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Cytotoxicity Elicited by Molybdenum Disulphide in Different Size of Particles in Human Airway Cells

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1. Introduction

Molybdenum disulphide (MoS_2) belongs to a class of layered materials well-known for their excellent lubrication performance. In the "bulk" form is used mainly in tribology area, as a dry and solid lubricant in, e.g. greases, dispersions, friction materials and bonded coatings. MoS_2 is used as an additive (in the amount of 0.5-30% by mass) for mineral oils, solid or liquid lubricants as well as composites. It can also constitute more than 80% of the mass of lubricants that exist in the form of powders or aerosols and which are available on the consumer market (IMOA 2018).

In recent years, the use of the nanoform of MoS_2 (MoS_2-NPs) has been increasing. Especially, two-dimensional nanoplates (2D nanomaterials) and fullerene-like structures are widely used in many tribological applications (Rapoport et al. 2005; Zhmud & Pasalskiy 2013; Feng & Cao 2016). The nanoplates/nanosheets of molybdenum disulfide are also used for the synthesis of analogues of such nanomaterials as: carbon nanotubes, fullerenes or graphene, in order to replace them in many consumer products (Teo et al. 2014; Jana & Rao, 2016). The use of MoS_2-NPs in dry lubricants is of particular importance in aviation, automotive, paper and food industries, in precision mechanics, electronics, chemical, glass, plastics and many other industries (Alazemi et al. 2016; Österle & Dmitriev 2016; Vidal-Abarca Garrido et al. 2016). The usage of MoS_2-NPs in lubricants in automotive and aviation is very beneficial for the environment, due to the reduction of particulate matter emission, which affects the smaller contamination of air, water and soil (Koppula et al. 2016; Vidal-Abarca Garrido et al. 2016). As a result, the reduction of emissions translates into a reduction in human morbidity, as solid particles (especially the fraction of ultrafine dust, with a diameter equivalent to those of nanoparticles) are responsible for the generation of respiratory, cardiovascular, allergic and cancer diseases. In the other hands, dry lubricants are used in the form of powders and aerosols, which can lead to their significant emission to the environment, including the working environment. For this reason, the determination of the toxicity of the compounds in the nano-form is extremely important. According to toxicological reports, the use of nanomaterials, beneficial for technological reasons, is associated with an uncertain health risk (Drew & Hagen 2015). Both *in vivo* and *in vitro* studies confirm that the particle size of the same chemicals can significantly affect their toxic potential (Drew & Hagen 2015; ECETOC 2014). There is a concern that even substances with low toxicity may adversely affect the body if used in the form of nanoparticles. Despite existing and the still-emerging applications of MoS_2-NPs, only a few investigations into their biocompatibility and toxicity have been performed. What is important, mainly their modified forms were evaluated (Wu et al. 2011; Hao et al. 2017; Liu et al. 2014; Teo et al. 2014; Appel et al. 2016; Pardo et al. 2014; Wang et al. 2015). The results of these studies are inconclusive and indicate cytotoxic effects of MoS_2-NPs at both low (Chng et al. 2014; Wang et al., 2015) and high concentrations (Corazzari et al. 2014; Teo et al. 2014; Pardo et al. 2015; Hao et al. 2017; Liu et al. 2014).

Taking into account the trend of adding nanoscale MoS_2 to many applications, there is a need for toxicity studies on their unfunctionalized forms, especially in terms of potential health effects after inhalation.

The basic step in assessing the safety of nanomaterials is to determine their cytotoxic effects in in vitro conditions (Zapór 2012). The respiratory tract is often represented by bronchial (BEAS-2B) and alveolar (A549) epithelial cells. The BEAS-2B cells retain metabolic competence of normal bronchial epithelial cells, therefore they are considered a sensitive model for toxicity testing of environmental pollutants as well as nanomaterials, including molybdenum compounds (Haniu et al. 2011; Ekstrand-Hammarstroem et al. 2012; Gilbert et al. 2012; Wang et al. 2015). A549 cells, despite their neoplastic origin, retain the properties of normal alveolar epithelial cells.

The purpose of this study was to assess the cytotoxic effect of unmodified molybdenum disulfide in nano- (MoS_2-NPs) and micro- (MoS_2-MPs) size of particle toward human bronchial (BEAS-2B) and alveolar (A549) cells.

2. Materials and methods

2.1. Chemicals and reagents

The molybdenum disulphides with particle size < 100 nm (MoS_2-NPs) and > 1 µm (MoS_2-MPs) originated from US Research Nanomaterials, Inc, Huston, Texas. The media for cell cultures were provided by Gibco BRL (Life Technologies Ltd. Paisley, UK). Foetal Bovine Serum (FBS), trypsin solution (0,25%) with EDTA, were purchased from Sigma Chemical Co. (St Louis, MO, USA). For cytotoxicity assays were used: 3-(4.5 dimethylthiazol-2-yl)-2.5 diphenyltetrazolium bromide (MTT), Neutral Red Solution (NRU), Hank's Balanced Salt Solution, Dulbeco's Phosphate Buffered Saline, dimethylsulphoxide (DMSO), Giemza solution, from Sigma.

2.2. Characterization of MoS_2-NPs and MoS_2-MPs

The particles of MoS_2-NPs and MoS_2-MPs were broken down and dispersed into colloidal form by means of ultrasonic gun (1 cycle, 15 min., 100% amplitude, water bath with ice). Then, an aqueous suspension of particles was stabilized with poly(vinylpyrrolidone) – PVP of molecular weight M = 360 000, in the ratio MoS2:PVP = 1:1. The choice of PVP as a stabilizer was dictated primarily by its physiological inertness, besides the compound being a non-ionic polymer does not change the pH of the culture media, and as non-toxic it is also used in medicine, pharmacology and cosmetics (Kariduraganavar et al. 2014). Not without significance is the fact that PVP is often used in tribology as a lubricant improving agent (Sułek et al. 2011).

The particle size and morphology was characterized using scanning electron microscopy (SEM, Nova NanoSEM 450 (FEI). Crystalline structure of particles was confirmed by X-ray diffraction (XRD), with Empyrean (PANalytical) diffractometer with CoKa line (1.78901 A). The measurement data was processed using ICDD PDF 4 database and HighScore Plus software. The particle size and size distribution was carried out in aqueous suspension of MoS_2 particles with stabilizer (PVP) using Dynamic Light Scattering (DLS) (Litesizer TM 500, Anton Paar). Particle suspensions with an initial concentration of 12.5 mg MoS_2/mL were prepared successively during the experiment. The preparation of nanoparticles, as well as the preparation of their suspensions and the characteristics was carried out at the Department of Materials Technology and Chemistry of the University of Lodz.

2.3. Cell culture and treatment

The normal bronchial epithelium cells BEAS-2B (CRL-9609) were purchased from American Type Culture Collection (LGC Standards Sp. z o.o.). The cells were grown in the LHC-9 serum free medium in the culture flasks coated with collagen type 1 (Greiner). The A549 cells were cultured in a DMEM medium supplemented with 7% FBS and with 1% antibiotic-antimycotic in sterile tissue culture flasks (Nunc, USA). The cells were maintained at 37°C in a humidified atmosphere with 5% CO_2. Before starting the experiment, the cells were removed from the flask by trypsinisation. Cell number and viability were determined in a Bürker chamber by the trypan blue exclusion method. Cells whose viability was over 90% were used in experiments. The cells were screened for *Mycoplasma sp.* infection using MycoAlert™ PLUS Mycoplasma Detection Kit (Lonza, Walkersville, Inc.).

2.4. Cytotoxicity studies

To assess cytotoxicity of MoS_2-NPs and MoS_2-MPs two assays were used. The MTT assay is based on the uptake and the reduction by mitochondrial succinate dehydrogenase of the soluble yellow MTT tetrazolium salt to an insoluble blue MTT formazan product (Denizot & Lang 1986; Mosmann 1983). The NRU assay is based on the uptake and lysosomal accumulation of the supravital dye, neutral red (Borenfreund & Puerner 1985). Cells were plated at a density of 1 x 10^4/well in a 96-well culture plate and cultured overnight to allow adherence and recovery. After this period, non-attached cells were aspirated and suspension of MoS_2-NPs or MoS_2-MPs in different concentrations (1÷200 μg/mL) were added, and incubated for 24. 48. or 72 hrs. Then, the medium was removed and reagents for cytotoxicity tests were added. Cytotoxicity tests were performed in at least three independent replications. Based on the absorbance values obtained in MTT and NRU tests, the viability ratio of cells exposed to the tested compounds, i.e. the percentage of viable cells compared to control was calculated. The possibility of interference nanoparticles with the test reagents was examined. To this end, nanoparticles were incubated in the absence of the cells and then MTT and NRU tests were performed (Kroll et al. 2012).

2.5. Clonogenic assay (Colony Forming Efficiency Assay, CFEA)

The clonogenic assay was conducted according the procedure described by Franken et al. (2006) and adapted from Kruszewski et al. (2013). Briefly: Exponentially growing cells were harvested and seeded in Petri dish 60 x 15 mm (21 cm^2) (Iwaki Cell Biology, Japan) at a density 500 cells/dish together with tested compound. Each dish finally contained 5 mL of cell culture medium with MoS_2-NPs or MoS_2-MPs in appropriate concentrations at least in three replicates for each treatment. Cells were exposed to particles over the time period they needed to form colonies, that is 10 days. After this period, particle solutions were removed, cells were washed with PBS, fixed (ethanol), stained (0.4% Giemza), and colonies were counted. Then plating efficiency (PE) and surviving fraction (SF) was calculated, as below:

PE = (number of colonies formed / number of cells seeded)

SF = no. of colonies formed after treatment / no. of cells seeded x PE

PE ratio for BEAS-2B cells calculated from three independent experiments was above 60%.

2.6. Data analysis

Three separate *in vitro* cytotoxicity experiments were conducted in which all samples of compounds were tested simultaneously. Each dose in separate experiment was tested in 9 replications (n = 9 wells per treatment). Replicates from 3 experiments were averaged. The CFEA test was carried out in the three separated experiments with three replications for each concentration of MoS_2-NPs or MoS_2-MPs. The results were presented as surviving fraction ratio (SF) ± standard deviation (SD). SF = 1 was set for the control. CFEA data were analysed by Student's test for comparison between two groups.

3. Results

3.1. Characterization of MoS_2-NPs and MoS_2-MPs

Before starting the cytotoxicity assessment of MoS_2-NPs and MoS_2-MPs, their properties were characterized in terms of morphology, particle sizes and size distribution. SEM analysis showed that MoS_2-NPs was a homogeneous material in its whole volume and consisted of disk-shaped particles (Fig. 1a). In the case of MoS_2-MPs, the SEM analysis showed that it was in the shape of multilayer hexagonal plates (Fig. 1b).

The histograms of particle size distribution indicated that the diameter of the disks of MoS_2-NPs was 97 ± 32 nm (the average of 500 counts) (Fig. 2a), while the thickness of the disks evaluated on the basis of XRD results was 8.5 nm ± 1.5 nm (data no shown). The size of MoS_2-MPs plates was 1.92 ± 0.64 μm (mean from 500 counts) (Fig. 2b), while the thickness evaluated on the basis of XRD results was about 10 nm (data no shown).

DLS analysis (in the natural colloid environment) indicated that the hydrodynamic diameter of MoS_2-NPs coated with PVP was d = 251 ± 94 nm, while MoS_2-MPs d = 0.7 ± 0.3 μm (data not shown). No peaks from large agglomerates were observed.

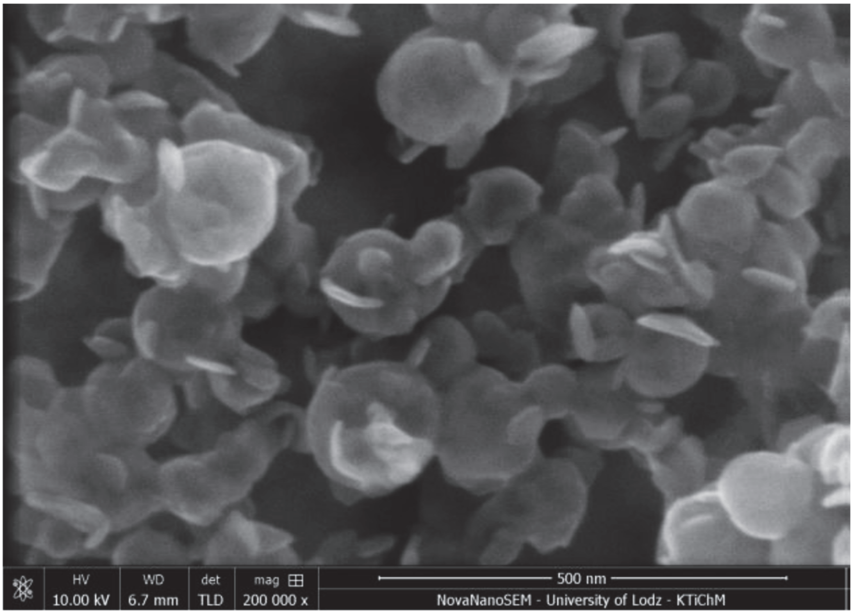

Fig. 1a. SEM image of MoS_2-NPs. Magnification and scale are present on the picture

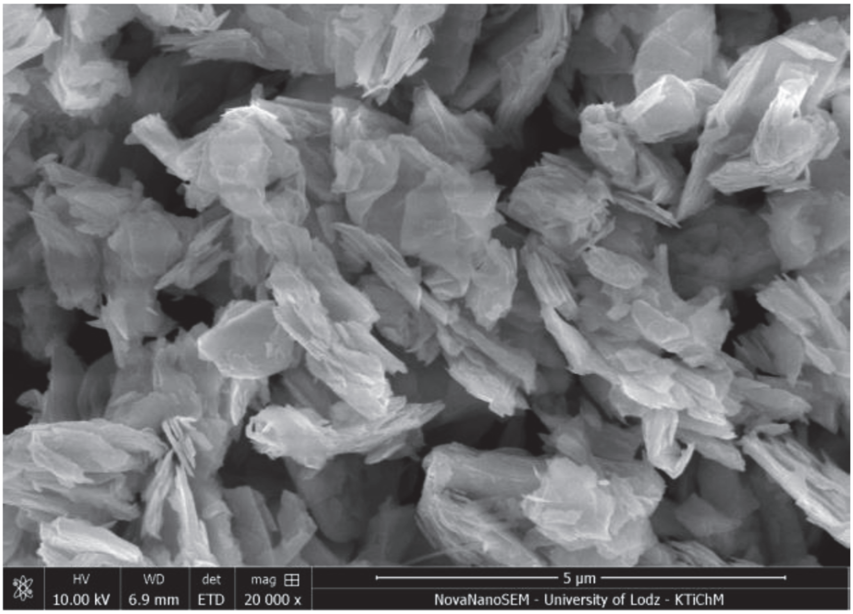

Fig. 1b. SEM image of MoS_2-MPs. Magnification and scale are present on the picture

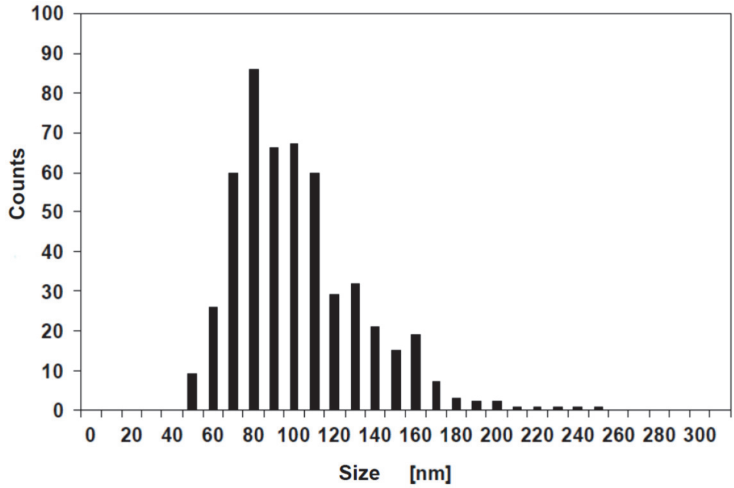

Fig. 2a. The histogram of particle size distribution of MoS_2-NPs

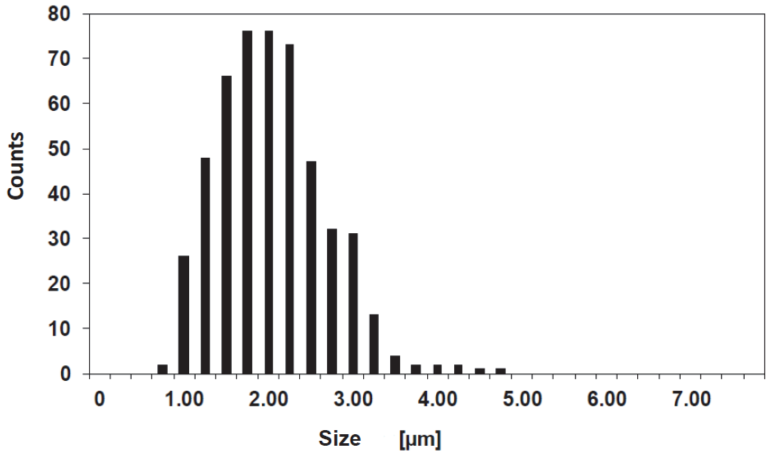

Fig. 2b. The histogram of particle size distribution of MoS_2-MPs

3.2. Effects of MoS_2-NPs and MoS_2-MPs on cell viability and proliferation

The effects of both MoS_2 on the viability of A549 and BEAS-2B cells assessed by MTT and NRU tests after 24, 48 and 72 h exposure are presented in Figures 3-6. The assessment of cytotoxicity performed in preliminary experiments did not show the effect of PVP on BEAS-2B and A549 cells in the range of concentrations used.

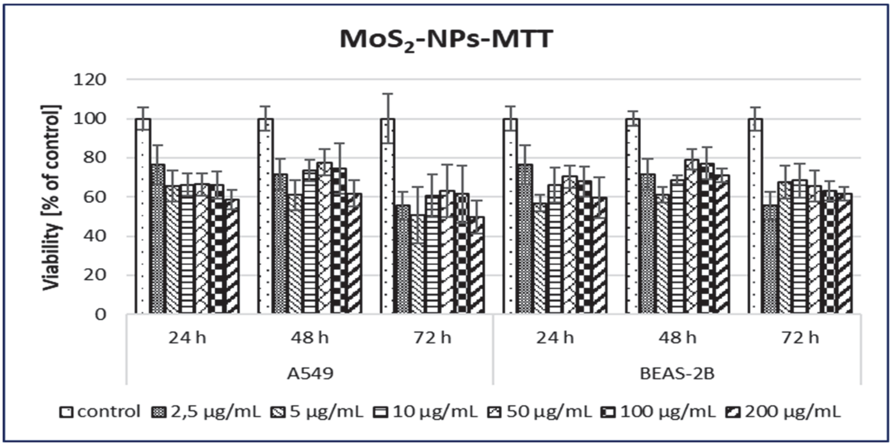

Fig. 3. Cytotoxic effect of MoS_2-NPs in A549 or BEAS-2B cells after 24 h, 48 h and 72 h exposure of the cells, assessed by MTT assay

MoS_2-NPs at a concentration of 2.5 µg/mL reduced the viability of both cell types assessed by the MTT reduction assay to about 70% after 24 and 48 h of exposure and to about 50% after 72 h compared to the control. Exposure of cells to higher concentrations of the substance did not result in a further decrease in their viability (Fig. 3). MoS_2-MPs had a similar effect. After 24 hours of exposure to the compound at a concentration of 5 µg/mL, cell viability was reduced to about 70% (A549) and about 60% (BEAS-2B). Higher concentrations and longer exposure time did not cause further decrease in cell viability (Fig. 4).

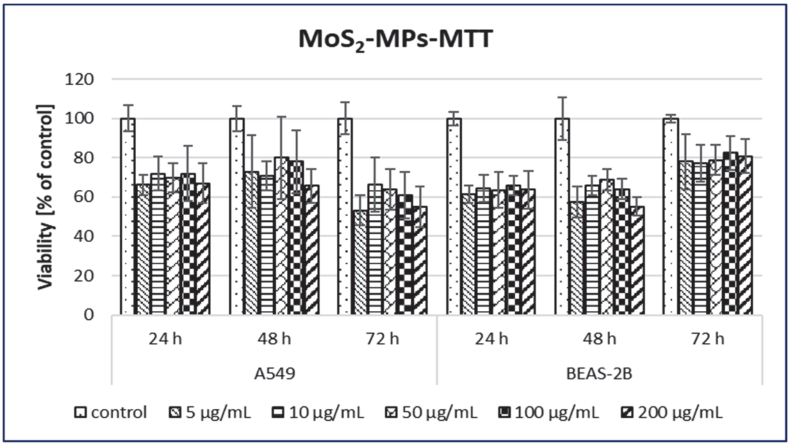

Fig. 4. Cytotoxic effect of MoS_2-MPs in A549 or BEAS-2B cells after 24 h, 48 h and 72 h exposure of the cells, assessed by MTT assay

Both MoS_2-NPs and MoS_2-MPs assessed by the NRU assay did not cause any decrease in cell viability relative to the control (on the contrary some of the measurements were above control values) (Fig. 5-6).

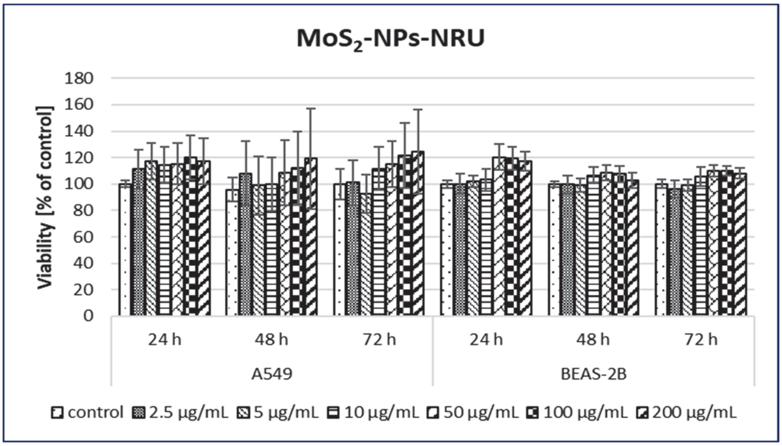

Fig. 5. Cytotoxic effect of MoS_2-NPs in A549 or BEAS-2B cells after 24 h, 48 h and 72 h exposure of the cells, assessed by NRU assay

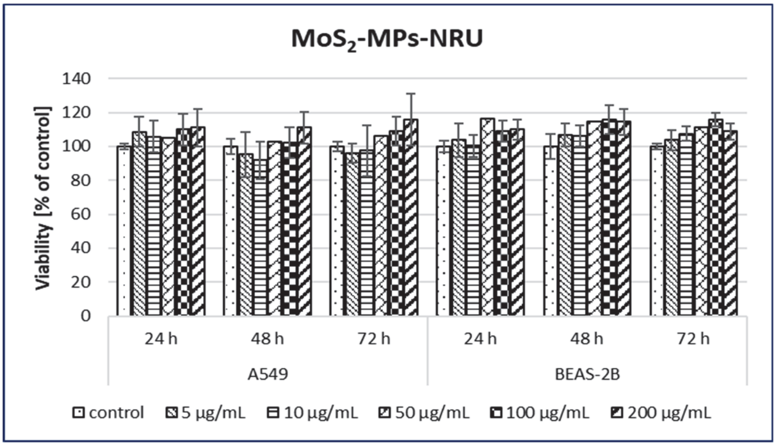

Fig. 6. Cytotoxic effect of MoS_2-MPs in A549 or BEAS-2B cells after 24 h, 48 h and 72 h exposure of the cells, assessed by NRU assay

3.3. Effects of MoS_2-NPs and MoS_2-MPs on colony formation ability of the cells

The Colony Forming Efficiency Assay (CFEA) was used to assess the toxic effects of the MoS_2-NPs and MoS_2-MPs, after long-term cell exposure. CFEA is based on ability of a single cell to grow into a colony (Puck & Marcus 1956). A colony being defined to consist as at least 50 clones of one cell (which corresponds to 6 mitotic divisions). This test is used to detect cells that retained the capacity for producing a large number of progeny after treatments that can cause reproductive death as result of damage to chromosomes, apoptosis, etc. (Herzog et al. 2007).

MoS_2-NPs at the lowest of the concentrations used (25 and 50 µg/mL) limited the proliferation of BEAS-2B cells to about 80%. Higher concentration (100 µg/mL) resulted in inhibition of growth of the culture to approx. 30%. The toxic effect of MoS2-NPs was also seen on A549 cells. However, the reduction of A549 culture growth to 80% occurred only in the highest concentrations of the compound (100 and 200 µg/mL) (Fig. 7).

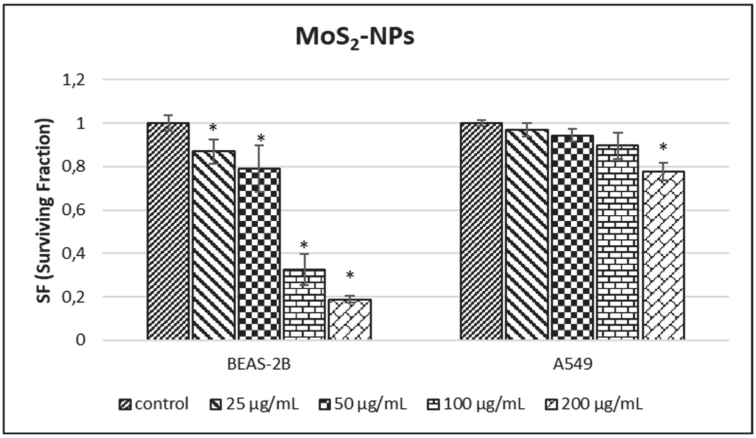

Fig. 7. Colony forming ability of BEAS-2B or A549 cells treated with different concentrations of MoS_2-NPs. Each bar represents the mean ± SD of 3 independent experiments. * $p < 0.05$ vs. control

MoS_2-MPs caused a greater (as compared to MoS_2-NPs) inhibition of BEAS-2B cell proliferation, however, the obtained results were very heterogeneous (high values of standard deviations). There was no toxic effect of the compound on the A549 cells (Fig. 8).

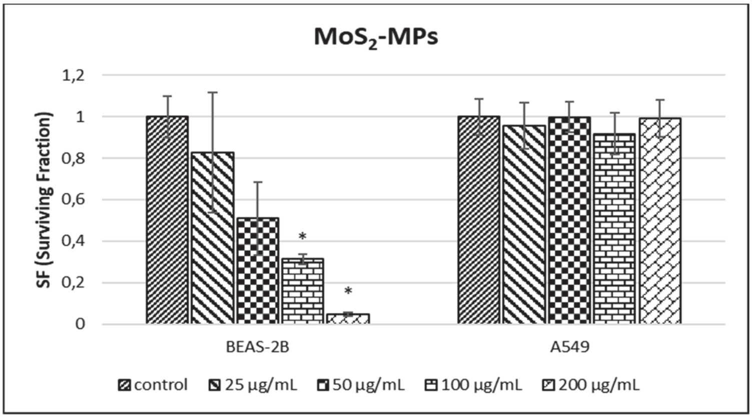

Fig. 8. Colony forming ability of BEAS-2B or A549 cells treated with different concentrations of MoS_2-MPs. Each bar represents the mean ± SD of 3 independent experiments. * $p < 0.05$ vs. control

4. Discussion

A wide range of applications of MoS_2-NPs in many industries, causes the possibility of occupational and environmental health implications of humans exposed to them. In the present study the comparison of the ability of MoS_2-NPs and MoS_2-MPs to induce cytotoxicity in two human lung epithelial cell models (BEAS-2B and A549) was carried out. The assessment of the cytotoxicity of nanomaterials is an essential tool in determining their potential effects at cellular level. It is the basis for the extrapolation of acute toxicity in animals and the determination of sub-lethal doses for in-depth toxicity studies (e.g. oxidative stress, inflammatory reactions, genotoxicity, etc.) (Stone et al. 2009). The studies of cytotoxicity *in vitro* are among the basic steps in Integrated Testing Strategy (ITS) for nanomaterials to predict their toxicity (Combes & Balls 2011; Stone et al. 2014). The results of the assessment of cytotoxicity often depend on the model used and applied research methods to assess cytotoxicity. In the studies carried out, BEAS-2B cells showed slightly higher sensitivity to the tested substances, while large differences in the levels of cytotoxic doses associated with the applied test method were observed. The test assessing the integrity of cell membranes and lysosomal activity (NRU) practically did not give any cytotoxic response, on the contrary, some results indicate a higher viability of exposed cells. It is difficult to explain such a phenomenon. Perhaps the smallest of the particles were accumulated in lysosomes and interfered with NR dye. This may be evidenced by large scatter of results, especially on A549 cells.

In MTT reduction assays the little trend in cytotoxicity profiles of MoS_2 was found: both sulphides at low concentrations (2.5 and 5 µg/mL) reduced the viability of the cells to about 60%, after which there was no further decrease in cell viability, despite being exposed to higher concentrations. Very similar results of MoS_2-NPs cytotoxicity received Chng et al. (2014) in MTT assay on A549 cells. Pristine MoS_2-NPs decreased viability of the cells in doses 3.125 and 6.25 µg/mL whereas higher concentrations did not cause changes in viability of the cells. Also, Wang et al. (2015) showed a slight (up to 80%) decrease in the viability of THP-1 cells and no cytotoxic effect in BEAS-2B cells exposed to various structural forms of MoS_2-NPs in concentrations of 10-50 µg/mL. It should be emphasised that MoS_2-NPs, despite the lack of cytotoxic effects, caused the release of pro-inflammatory mediators in cells and, in vivo inflammation and fibrosis. In turn, Quereshi et al. (2015) observed a minimal decrease in the survival rate of HeLa cells with increase of concentration of MoS_2-NPs, but they use higher doses, i.e. from 32.5 to 300 µg /mL. Likewise, Corazzari et al. (2014) and Theo et al. (2014) in the studies on A549 cells demonstrated cytotoxic activity of MoS2-NPs only in high concentrations (400 mg/mL).

In order to study possible long-term toxic effects of MoS_2-NPs and MoS_2-MPs the clonogenic assay was used, which is performed within 7-10 days. Recently, the clonogenic assay is considered a promising test to study toxicity of nanomaterials, as it makes use of no cellular dyes, that have been demonstrated to be a possible reason for invalid results due to their biochemical interaction with the nanomaterials tested (Casey et al. 2007, Herzog et al. 2007, Ponti et al. 2010,). The results from an interlaboratory comparison study performed in the frame of OECD's Working Party of Manufactured Nanomaterials (WPMN) showed that the CFE assay is a suitable and robust *in vitro* method to assess cytotoxicity of nanomaterials (JRC Report 2014). In this experiment both, MoS_2-NPs and MoS_2-MPs were able to significantly decrease the clonogenic survival and cell proliferation in a dose-dependent fashion in a wide range of concentrations to 200 µg/mL, when exposed constantly over 10 days, but this effect was visible mainly in BEAS-2B cells. The MoS_2-NPs were slightly more cytotoxic than MoS_2-MPs. Both MoS_2 did not cause inhibition of colony forming ability of A549 cells.

Inhibition of the ability of BEAS-2B cells to proliferate under the influence of both MoS_2 particles may be an unfavourable phenomenon for predicting their long-term effects of exposure. At the body level, these cells are a kind of barrier to xenobiotics. Thanks to the ability to create tight junctions and the ability to adhere "foreign" particles on the surface of cell membranes, these cells form the body's defence line against the penetration of particles into cells (Heijink et al. 2010).

5. Conclusion

The obtained data with regards cytotoxic and clonogenic effects of MoS_2-NPs and MoS_2-MPs suggest rather their low hazardous potency with an indication of higher toxicity of MoS_2-NPs. Such result, although it needs to be confirmed in *in vivo* studies, is promising due to the predicted wide use of molybdenum disulfide nanoparticles. Especially that molybdenum disulphide is one of the most promising post-graphene nanomaterials.

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Abstract

The present investigation was aimed to study the cytotoxic response induced by molybdenum disulfide in nano- (MoS_2-NPs) and micro- (MoS_2-MPs) size of particle in human bronchial (BEAS-2B) and alveolar (A549) cells. The cells were exposed with different particle size of MoS_2 in concentrations range 1-200 µg/mL for 24, 48, and 72 h, and then the cytotoxicity assays (MTT and NRU) was performed. Afterwards, long-term toxicity was assessed by colony forming efficiency assay (CFEA) during 10 days exposure of the cells.

Both MoS_2-NPs and MoS_2-MPs showed similar, weak cytotoxic effects on BEAS-2B and A549 cells assessed by MTT assay, that is reduction of cell viability to approx. 60-70% at concentrations of 2.5 and 5 µg/mL. The percentage viability remained relatively constant at this level across all concentrations above 5 µg/mL. In long-term exposure, both MoS_2 inhibited colony formation in a wider range of concentrations to 200 µg/mL. MoS_2-NPs were slightly more cytotoxic than MoS_2-MPs. The data suggest the low potential hazardous nature of both MoS_2 tested with an indication of higher toxicity of MoS_2-NPs.

Keywords:
molybdenum disulphide, nanoparticles, cytotoxicity

Ocena cytotoksycznego działania cząstek disiarczku molibdenu na komórki układu oddechowego

Streszczenie

Celem badań była ocena cytotoksycznego działania nano- (MoS_2-NPs) i mikrometrycznego (MoS_2-MPs) disiarczku molibdenu na ludzkie komórki nabłonka oskrzelików (BEAS-2B) i pęcherzyków (A549) płuc. Komórki narażano na różnej wielkości cząstki MoS_2 w zakresie stężeń 1-200 µg/ml przez 24, 48 i 72 h. Badano wpływ obu rodzaju cząstek MoS_2 na integralność błon komórkowych (test NRU) oraz aktywność metaboliczną komórek (test MTT). Oceniano również zdolność komórek do proliferacji po długotrwałym (10 dni) narażeniu na podstawie testu efektywności formowania kolonii (CFEA).

Oba MoS_2 powodowały podobne, słabe działanie cytotoksyczne na komórki oceniane testem MTT, tj. obniżenie przeżywalności komórek do ok. 60-70% w stężeniach of 2,5 and 5 µg/mL po 24 h, które w niewielkim stopniu nasilało się z czasem narażenia, natomiast nie obserwowano wzrostu cytotoksyczności ze wzrostem stężenia. Po długotrwałej ekspozycji (10 dni) oba MoS_2 hamowały zdolność tworzenia kolonii w szerszym zakresie stężeń tj. do 200 µg/mL, przy czym MoS_2-NPs wykazywały silniejsze działanie ograniczające zdolność komórek do proliferacji niż MoS_2-MPs. Dane wskazują na niski potencjał toksyczny obu badanych MoS_2 ze wskazaniem wyższej toksyczności MoS_2-NP.

Słowa kluczowe:
disiarczek molibdenu, nanocząstki, cytotoksyczność

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Physicochemical Properties of Copper Modified Zeolite

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1. Introduction

Zeolites have been used in environmental engineering mainly in catalytic processes and as ion exchangers in water and wastewater treatment. A number of papers on the application of natural zeolites in chemical processes, especially modified zeolites, as heterogeneous catalysts (or their supports) have been published during last decades (Amiri & Nezamzadeh-Ejhieh 2015, Świderska-Dąbrowska & Schmidt 2014, Świderska-Dąbrowska 2015, Świderska-Dąbrowska et al. 2017). Moreover, modified zeolites have been increasingly often used in processes of water and wastewater treatment, as selective adsorbents (Hawash et al. 2018, Inglezakis et al. 2004, Li et al. 2009, Liu et al. 2017, Schmidt & Anielak 2011) or antibacterial material (Yao et al. 2019). Selective modified zeolites allow significant improvement in the effectiveness of impurities' removal without introducing additional reagents to the environment. The final effect of treatment of water solutions is determined by the catalyst used, its physicochemical properties and the process parameters. The catalytic activity of zeolites and their chemical stability strictly depend on the method of their modification and calcination temperature.

Modification of zeolites' surface is most often carried out using ion exchange, wet impregnation or precipitation methods. Aqueous ion exchange allows introduction of metal ions in place of interstitial cations, however, it requires a long time of zeolite contact with the salt solution and generates significant amount of residual solvent. The problem of wastewater, often containing heavy metals, harmful to the natural environment, may be solved by application of wet-impregnation method. Moreover, this method allows to control the amount of metal ions introduced into the zeolite framework (Singh et al. 2018). The third method – precipitation – creates deposits of metal oxides on the surface of zeolites. They are formed using a precipitation agent, e.g. NaOH, Na_2CO_3 or NH_3.

Depending on the used zeolite modification method, metal ions, hydroxocomplexes or oxides may form on its surface. Singh et al. used Cu/Zeolite Y (obtained using various methods) for the oxidation of quinoline in the catalytic wet peroxide oxidation process. They proved that the ion exchange and wet-impregnation methods lead to the formation of isolated Cu(I)/Cu(II) species. Such zeolites show bigger catalytic activity than zeolite modified with precipitation-impregnation method, despite increase of its specific surface, due to the deposition of large CuO crystallites on its external area (Singh et al. 2018).

The catalytic activity of metal oxide-based heterogeneous catalyst largely depends on the degree of dispersion of metal oxides on the surface of the zeolite. Xin et al. modified the SBA-15 zeolite with Cu(II) ions using NH_3 as a precipitation agent. It was dosed in a Cu/NH_3 ratio from 1/3 to 1/6. The highest CuO dispersion on external area was obtained at the highest Cu/NH_3 ratio. Strong interactions between Cu and zeolite, in such case, increased the thermal stability of the catalyst up to 700°C (Xin et al. 2018).

The dispersion of metal on the surface of zeolite also depends on the type of metal salt applied. Xuanwen et al. achieved higher degree of Cu dispersion on the surface of 13X zeolite using $CuCl_2$ for impregnation than $Cu(NO_3)_2$. For copper (II) chloride, Cu(II) species were found on the zeolite surface, while in the other case it might be CuO or basic cupric nitrate, which during calcination showed a tendency for aggregation (Xuanwen et al. 2017).

Batistela et al. noticed that the location of metal oxides on the zeolite surface also depends on the size and volume of its pores (Batistela et al. 2017). They conducted humid impregnation with zinc nitrate of three types of zeolites: NaY, NaA and ultrastable Y zeolite (containing Na^+ and H^+ ions) – USY, which were then calcined at 550°C. Studies of the surface structure of modified zeolites showed the presence of ZnO in micropores, which caused a decrease in the specific surface of zeolites. However in the case of NaA zeolite (which has a small volume of micropores), after full cavity saturation of micropores, ZnO crystallization also took place on the external surface of NaA. Supporting of ZnO on NaY and NaA did not significantly affect their photocatalytic activity – the bandgap value of ZnO/zeolite is similar to ZnO only (3.2 mV). On the contrary, an increase in the band gap value in relation to ZnO, was noted for USY. This requires usage of a stronger source of radiation and may cause the photocatalysis process to be unprofitable (Batistela et al. 2017).

Research conducted by Batistela et al. proved that the efficiency of zeolite modification is significantly affected by the first stage – pretreatment, i.e. preparation of the initial form of zeolite. Liu et al. showed that washing of the natural zeolite with acid causes unblocking of its pores (due to removal of impurities) and increase of the specific surface area of zeolite as well as increasing the number of active sites for adsorption process. The exchange of interstitial cations (mainly metals of I and II groups of the periodic table) for H^+ ions causes strong protonization of zeolite, which promotes adsorption of NO_2^- anions on the surface of the obtained zeolite (Liu et al. 2017).

Sometimes it is also advisable to carry out calcination process before modification of the zeolite surface with metal ions. Studies of Sushkevich & van Bokhoven proved that the removal of carbonaceous impurities during the calcination of modernite prevents the loss of active Cu(II) ions, which can be reduced to Cu(I) during reaction with carbonaceous compounds. Moreover, calcination in pure oxygen atmosphere is preferred over the air. Air contains traces of organic substances that can be adsorbed on the surface of modernite (Sushkevich & van Bokhoven 2018).

Calcination is usually the last stage of modification of zeolites surface. A slight change of calcination temperature brings about considerable changes in its structure. Chen et al. (Chen et al. 2008) proved that zeolite catalytic activity and their chemical stability strictly depend on the method of their modification and temperature of calcination. Considerable decrease of catalytic activity of a zeolite after calcination at the temperature of 550°C, resulting from total dealumination of the zeolite was observed.

Effectiveness of modified zeolites in water and wastewater treatment also depends on surface charge, which is affected by forms of particles and molecules occurrence on its surface in function of calcinations temperature. Surface charge of zeolite is also affected by potential-forming ions, present in the treated solution, such as H^+ and OH^- (Ates et al. 2018, Świderska-Dąbrowska & Schmidt 2012a).

Removal of individual impurities depends on their size, which determines easiness of their migration via the channels of clinoptilolite (Inglezakis et al. 2004, Erdem et al. 2004). However, there are only a few publications on the physicochemical properties of modified zeolites and their effect on aqueous solutions. It is very important in terms of their practical and technological application because the mechanism of impurities' removal from aqueous solutions using zeolites, for example in hydrogenous form (Liu et al. 2017) is different than that on a zeolite modified with Fe ions (Akgul 2014, Hawash et al. 2018, Świderska-Dąbrowska et al. 2012b), Mn ions (Anielak & Schmidt 2015, Skoczko et al. 2015) or Co ions (Świderska-Dąbrowska & Schmidt 2013, Andriyevskyy et al. 2018).

Practical application of a zeolite modified with Cu(II) ions in water and wastewater treatment may significantly increase effectiveness of sorption and oxidation of organic pollutants. Therefore, the aim of this study was to compare the physicochemical properties of natural zeolites modified by Cu(II) ions using two precipitating reagents: sodium hydroxide and sodium carbonate. This study evaluates the effectiveness of zeolite modification methods as well as their physical and chemical stability, taking into account the changes that take place during the process of calcination within the temperature range from 250°C to 650°C.

2. Research methodology

2.1. Materials

Natural zeolite – clinoptilolite from Slovakia, with granulation size from 0.40 mm to 0.75 mm, containing 64.9% of SiO_2, 9.9% of Al_2O_3, 2.9% of K_2O, 2.5% of Na_2O, 1.4% of CaO, 1.4% of Fe_2O_3 and 0.3% of MgO, was used in the experiments.

All chemical reagents of an analytical grade: copper (II) sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$), sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$) and sodium hydroxide (*NaOH*) were purchased from POCh Gliwice. Model solutions were prepared using ultrapure water (Hydrolab, Polska).

2.2. Modification of zeolite

The natural zeolite was transformed into the hydrogenous form by shaking it for 2 hours in 5% HCl solution of volume three times of zeolite volume and was subsequently modified with copper (II) ions by precipitation using two precipitating agents: sodium hydroxide or sodium carbonate.

Method with NaOH – the zeolite was stirred with 0.05 mol/L of $CuSO_4$ for 4 hours at pH = 3 and at temperature of 50°C; subsequently pH was increased up to 9.5 with 2 mol/L of NaOH and the solution was stirred for another hour. The zeolite was washed with deionised water three times and dried at a temperature of 105°C.

Method with Na_2CO_3 – solid Na_2CO_3 was added to 0.05 mol/L of $CuSO_4$ (1 mol:1 mol). After 1 hour of stirring at a temperature of 50°C, zeolite was added to the solution and stirred for another 4 hours. Subsequently, the zeolite was separated, washed with three portions of deionised water and dried at a temperature of 105°C.

Those procedures were repeated three times, and each time the content of copper in the zeolite increased. Then zeolite, modified by precipitation with NaOH (ZCu-1) or Na_2CO_3 (ZCu-2), was calcinated for 2 hours in a muffle furnace, at the temperature of calcination ranging from 250°C to 650°C.

2.3. Analytical methods

The electrokinetic potential (zeta potential ζ) of the zeolite particles (in suspension of finely ground zeolite $d < 0.04$ mm with concentration of 0.1 g/L) was measured by the method of phase analysis of dispersed laser beam using zeta potential analyser ZetaPALS (Brookhaven Instrument Corp., USA).

The microstructure of the zeolite surface and its qualitative composition were examined using JSM 5500 LV scanning electron microscope (JEOL, Japan), with EDS method.

Cu concentration was determined using Varian Spectr AA 20 plus atomic absorption spectrometer.

2.4. Leaching test

In processes of heterogeneous catalysis, which are carried out in the liquid phase, active species (e.g. metal ions) can pass from the catalyst surface to the liquid. Determination of the amount of leached metal ions can be helpful in assessing the chemical stability of the catalyst, its activity and its reusability (Sádaba et al. 2015). In addition, Yang et al. (Yang et al. 2017) proved that Cu(II) ions leached out during heterogeneous catalytic ozonation of organic pollutants may act as a homogeneous catalyst and affect the mechanism of the oxidation reaction. They also observed a significant effect of the solution matrix on the metal leaching process.

The leaching of metallic ion from the zeolite was determined in static tests, which involved stirring an aqueous suspension of zeolite (10 g/L) with the initial pH of 3, 6 and 9, for 24 hours. The pH of the solution was adjusted with 0.1 mol/L of NaOH or 0.1 mol/L of HCl. The resulting variables were pH and the concentration of copper in a decanted solution after a 24-hour shaking of zeolite with water solution.

3. Results and discussion

The method of zeolite modification significantly affects the copper content in a zeolite. Increase in the number of modification cycles is accompanied by an increase in the content of copper in ZCu-2 from approx. 3.5 to 9.5 mg/g of dry zeolite. On the contrary, Cu content in ZCu-1 is approx. 4 mg/g of zeolite and it does not change despite repeating the analytical modification procedure.

The process of precipitation at the final stage of modification of ZCu-1 zeolite was conducted at pH = 9.5 (pH was adjusted with NaOH solution). At this pH value, hydrated precipitable hydroxo complexes $Cu(OH)_{2aq}$ dominate, increasing their concentration on the surface of zeolite (Fig. 1).

After 60 minutes of contact time of ZCu-1 zeolite with the precipitating solution, its pH decreased from 9.5 to approx. 5, when dissociated Cu^{2+} aqua ions dominate, whereas share of $Cu(OH)^+$ is low (Fig. 1). Decrease of the solution's pH was a consequence of migration of protons from the zeolite matrix (zeolite in H form); they neutralised hydroxyl groups from dissociation of NaOH. Reactions (1) and (2) take place as a result of protons leaching:

$$Cu(OH)_2 + H^+ = Cu(OH)^+ + H_2O \tag{1}$$
$$Cu(OH)_2 + 2H^+ = Cu^{2+} + 2H_2O \tag{2}$$

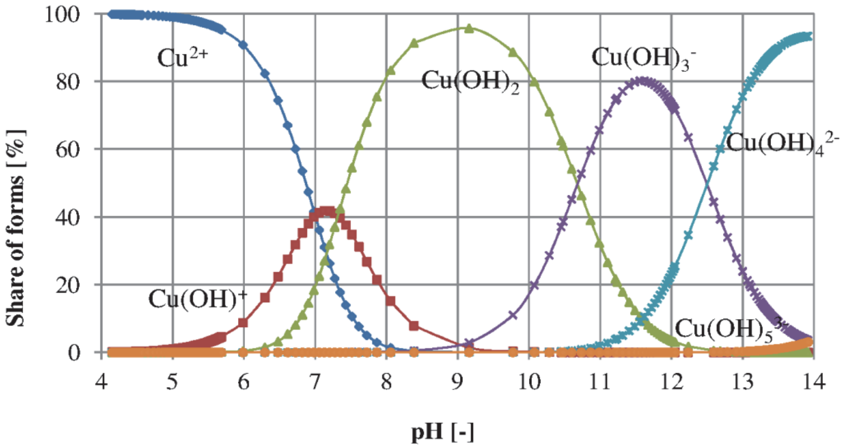


Fig. 1. Impact of solution pH on occurrence of Cu(II) complexes in aqueous solutions

As a result of proton migration processes the solution's pH decreases and precipitable complexes $Cu(OH)_{2aq}$ (which occur on the surface of the zeolite) dissolve to $Cu(OH)^{+}$ and Cu^{2+} (Cu^{2+} ions migrate into the solution). Such mechanism causes decrease of Cu concentration in zeolite, and copper present in the zeolite comes mostly from ion exchange processes.

ZCu-1 zeolite was modified in the following system: removal of ions from the zeolite with 5% solution of HCl (mainly Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}), which comprise so-called zeolite contamination, modification with Cu(II) ions using method of co-precipitation and calcination. The process of calcination has a fundamental effect on the surface charge of a zeolite; it can either increase or decrease it. At the same time catalytic activity as well as the sorption capacity of ZCu-1 change. The results presented in Figure 2a indicate variable values of the zeta potential of examined ZCu-1 zeolite as the function of calcination temperature.

The ζ potential values of the ZCu-1 zeolite ranged from -25 to -45 mV in the pH range from 3 to 10.2. With the solution's pH increase from 3 to approx. 7.5, the potential decreased from -30 mV to -20 mV for ZCu-1 after calcination at temperature of 650°C, whereas its negative charge on the surface is higher and increases throughout the entire pH range after calcination at temperatures 450°C and 550°C. The difference probably results from dealumination process of the zeolite at the temperature 650°C, which change the Si/Al ratio in the zeolite and causes decrease of negative charge of zeolite surface. Changes in the structure of natural zeolite (modernite-clinoptilolite) during its calcination in the temperature range from 400 to 1000°C were studied by Wahono et al. (Wahono et al. 2019). They observed that at temperatures above 600°C the specific surface area of zeolite significantly decreased and the average pore size increased almost 4 times. However, at 1000°C the zeolite crystal transforms into cristobalite. Along with increasing calcination temperature, the Si/Al ratio did not change significantly. In turn, according to Tomazović et al., clinoptilolite in ammonium form undergoes the dealumination process at the temperature ≥400°C. In addition, they found that different cationic forms of Al are formed depending on the calcination temperature (Tomazović et al. 1996).

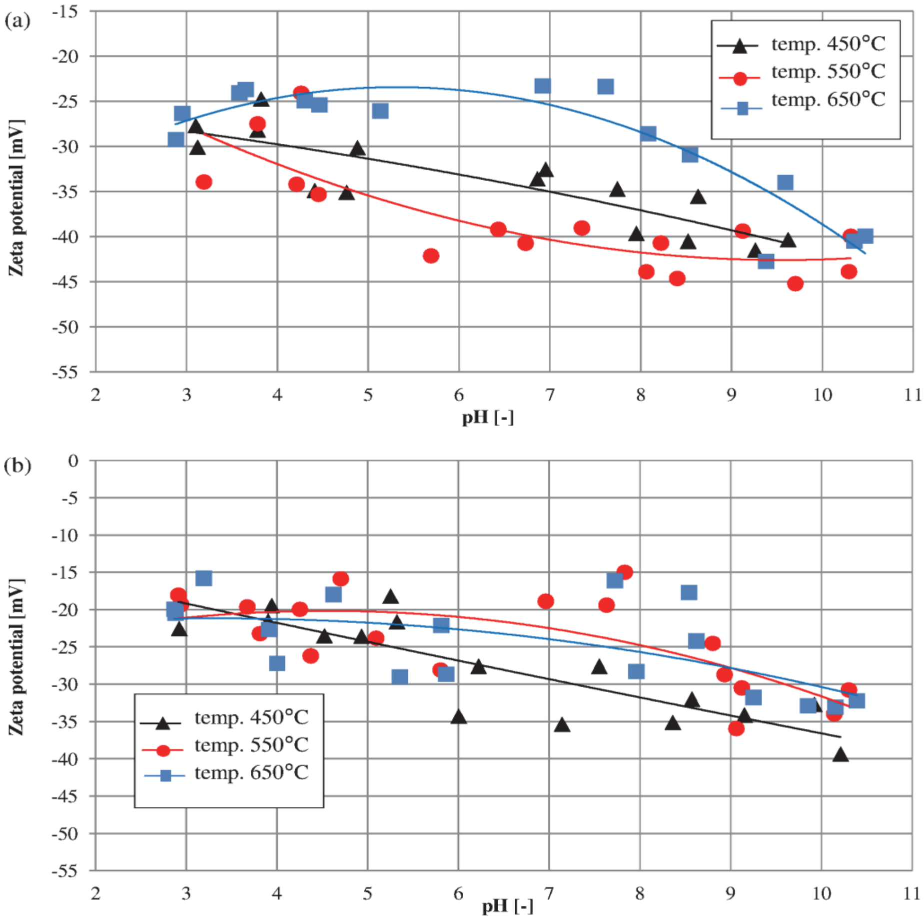


Fig. 2. Impact of solution pH on zeta potential of modified zeolite in function of calcination temperature: (a) ZCu-1, (b) ZCu-2

Moreover, our experiments have shown that the temperature of calcination from 250°C to 550°C does not significantly affect the zeta potential. Its value depends on the concentration of potential-forming ions and presence of other ions in the solution. However, the surface charge of the zeolite is determined by H^+ and OH^- ions.

Changes of the solution's pH on the zeolite surface and in its pores can cause reactions (3-6):

$$Z\text{-}Cu^{2+} + H_2O = Z\text{-}CuOH^+ + H^+ \quad (3)$$
$$Z\text{-}O^- + CuOH^+ = Z\text{-}OCuOH \quad (4)$$
$$2Z\text{-}OH + Cu^{2+} = (Z\text{-}O)_2\text{-}Cu + 2H^+ \quad (5)$$
$$ZO^- + Cu^{2+} = (Z\text{-}O)_2\text{-}Cu \quad (6)$$

Apart from migration of protons from the zeolite matrix, pH decrease is caused by reactions (3) and (5). According to reactions (3-6), Cu detainment in ZCu-1 is caused by electrostatic interactions between Cu(II) cations and the electronegative surface of the zeolite. Brönsted acid centres in the zeolite structure can lead to formation of $[Cu\text{-}O\text{-}Cu]^{2+}$ bridges. At pH < 6, when Cu(II) aqua ions dominate (Fig. 1), Cu is detained according to reactions (5) and (6).

Modification of zeolite with Cu(II) ions by coprecipitation with Na_2CO_3 results in the formation of insoluble, green-blue complex $Cu_2(OH)_2CO_3$ and $Cu_n(OH)_{2n-2}^{2+}$ in the aqueous solution. The pH value of the $CuSO_4$ solution from the initial value of 4.3 increased after adding Na_2CO_3 to pH = 8, and decreased to pH = 7 after 4 hours of contact time with zeolite. There were therefore favourable conditions for the precipitation of hydrated $CuCO_{3aq}$ ($pK_a = 6.5$), which could be adsorbed on the surface and in the pores of ZCu-2. The copper content in ZCu-2 zeolite increased steadily, reaching a value of about 9.5 mg/g of zeolite after the third cycle. The zeta potential analysis of ZCu-2 indicates that the zeolite had a lower negative surface charge throughout the entire range of pH changes as compared to ZCu-1 (Fig. 2). The zeta potential of the ZCu-2 zeolite ranged from -15 to -35 mV at pH range from 3 to 10.2.

In case of ZCu-2, the negative charge on its surface increases with the increase of solution pH and the decrease of calcination temperature (from 250°C to 650°C). The ζ potential of ZCu-1 within the specific pH range has much greater absolute values, which vary from -30 mV to -45 mV. It can be concluded that electrostatic activity of ZCu-1 is higher than that of ZCu-2.

These relationships can be explained basing, among others, on formation of polymorphic species of copper (II) oxide. On the surface of ZCu-2 zeolite, which was obtained in precipitation with Na_2CO_3 method and calcined at temperature of 450°C, CuO dominates, hardly soluble in water. In an aqueous solution, the surface of the zeolite is hydrated, changing its surface charge. At pH = 5, when Cu^{2+} ions dominate (Fig. 1), the zeta potential was about -25 mV. As the pH increases further concentration of hydroxyl ions occurs in the diffusion layer of zeolite, and negative electrokinetic potential also increases.

At calcination temperature of 650°C, on the surface of ZCu-2 zeolite and in its micropores, dominate copper oxides γ-CuO and probably copper hydroxo oxide occurs (according to Wells) (Wells 1993). They form more stable connections with the zeolite matrix as compared to hydrated Cu compounds. A comparison of Figure 3a and 3b shows that Cu compounds, which form on ZCu-2 at lower calcination temperatures, migrate to the solution more readily at pH > 6. This may be caused by: (i) mechanical abrasion of copper oxide crystallites from the external surface of zeolite ZCu-2 during mixing, (ii) higher Cu concentration on the ZCu-2 zeolite surface (occurring in the form of CuO) than on ZCu-1.

Less Cu compounds migrate at lower initial pH (Fig. 3b), which is a consequence of the formation of acidic Brönsted active sites and detention of Cu in the zeolite matrix. Changes in the initial pH from 3 to 9 can result in reactions (3) and (4), which reduce the amount of copper leached to the solution.

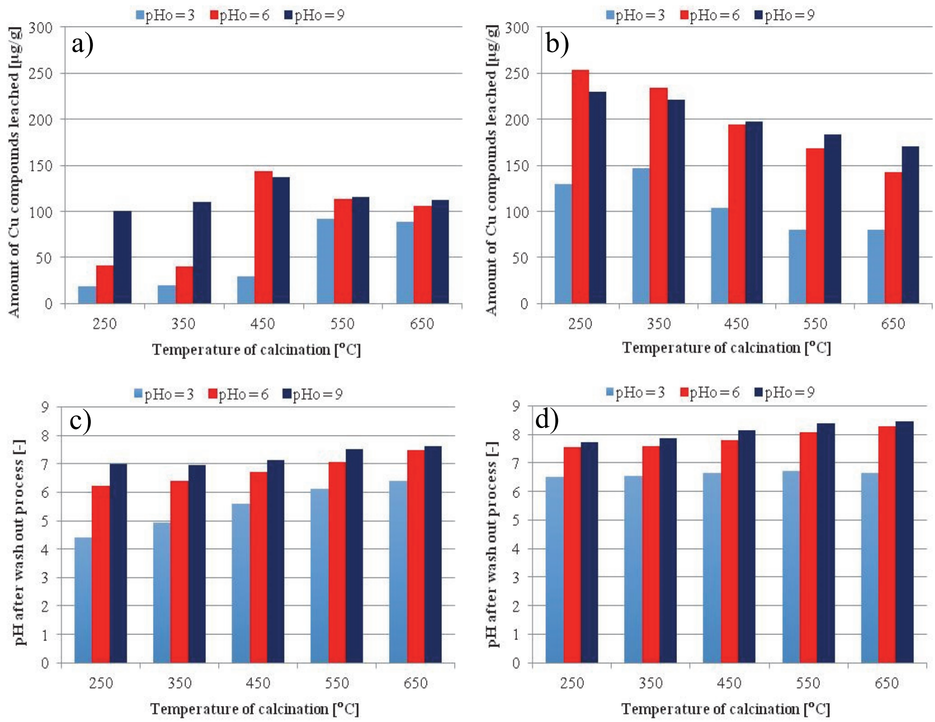


Fig. 3. Impact of calcination temperature of zeolite on amount of leached Cu compounds and pH after wash out process in function of initial pH of solution after 24 hour contact of zeolite with aqueous solution: (a, c) ZCu-1, (b, d) ZCu-2

Different relationships were observed for ZCu-1 zeolite (Fig. 3a and 3c). Migration of copper compounds from the zeolite matrix to the solution increases significantly only after calcination at temperature of 450°C. The copper content at lower calcination temperatures, at pH ≤ 6, remains at a level of about 40 μg/g of ZCu-1.

Compounds of copper (II) present on the zeolite surface (for the calcination temperature < 450°C) undergo hydration to $Cu(OH)_{2aq}$ in solution, which pH_{PZC} is from 9.5 to 10.2 (Kosmulski 2001). That is why, there is an excess of positively charged $Cu\text{-}OH_2^+$ groups in the solution and on the zeolite surface. Decreasing of the pH value below 5 brings about the process of jamming copper in the zeolite:

$$Z\text{-}CuOH^+ + H^+ = Z\text{-}Cu^{2+} + H_2O \quad (7)$$

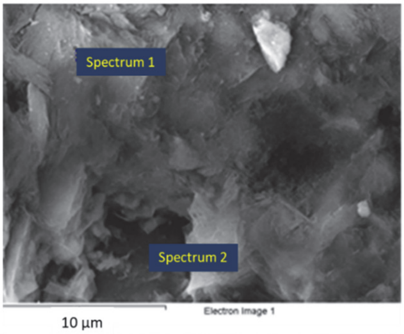
At higher calcination temperatures, stable forms of copper oxides γ-CuO (pH_{PZC} 7,5) are formed on the zeolite surface (Kosmulski 2001), which can migrate to the solution as suspension, increasing the Cu concentration.

Study of the surface and pores of zeolites calcinated at temperature 650°C, performed with an electron scanning microscope, showed that ZCu-2 zeolite contains much more copper (approx. 5% wt.) as compared to ZCu-1 (0.12% wt.) – Figure 4.

Modification of zeolite using Na_2CO_3 as a precipitation agent resulted in sorption copper (II) carbonates on the surface of the zeolite, which during calcination decomposed into CuO, CO_2 and water. SEM images show numerous crystallites, mainly CuO, which is also confirmed by EDS analyses (high concentration of copper and oxygen) – Fig. 4b.

Analysis of the surface of ZCu-1 zeolite showed that it was covered with copper compounds in a small range (0.12% wt.). SEM image clearly shows crystals of clinoptilolite, the main component of natural zeolite, with a lamellar structure. However, several times larger amounts of copper were observed in its pores (0.72% wt.) – Fig. 4a, spectrum 2. Due to the low pH after the modification process, which favors creation of aqua and hydroxy ions of Cu(II), copper retention took place mainly due to ion exchange process. Cu (II) ions stuck in the zeolite channels were more strongly bound to the zeolite matrix than copper (II) ions retained at the external surface of zeolite. This a probable cause of their higher concentration in zeolite micropores.

(a)



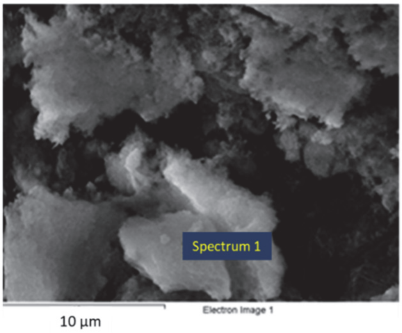
Spectrum 1

Element	Weight%	Atomic%
C K	16.25	22.94
O K	58.21	61.69
Na K	1.02	0.75
Al K	3.21	2.02
Si K	19.91	12.02
K K	1.02	0.44
Ca K	0.27	0.11
Cu K	0.12	0.03
Totals	100.00	

Spectrum 2

Element	Weight%	Atomic%
O K	31.96	46.23
Na K	1.10	1.10
Al K	4.53	3.88
Si K	55.29	45.56
K K	1.75	1.03
Fe K	4.66	1.93
Cu K	0.72	0.26
Totals	100.00	

(b)



Spectrum 1

Element	Weight%	Atomic%
C K	16.53	24.34
O K	52.42	57.94
Na K	0.98	0.75
Al K	3.34	2.19
Si K	20.17	12.70
K K	1.11	0.50
Ca K	0.33	0.14
Cu K	5.13	1.43
Totals	100.00	

Fig. 4. Qualitative characteristics of examined zeolites after calcination at temperature 650°C: (a) analysis of ZCu-1 zeolite surface (spectrum 1) and inside of the pores (spectrum 2), (b) analysis of ZCu-2 zeolite surface

4. Conclusions

The results presented in this paper showed considerable differences in the physicochemical properties of clinoptilolite modified with Cu(II) ions by precipitation with NaOH (ZCu-1) and Na_2CO_3 (ZCu-2). Concentration of copper in the matrix of ZCu-2 zeolite is nearly three times higher compared to ZCu-1 as early as after the third modification cycle. Low concentration of Cu in ZCu-1 was caused by dissolution of precipitable complexes $Cu(OH)_{2aq}$ to $Cu(OH)^+$ and Cu^{2+} in the presence of proton derived from H-form zeolite. Cu was detained in ZCu-1 as a result of electrostatic interactions between Cu(II) cations and the electronegative surface of zeolite. In ZCu-2 zeolite detention was caused by precipitation and coprecipitation of hydrated copper (II) carbonates (IV). Moreover, a significant effect of calcination process (at temperatures from 250°C to 650°C) has been confirmed, both on the surface charge of zeolite and on the amount and type of adsorbed copper. Various crystalline forms of Cu are formed. After calcination, on the surface of ZCu-2 in the function of temperature, polymorphic species of copper (II) oxide occur, which form more stable connections with the zeolite matrix as compared to ZCu-1. After modification process, the electrostatic activity of zeolite ZCu-1 is higher than that of ZCu-2. Its value depends on the concentration of potential-forming ions (pH) and the presence of co-ions, which also affect leaching of Cu from the zeolite matrix to the solution. It was proved that migration of Cu was affected by reactions of hydration, hydrolysis and complexing of Cu with the zeolite matrix. Depending on the solution's pH, corresponding Cu complexes are formed which significantly reduces their content in the zeolite structure.

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Abstract

Zeolites have been used in environmental engineering mainly in catalytic processes and as ion exchangers in water and wastewater treatment. Selective modified zeolites allow significant improvement in the effectiveness of impurities' removal without introducing additional reagents to the environment. The final effect of treatment of water solutions is determined by the catalyst used, its physicochemical properties and the process parameters.

In this work effectiveness of zeolite modification methods as well as their physical and chemical stability, taking into account the changes that take place during the process of calcination within the temperature range of 250°C to 650°C is presented. A natural clinoptilolite used in the experiment was transformed into the hydrogenous form and subsequently modified with copper (II) ions by coprecipitation with NaOH and Na_2CO_3. The effect of the method of the zeolite modification on Cu content, the zeolite Leaching capacity and surface charge was evaluated. An analysis of experimental results has shown that calcination temperature does not significantly change the surface charge, but does affect copper speciation. Analysis of EDS spectra by a scanning microscope, which showed that new and regular forms of copper compounds had been formed along the zeolite lattice structure is also presented.

The experimental results show that retention of Cu in zeolites was caused by electrostatic interactions between Cu(II) cations and the electronegative surface of the zeolite and coprecipitation of Cu(II) complexes.

Physicochemical properties of examined zeolites were affected by processes of hydration, hydrolysis and complexing of Cu with the zeolite matrix as a function of the solution's pH. Results show that the process of impurities' removal from water and wastewater depends on the method of zeolite modification and on the solution's pH.

Keywords:
zeolite, precipitation, surface modification, calcination, zeta potential, leaching

Właściwości fizykochemiczne zeolitu modyfikowanego miedzią

Streszczenie

W inżynierii środowiska zeolity stosowane są przede wszystkim jako wymieniacze jonowe w oczyszczaniu wody i ścieków oraz w procesach katalitycznych. Selektywne modyfikowane zeolity pozwalają na znaczące zwiększenie skuteczności usuwania zanieczyszczeń, jednocześnie nie wprowadzając dodatkowych reagentów do środowiska. O końcowym efekcie decyduje rodzaj zastosowanego katalizatora, jego właściwości fizykochemiczne oraz parametry prowadzenia procesu.

W pracy przedstawiono efektywność metod modyfikacji zeolitów oraz ich stabilność fizyczną i chemiczną, z uwzględnieniem zmian zachodzących podczas procesu kalcynacji w zakresie temperatur od 250°C do 650°C. W badaniach zastosowano zeolit naturalny klinoptylolit, który przeprowadzono w formę wodorową roztworem HCl, a następnie poddawano modyfikacji jonami miedzi (II) metodą współstrącania z użyciem NaOH i Na_2CO_3. Oceniono wpływ sposobu prowadzenia modyfikacji zeolitu na zawartość Cu, jego rozmywalność oraz ładunek powierzchniowy. Analiza wyników badań wykazała, że temperatura kalcynacji nie wpływa istotnie na zmianę ładunku powierzchniowego, ale na formę występowania związków miedzi. W pracy przedstawiono również analizę widm EDS wykonanych mikroskopem skaningowym, która pokazała, że wzdłuż struktury krystalicznej zeolitu zostały utworzone nowe i regularne formy związków miedzi.

Wyniki badań wykazały, że zatrzymywanie Cu w zeolitach zachodziło na skutek oddziaływań elektrostatycznych między kationami Cu(II) i elektroujemną powierzchnią zeolitu oraz w wyniku strącania i współstrącania kompleksów Cu(II).

Czynnikami wpływającymi na właściwości fizykochemiczne badanych zeolitów są procesy hydratacji, hydrolizy i kompleksowania Cu z matrycą zeolitu w funkcji pH roztworu. Przedstawiona w pracy analiza wyników badań wykazała, że proces usuwania zanieczyszczeń z wód i ścieków uzależniony jest od sposobu modyfikacji zeolitu oraz od pH roztworu.

Słowa kluczowe:
zeolit, strącanie, powierzchniowa modyfikacja, kalcynacja, potencjał dzeta, rozmywalność

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A Weibull Analysis of the Reliability of a Wastewater Treatment Plant in Nowy Targ, Poland

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1. Introduction

The technological reliability of a wastewater treatment plant (WWTP) can be defined as the probability that the facility will meet the requirements regarding the maximum permissible limits for pollution parameters in a given unit of time (Oliveira & Von Sperling 2008, Andraka & Dzienis 2003, Rak et al. 1989). In practice, the reliability of WWTPs is most often determined as a percentage reduction rate i.e. the difference between the values of pollution parameters in influent and effluent wastewater (Chmielowski & Ślizowski 2010, Młyński et al. 2016, Masłoń & Tomaszek 2013). Another, more advanced, method of reliability assessment used by many researchers in recent years is the method based on the three-dimensional Weibull distribution (Bugajski et al. 2012, Nastawny & Jucherski 2013, Bugajski 2014a, Bugajski et al. 2016, Marzec et al. 2018). In the case of WWTPs, the reliability obtained should be compared to the guidelines set out in the water quality permit, and if the facility turns out to be unreliable with respect to pollutant removal, measures should be taken to identify and then correct the deficiencies in the operation of the facility (Krzanowski & Wałęga 2006, Kuśnierz 2018). The technological reliability of treatment plants with a biological reactor with activated sludge in regard to pollution removal is affected by many factors, both dependent and independent of the operators of those facilities; the most important of these factors are the high variability in the quantity and quality of influent wastewater, its temperature, the ratio of organic carbon concentration to nitrogen and phosphorus concentrations, the content of toxic substances, and even the content of antibiotics in wastewater (Sadecka & Płuciennik-Koropczuk 2011, Takács 2008, Kaczor & Bugajski 2012, Vaiopoulou & Gikas 2012, Smyk et al. 2017). In Poland, one of the most important factors that have an adverse effect on the operation of WWTPs is the illegal discharge of stormwater into sewerage systems (Kaczor 2012, Pecher 1999). Stormwater, which is extraneous water, causes hydraulic overloads in wastewater treatment plants and leads to the cooling down of wastewater in winter (Kaczor et al. 2017, Michalska & Pecher 2000). To increase the reliability of WWTPs and thus reduce the risk of excessive amounts of pollutants being discharged into the environment, measures should be taken to eliminate the illegal discharge of meltwater and industrial wastewater into sewerage systems and to raise the ecological awareness of sewage system users (Kallas et al. 2015, Ren et al. 2018).

The aim of the present study was to assess the reliability of a wastewater treatment process with the use of a modified Weibull method. The experiments were conducted in a collective wastewater treatment plant in Nowy Targ, Poland. The obtained pollution removal reliabilities were compared to maximum permissible limit values specified in the water quality permit for this facility. Moreover, relative exceedance frequency values were determined for the individual parameters. The following parameters were analyzed: biochemical oxygen demand (BOD_5), chemical oxygen demand (COD_{cr}), total suspension (TS), chromium ions (Cr), total nitrogen (TN) and total phosphorus (TP).

2. Material and methods

2.1. Study site

The sewerage system in Nowy Targ has a length of 86.9 km, The system is divided into two water catchment areas: the Szaflary Axis and the Ludźmierz Axis. The sanitary network is built of stoneware (about 40%), concrete (about 10%) and reinforced concrete WIPRO pipes (about 10%) with diameters from DN 200 to 400 mm. At present the sewerage system is being modernized/recently the system has been modernized using new technologies, mainly PVC pipes as well as new generation stoneware and composite pipes made of fiberglass-reinforced plastic. Wastewater from the sanitary sewage network is drained to the WWTP mainly by gravity, but four sewage pumping stations are also used to support the gravity-driven flow. Currently, the sewerage system is used by 47 537 residents. Additionally, 60 legally operating fur companies are connected to the sewerage system. They discharge industrial wastewater. The household and industrial sewage flows into the collective mechanical and biological wastewater treatment plant with a designed flow capacity of $Q_{m.d..} = 21\ 000\ m^3 \cdot d^{-1}$ and a PE (population equivalent) = 116 000. The sanitary sewage system also receives illegal discharge of storm water, which, according to the data provided by the employees of the WWTP in Nowy Targ, represents 12% of the total amount of influent wastewater.

2.2. Characteristics of the wastewater treatment plant

The wastewater treatment plant in Nowy Targ was established in 1995 and is located at 49°29'N, 20°3'E. Sewage from the municipal sewerage network is conveyed via a collector with a diameter DN = 1.2 m to a pumping station. The main pumping station operates two pumps with a capacity of 1400 $m^3 \cdot h^{-1}$. The pumps lift sewage to a height of 7.5 m for easy gravity flow through the entire process line. The sewage flows from the pumping station to a screen room, where screenings are caught on two step-screens with a slot width of 3 mm and a rated power of 1.5 kW. Then, the wastewater flows into two sand traps, where mineral substances such as sand or gravel are sedimented. The sand separated by sedimentation is discharged into a sand scrubber separator, and after cleaning and dewatering, is fed into a container. The wastewater leaving the sand traps is conveyed by an 800 mm DN pipeline to two primary settling tanks. The horizontal-flow settling tanks are 42.0 m long, 6.0 m wide and 3.6 m high. Primary sludge is collected in sludge hoppers and cyclically removed to a gravity thickener. Biological treatment is performed using the sequencing batch reactor method. In the biological treatment section, three bioreactors are installed, which work in 8-hour cycles. Each of them is 70 m long, 23 m wide and 4.5 m deep. Treated wastewater, after decanting, is discharged through a 1000 mm DN collector pipe to the receiver, the Dunajec river.

The permissible limits (concentrations or minimum reduction rates) of pollutants for water leaving the wastewater treatment plant, as specified in the water quality permit for the Nowy Targ facility, are given below:

- BOD_5 – 15 $mg \cdot dm^{-3}$
- COD – 125 $mg \cdot dm^{-3}$
- Total suspension – 35 $mg \cdot dm^{-3}$
- Chromium – 0.5 $mg \cdot dm^{-3}$

Maximum permissible limit in concentration units

- Total nitrogen – 70%
- Total phosphorus – 80%

Minimum reduction rate in percent

2.3. Analytical and statistical methods

The study was conducted over two years (2016-2017). During this period, 87 samples of raw and treated wastewater each were collected and analyzed. Samples of influent wastewater were collected from the inlet channel using an autosampler programmed with respect to the wastewater flow rate. Effluent samples were taken from the outfall to the Dunajec river, which receives wastewater from the investigated treatment plant. Samples of wastewater were subjected to physical-chemical analysis in accordance with the reference methods set out in the applicable legal acts (Dz.U./2014/1800).

- BOD_5 – oxygen content was measured after 5 days of incubation at 20°C in OXI TOP – 197 WTW
- COD_{cr} – the dichromate test according to PN-ISO 6060:2006
- Total suspension – samples were filtered through GF/A glass fiber filters, dried for 1 hour at 105°C and weighed on a Santorius BA 210S analytical balance according to PN-EN 872:2007
- Chromium – Hach DR 2800 spectrophotometer using LCK 313 cuvette tests
- Total nitrogen (Kjeldahl) – according to PN-EN 25663:200
- Total phosphorus – Hach DR 2800 spectrophotometer using LCK 349 and LCK 350 cuvette tests.

The technological reliability of the WWTP in Nowy Targ was determined using the Weibull method. As Bugajski demonstrated in his previous studies (Bugajski et al. 2012, Bugajski 2014b), the Weibull distribution is a general probability distribution that can be successfully used to determine the technological reliability of WWTPs. The Weibull distribution can be used when the failure rate (in the case of a wastewater treatment plant, the exceedance rate) follows a monotonic trend. The Weibull distribution is characterized by the probability density function (1) with parameters b, c and θ (Bugajski et al. 2012):

$$f(x) = \frac{c}{b} \cdot \left(\frac{x-\theta}{b}\right)^{(c-1)} \cdot e^{-\left(\frac{x-\theta}{b}\right)^{c}} \tag{1}$$

where:
x – variable defining the concentration of a pollutant in treated wastewater,
b – scale parameter,
c – shape parameter,
θ – location parameter,
under the assumption that θ <x, b> 0, c> 0.

The reliability function R(x), as a complement to unity of the distribution function F(x), is given by the formula (Bugajski 2012):

$$R(x) = 1 - f(x) \tag{2}$$

where:

$$F(x) = 1 - exp\left[-\left(\frac{x-\theta}{b}\right)^{c}\right] \tag{3}$$

The Weibull distribution parameters were estimated using the maximum likelihood method. Goodness of fit of the Weibull distribution to empirical data was assessed with the Hollander-Proschan test. The results obtained in this part of the study were analyzed using STATISTICA 8 software.

In the analytical part of the study regarding the frequency of occurrence of characteristic values/concentrations of the analyzed parameters, the magnitudes and widths of class intervals were determined according to the guidelines provided by Jóźwiak & Podgórski (2001).

$$\mathbf{k = 5logn} \tag{4}$$

where:
k – number of class intervals (5 < k < 20),
n – sample size

The class intervals for the particular pollution parameters were selected so that the frequency distribution would provide a detailed and clear picture of the structure of the statistical set. The maximum permissible limits of the pollutant parameters were used as class boundaries.

3. Results and discussion

3.1. The quality of raw sewage

In the initial part of the analysis, the values of the investigated pollution parameters were determined in influent wastewater. The mean and median BOD_5, total nitrogen and total phosphorus values for the influent were similar to the typical values of these parameters in domestic wastewater, as given in the literature (Kaczor 2009, Gajewska 2015, Henze et al. 2010, Koutsou et al. 2018). In the case of COD and total suspension, the mean and median values exceeded the values typically reported for domestic wastewater (Kaczor 2009, Gajewska 2015, Henze et al. 2010, Koutsou et al. 2018, Abbassi et al. 2018, Stańko et al. 2016). As shown by previous studies on the characteristics of wastewater in the Nowy Targ WWTP, the increased values of some of the pollution parameters in raw sewage were due to the substantial share of industrial wastewater coming from fur companies

(Nowobilska-Majewska 2017, Bugajski et al. 2017). BOD_5, COD and TN values in the influent showed moderate variability according to the scale given by Wawrzynek (2007), with the coefficient of variation Cv ranging from 0.3 to 0.35. In the case of Total suspension, TP and chromium ions, a large variation (according to the Wawrzynek scale (2007)) was found, with Cv for these parameters ranging from 0.43 to 0.51. The statistics for the investigated pollution parameters of influent wastewater are given in Table 1.

Table 1. Descriptive statistics for the investigated pollution parameters of raw sewage

Parameter	Unit	Statistics					
		Average	Median	Min.	Max.	Standard deviation	Coefficient of variation
BOD_5	$mg \cdot dm^{-3}$	498.5	485.1	206.5	935.0	148.4	0.30
COD		1615.9	1559.0	552.0	3074.0	559.7	0.35
TS		1079.5	980.0	2650.0	2210.0	478.4	0.44
Cr		7.75	6.84	2.04	20.90	3.92	0.51
TN		106.6	104.2	44.2	209.3	31.5	0.30
TP		18.2	17.2	5.4	51.8	7.9	0.43

3.2. Technological reliability of the WWTP

The technological reliability of the wastewater treatment plant with regard to pollutant removal was determined using the Weibull distribution. A hypothesis was tested for the estimated distribution parameters that the Weibull distribution could be used to approximate the empirical data. An analysis of the p-value of the investigated parameters showed that the null hypothesis was true. The results of the Hollander-Proschan goodness-of-fit test along with scale, shape and location parameters are shown in Table 2.

The minimum (permissible) reliability limit adopted in this study was 93.72% (at the manufacturer's risk of $\alpha = 0.05$), a value established by Andraka and Dzienis (2003) for WWTPs of above 50.000 PE. According to those authors (2003), the permissible failure rate (exceedance rate) of a facility of this size is 22 days per year at a risk level $\alpha = 0.05$.

The technological reliability of BOD_5 reduction to the limit value of 15 $mg \cdot dm^{-3}$ was 72.5%, as shown in Fig. 1A. In other words, the probability of exceedance for BOD_5 in treated wastewater was 27.5%. A comparison to permissible reliability values shows that the BOD_5 removal reliability during the investigated period was 21.22% lower than required. A BOD_5 removal reliability of 72.5% means that the maximum permissible limit of this parameter in treated wastewater may be exceeded on nearly 100 days a year (365 days). The difference between the number of exceedances for BOD_5 and the allowable number of days on which the facility fails to operate properly, at $\alpha = 0.05$, was 78 days a year.

Table 2. Results of the estimation of the Weibull distribution parameters together with the measures of goodness of fit to empirical data

Parameter	Unit	distribution parameters			Hollander-Proschan test	
		b	c	θ	Test value	p
BOD_5	$mg \cdot dm^{-3}$	12.641	1.5330	3.3384	0.647505	0.51730
COD		97.315	2.9992	39.9490	0.569031	0.56934
TS		34.269	1.4892	3.5909	0.675626	0.49928
Cr		0.44481	2.3524	0.0000	0.372182	0.70976
TN	%	90.657	14.095	−5.0000	−1.34174	0.17968
TP		94.224	25.668	−10.0000	−0.624557	0.53226

COD removal reliability to the limit value of 125 $mg \cdot dm^{-3}$ was 88%, as shown in Figure 1B. The difference between the minimum required reliability (93.72%) and the measured reliability (88%) was 5.72%. This means that the treatment plant did not meet the requirements for effluent COD concentrations on about 44 days a year. When one subtracts from this number the number of allowable exceedances per year (22 days), it turns out that the maximum permissible COD concentration in treated wastewater was in excess of the standard on 22 days a year.

In the case of total suspension, the technological reliability of the plant relative to the permissible concentration of 35 $mg \cdot dm^{-3}$ was 65% (Fig. 2C). The number of exceedances per year was 128 days. Given that the allowable number of exceedances is 22 days, the plant exceeded the standards for total suspension on 106 days a year.

In the case of chromium (Cr), the removal reliability was 72.5% (Fig. 1D). This is the same level of reliability as in the case of BOD_5. The maximum permissible concentration of Cr in wastewater, which is 0.5 $mg \cdot dm^{-3}$, was exceeded on about 100 days a year. When one subtracts from this number the number of allowable exceedance days (22 days), it transpires that Cr concentration norms were exceeded at the study site on 72 days a year.

The coefficients of determination R^2 for the parameters whose reliabilities are described by the cumulative distribution functions in Figs. 1A, 1B, 1C and 1D are as follows: BOD_5 – 0.9884, COD – 0.9919, TS – 0.9421, Cr – 0.9327. These results show that the Weibull model of reliability described by the cumulative functions in Figs. 1A, 1B, 1C and 1D shows a very high goodness-of-fit.

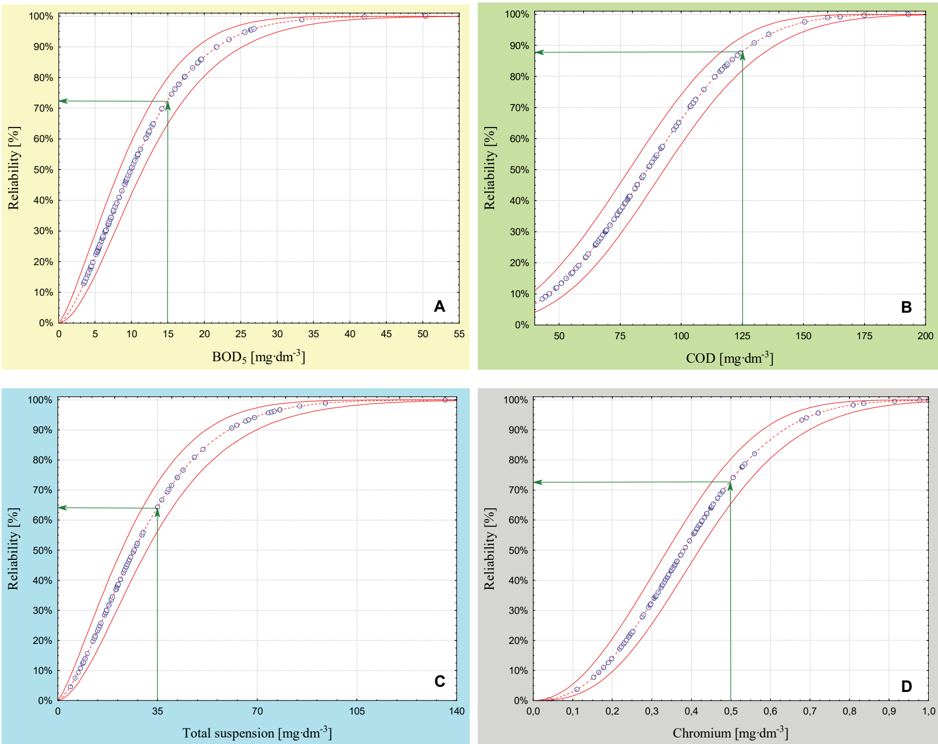

Fig. 1. Weibull cumulative distribution functions and the technological reliabilities determined for the pollution parameters expressed as a concentration

In the case of biogenic elements (TP and TN), for which permissible limits were defined as minimum reduction rates, the following reliabilities were obtained based on Weibull reliability analysis: 97.5% for total nitrogen removal to the minimum effluent discharge limit of 70% (Fig. 2A), and 98% for total phosphorus removal to the required minimum level of 80% (Fig. 2B). In both cases, the reliability values were higher than the minimum required removal reliability of 93.72%. It should be pointed out, however, that the reliability data also show that total nitrogen and total phosphorus reduction rates were lower than the required minimum on 9 and nearly 7 days a year, respectively.

The coefficients of determination R^2 for the biogenic elements were: TN – 0.8521 and TP – 0.7986, which shows that the Weibull model of TN and TP removal reliabilities described by the cumulative distribution functions in Figs. 2A and 2B had a high goodness-of-fit, which was, however, lower than in the case of the four previously analyzed parameters.

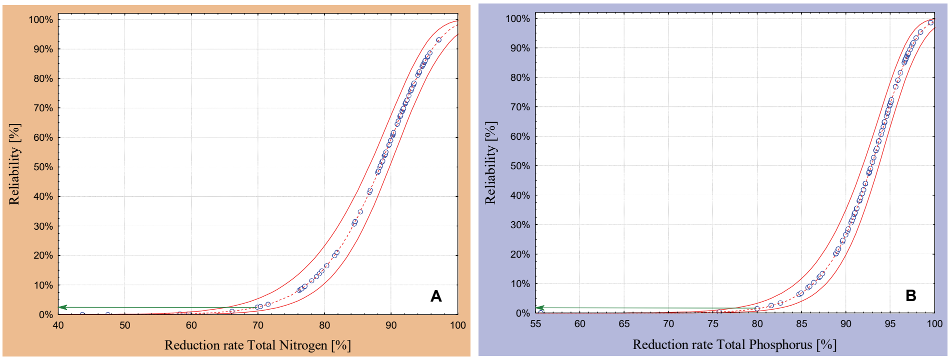

Fig. 2. Weibull cumulative distribution functions and the technological reliabilities determined for the pollution parameters whose limit values are expressed in percent

The analysis of the technological reliability of the WWTP in Nowy Targ performed using the Weibull model confirms literature reports that the Weibull method aptly describes the reliability of various technologies used in wastewater treatment plants (Bugajski et al. 2012, Nastawny & Jucherski 2013, Bugajski 2016, Jóźwiakowski et al. 2018, Marzec 2017, Marzec et al. 2018). The removal reliabilities for Total suspension, BOD_5 and COD of 65%, 72.5% and 88%, respectively, are lower than those described by Marzec et al. (2018) and Nastawy & Jucherski (2013). In the case of biogenic parameters, the reliability of the investigated facility is comparable to that reported by Bugajski (2014) and Jóźwiakowski et al. (2018).

3.3. Relative exceedance frequency

According to the literature, valuable information for purposes of maintenance and potential modernization of wastewater treatment systems can be obtained by determining exceedance frequency values for pollution parameters of effluent wastewater (Henze et al. 2010, Kaczor 2001). Frequency analysis is a very useful statistical tool for the interpretation of results of regularly and irregularly performed measurements.

In this part of the study, the frequency of occurrence of specific concentrations/reduction rates and exceedance frequencies of the analyzed pollution parameters were determined in treated wastewater. This allowed us to determine the relative exceedance frequencies (%) for the investigated pollution parameters. Also, based on this analysis, we were able to identify the modal class intervals (ones with the highest frequency of observations) for the individual effluent parameters. After calculating the frequency of occurrence of the values of the particular pollution parameters, the number of frequency distribution classes was determined for each parameter. Five interval classes were adopted for BOD_5, with a class width of 5 mg·dm^{-3} (Fig. 3A). Also five classes were delimited for COD, but class width was 25 mg·dm^{-3} (Fig. 3B). In the case of COD, the lowest interval class was 0 to 75 mg·dm^{-3}, as COD concentrations lower than 50 mg·dm^{-3} were not recorded in this study. The same number of classes (five) was established for Total suspension, and the class width was calculated at 17.5 mg·dm^{-3} (Fig. 3C). For chromium ions, four classes with a width of 0.25 mg·dm^{-3} (Fig. 3D) were considered. In the case of biogenic parameters, measured as a reduction rate, six classes with a width of 10% were established for total nitrogen (Fig. 4A) and five classes with a width of 10% were adopted for total phosphorus (Fig. 4B). For all the investigated parameters, class limits were defined so that the permissible limit or the minimum reduction rate should constitute a closed limit of the class interval. This allowed us to determine the relative frequency as percentage of the number of exceedances of a given parameter in relation to its permissible limit.

For BOD_5, the percentage of observations (samples) in the classes from 15 to 20 mg·dm^{-3} and above 20 mg·dm^{-3} was 12.6% and 10.3%, respectively (Fig. 3A). In total, 23.0% of all wastewater samples fell in these two intervals. The analysis of the relative exceedance frequency for BOD_5 showed that the largest number of observations for this parameter were in the interval from 5 to 10 mg·dm^{-3}. For COD, the frequency of occurrence in the two class intervals above the limit of 125 mg·dm^{-3} totaled 8.0% of all wastewater samples (Fig. 3B). No modal interval was observed for effluent COD, which indicated that COD removal processes in the investigated treatment plant were unstable. The frequency of occurrence of Total suspension concentrations from 35 to above 70 mg·dm^{-3} (Fig. 3C) in sewage samples was 25.3%. The modal class interval for Total suspension was the interval from 17.5 to 35.0 mg·dm^{-3}, which contained 48.3% of all observations. Concentrations of chromium ions in treated wastewater in excess of the permissible limit were observed in 16.1% of cases, i.e. all observations in the intervals from 0.5 to 1.0 mg·dm^{-3} (Fig. 3D). The modal class interval for Cr was 0.25 to 0.50 mg·dm^{-3}, which contained 64.4% of all effluent chromium ion concentrations.

An analysis of the frequency of occurrence of biogenic parameters, whose levels are expressed as a reduction rate, showed that TN and TP reduction rates below the adopted minimum limits (70% and 80%, respectively) constituted 6.9% and 2.2% of all events, respectively (Figs 4A and 4B). In the case of TN, the largest number of events (52% of all observations) was recorded in the interval above 90%. Similar results were obtained for TP, for which 78.2% of all observations fell in the interval above 90%. These findings show that the reduction rates of total nitrogen and total phosphorus were high. Nevertheless, cases of a low reduction rate should be identified and measures should be taken to increase the rate of removal of biogenic waste.

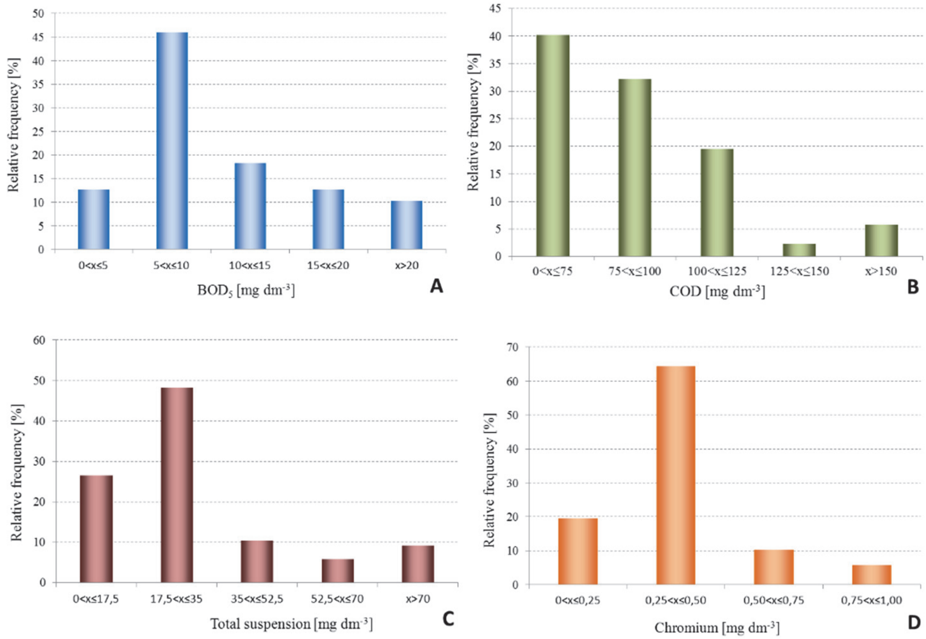

Fig. 3. Histograms of relative frequency for the pollution parameters measured in concentration units (mg·dm^{-3}) – BOD$_5$, COD, TS, Cr

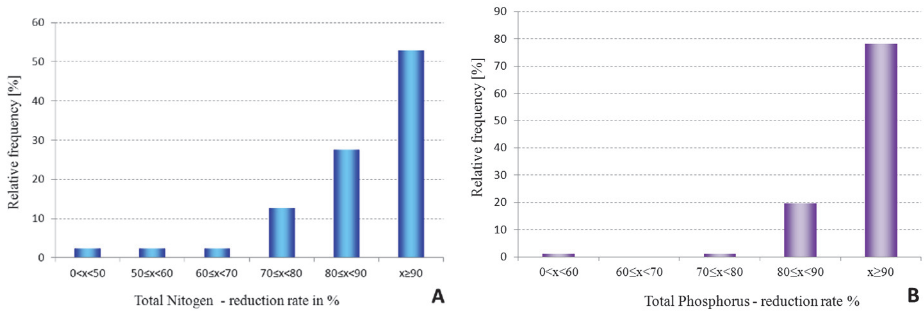

Fig. 4. Histograms of relative frequency of TN and TP reduction rates (%)

As a last step of the analysis of the results obtained in this study, we determined the number of exceedances for the analyzed parameters in relation to the permissible number of exceedances laid down in the applicable legal provisions. In accordance with the Regulation of 18 November 2014 (Dz.U./ 2014/1800) Annex 7, current Polish legislation specifies the number of sewage samples collected during the year which are allowed not meet the specific water quality permit requirements. This can be defined as the "tolerance limit". Given that we collected 43 wastewater samples in 2016 and another 44 samples in 2017, according to the provisions of Annex 7 (line 6) to the abovementioned Regulation, the allowable number of exceedances which did not adversely affect the operation of the treatment plant was five. The exceedance frequency data show that in each research year the permissible limits were exceeded on 84 days for BOD_5, 29 days for COD, 92 days for Total suspension, 59 days for Cr, 25 days for TN and 8 days for TP. This means that the tolerance limit of five exceedance events was exceeded for all the analyzed parameters.

4. Conclusions

The Weibull analysis of the technological reliability of the wastewater treatment plant in Nowy Targ demonstrated that the facility was the most reliable with regard to the removal of the biogenic components: total nitrogen and total phosphorus. The plant was 97.5% reliable in achieving the minimum TN reduction rate of 70% and 98.0% reliable in achieving the minimum TP reduction rate of 80%. The reliabilities obtained for the parameters measured as concentrations were as follows: 72.5% for BOD_5, 88% for COD, 65% for Total suspension and 72.5% for chromium ions. The relative exceedance frequency values for these parameters were 23%, 8%, 25.3% and 16.1% of all analyzed wastewater samples, respectively. For the biogenic parameters, whose permissible limit values are expressed as minimum reduction rates, values lower than the required minimum were found in 2.5% of all observations for total nitrogen and in 2% of all observations for total phosphorus. The number of exceedances per year for all the investigated parameters was larger than the "tolerance limit" of five days laid down in the legal provisions in force in Poland. When analyzing the causes of the malfunction of the investigated WWTP in Nowy Targ, which is part of a combined sewerage system, it is first necessary to determine which of those causes are the result of improper operation of the plant and which are independent of the operator. Then appropriate corrective actions should be taken.

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Abstract

In the study, the Weibull method was used to determine the technological reliability of a collective wastewater treatment plant in Nowy Targ in Poland in regard of its ability to meet effluent discharge standards for selected pollution parameters. In addition, relative exceedance frequencies were calculated for this facility. The experiments were conducted in 2016 and 2017. During this period, 87 samples of influent and effluent wastewater were collected and analyzed. The parameters investigated in the study included BOD_5, COD, Total suspension and chromium Cr, for which the maximum permissible limits specified in the water quality permit are expressed as concentrations, and TN and TP, for which limit values are defined as minimum reduction rates (%). The technological reliability values for the parameters measured in concentration units were 72.5% for BOD_5, 88% for COD, 65% for Total suspension, and 72.5% for Cr. The relative exceedance frequency was 23% of all measurement series for BOD_5, 8% for COD, 25.3% for Total suspension, 16.1% for Cr, 2.5% for TN, and 2.0% for TP. It was found that the number of exceedances per year for all the investigated parameters was larger than the "tolerance limit" of five days laid down in the legal provisions in force in Poland relating to the quality of wastewater discharged to a reservoir. The results show that measures should be taken to identify the causes of the observed deficiencies in the reduction of the analyzed pollution parameters in the technological line of the treatment plant and that corrective action should be pursued.

Keywords:
wastewater, wastewater treatment plant, technological reliability,
frequency of occurrence

Analiza niezawodności funkcjonowania oczyszczalni ścieków w Nowym Targu (Polska) z zastosowaniem metody Weibulla

Streszczenie

Celem pracy jest wykorzystanie metody Weibulla w celu określenia niezawodności technologicznej odnośnie uzyskania wartości normatywnych w ściekach oczyszczonych dla wybranych wskaźników zanieczyszczeń w zbiorczej oczyszczalni ścieków w Nowym Targu. Ponadto w pracy określono częstość względną występowania ponadnormatywnych wartości analizowanych wskaźników. Badania prowadzono w latach

2016 i 2017, gdzie w tym okresie pobrano i poddano analizie po 87 próbek ścieków dopływających i odpływających. W pracy uwzględniono wskaźniki, dla których wymagania w pozwoleniu wodno-prawnym podano jednostce wagowej i są to: BZT_5, ChZT, zawiesina ogólna i chrom Cr oraz wskaźniki, dla których wymagania określono, jako minimalny stopnień redukcji (%) i są to: azot ogólny oraz fosfor ogólny. Niezawodność technologiczna dla wskaźników, których miarą jest jednostka wagowa wynosi dla BZT_5 – 72.5%, dla ChZT – 88% dla zawiesiny ogólnej – 65% i dla chromu Cr – 72.5%. Częstość względna występowania ponadnormatywnych wartości lub stopnia redukcji dla analizowanych wskaźników wynosi dla BZT_5 – 23%, dla ChZT – 8%, dla zawiesiny ogólnej – 25.3%, dla jonów chromu Cr – 16.1%, dla azotu ogólnego – 2.5% i dla fosforu ogólnego – 2.0% przypadków w stosunku do wszystkich serii pomiarowych. Stwierdzono, że liczba dni w roku, w których występują wartości ponadnormatywne dla badanych parametrów przekracza liczbę 5 dni, czyli „granicę tolerancji" wskazaną w obowiązującym w Polsce akcie prawnym dotyczącym jakości ścieków odprowadzanych do odbiornika. Na terenie analizowanego systemu kanalizacyjnego zaleca się podjąć działania w celu identyfikacji przyczyn występujących nieprawidłowości unieszkodliwiania analizowanych wskaźników w ciągu technologicznym oczyszczalni i podjąć działania naprawcze.

Słowa kluczowe:
ścieki, oczyszczalnia ścieków, niezawodność technologiczna, częstość występowania

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Bacteriological Air Quality at Animal Veterinary Practice

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1. Introduction

In recent years, biological factors are becoming a serious problem of occupational medicine and public health. Hazards caused by these factors are related to specific professions, as well as to the presence and properties of individual factors. The microorganisms present in the air, such as bacteria and fungi can cause adverse health effects (infections, immunotoxic diseases and allergies) (Thorne et al. 1992, Kalogerakis et al. 2005, Frączek et al. 2018). The disease effect, ensuing from the inhalation of various molecules in the air, depends primarily on their size, chemical composition, microbiological properties and the place of their depositing in the human respiratory tract (Kelly & Fussell 2012). Carrying out duties by vet or veterinary technician during contact with the animals and work with products of animal origin are considered to be related to exposure to harmful biological agents (Rim & Lim 2014). Despite the relatively low prevalence of serious zoonotic diseases, veterinarians must remain vigilant. Small animal veterinary practitioners must be aware of the risks of zoonotic diseases for their own safety. The reservoir for microorganisms that can cause disease are wild, farm and home animals. The cause of the disease may be contact with an sick animal as well as contact with its excretions and secretions, such as: faeces, urine, mucus or contact with material of animal origin (Weese et al. 2002).

Due to the fact that the microbiological quality of air is a very important factor in the workplace, the aim of this study was to characterize this property of air at the small animal veterinary practice based on the number and species composition of the bacterial population.

2. Materials and methods

The study was carried out at the premises of the animal veterinary practice in Krakow (Poland) in 2017, in two measuring rounds, during the contractually agreed „summer" season (6-month period from April to September), with average outside air temperature above 10°C persisting for at least 7 days (in the summer period, in the temperate climate zone, a higher concentration of fungal aerosol is observed, both in the indoor and outdoor air). The veterinary practice takes care of pets, mainly dogs and cats. The tests were carried out at one veterinary practice, which was selected as a „model" object (on the basis of previous studies). The samples of air were collected in duplicate at four measuring points. A total of 96 air samples were analyzed. The selected rooms were those in which animals were housed or through which there was a regular flow of animals on a daily basis (treatment room, a room with cages in which animals are housed after treatments and waiting room) inside the building. Air samples were collected before opening, five hours after opening and after the veterinary practice work. All studied rooms were naturally ventilated.

Additionally, the air samples were collected at a point situated outside the building (as the "background"). The air samples were collected by using a six-stage Andersen cascade sampler (model 10-710, Graseby-Andersen, Inc., Atlanta, GA). The sampler was placed at a height of 1.5 m above the floor or ground (outdoor measurements) to simulate the aspiration from the human breathing zone. A 5-minute sampling period and the flow rate of 28.3 $dm^3 \cdot min^{-1}$ were applied for the collection of air samples. Bacteria were collected on tryptic soy agar (TSA LAB-AGARTM, Biocorp), EMB medium (Biocorp) for Gram-negative bacteria and Chapman's medium (Biocorp) for mannitol-positive staphylococci. During sampling, the air temperature and relative humidity were measured using a hygrometer Kestrel 4000. The TSA plates were incubated for 24 hour at 37°C, then 3 days at 22°C and another 3 days at 4°C. The EMB and Chapman's plates were incubated for 24 hours at 37°C. The prolonged incubation of samples for culturing of bacteria or fungi enables the growth of slowly growing strains at a lower temperature range. After incubation, the bacterial colonies were counted. The concentration of bioaerosol was calculated as the number of colony forming units per cubic meter of air ($cfu \cdot m^{-3}$) (Wlazło et al. 2008, Bulski 2017, Frączek et al. 2018).

Due to the specificity of the studied environment, randomly selected bacterial strains, differing from each other macroscopically, were preliminary identified by Gram staining for their morphology and, finally, by the mass spectroscopy (MALDI TOF MS), using laser desorption/ionization, with matrix-assisted and time-of-flight analyzer, by using MALDI Biotyper analyzer (Bruker).

The results were statistically analysed using Statistica 13.1 (StatSoft, Inc., Tulsa, OK, USA). The collected data was characterized by parametric distribution (Shapiro-Wilk test). The analysis of variance (one-way and two-way ANOVA) was performed and the significance of differences between means was verified by the Tukey's test ($\alpha = 0.05$). The results showing the effect of microclimatic parameters (temperature and relative humidity) on the prevalence of airborne microorganisms were evaluated using the r coefficient of the Pearson's correlation.

3. Results

The concentrations of bacterial aerosol are presented in Table 1, Table 2 and Figure 1. Concentrations of total number of bacteria in the studied premises ranged from 256 to 1123 cfu·m^{-3}. The results showed that the highest average concentration value of bacterial aerosol was observed in the treatment room and the lowest concentration was observed in the waiting room. The analysis (one-way ANOVA) showed a significant differences in the concentrations of bacterial aerosol between the treatment room and outdoor air (Tukey's test: $p < 0.05$). The concentrations of bacterial aerosol were higher in the indoor air than in the outdoor air, but the differences between waiting room, room with cages and outdoor air were not statistically significant (Tukey's test: $p > 0.05$). The analysis of two-way ANOVA showed that the higher concentration of total number of bacteria in the studied rooms was observed in the treatment room after veterinary practice work and the lowest concentration was observed in the waiting room, five hours after opening. The analysis showed that there were no significant differences in the concentration of total number of bacteria in treatment room taking into account the measuring time (Tukey's test: $p > 0.05$). The same results were observed in waiting room. There were significant differences in concentration of total number of bacteria only in room with cages before opening and five hours after opening (Tukey's test: $p < 0.05$).

Concentrations of Gram-negative bacteria in the studied premises ranged from 0 to 398 cfu·m^{-3}. The results showed that the highest average concentration value of Gram-negative bacteria was observed in the treatment room and the lowest concentration was observed in the room with cages. The concentrations of Gram-negative bacteria aerosol were higher in the outdoor air than in the indoor air, but the analysis (one-way ANOVA) showed a non-significant differences in the concentrations of Gram-negative bacteria between indoor and outdoor air (Tukey's test: $p > 0.05$). The analysis of two-way ANOVA showed that the higher concentration of Gram-negative bacteria in the studied rooms was observed in the treatment room five hours after opening and the lowest concentration was observed in room with cages, after practice work. The analysis showed that there were no significant differences in the concentration of Gram-negative bacteria in indoor air taking into account the measuring time (Tukey's test: $p > 0.05$).

Table 1. Bacterial aerosol concentrations (cfu·m^{-3}) at animal veterinary practice and outdoor air

Environment		Total number of bacteria		Gram-negative bacteria		Mannitol-positive staphylococci	
		Range	Median	Range	Median	Range	Median
Indoor air	Treatment room	567-1123	699	9-398	27	151-1404	474
	Room with cages	468-1016	628	0-27	9	196-804	469
	Waiting room	256-725	469	18-115	45	159-645	381
Outdoor air		397-496	447	9-239	124	159-447	318

Table 2. Average bacterial aerosol concentration (cfu·m^{-3}, ±SD) in indoor air at animal veterinary practice (two-way ANOVA)

Measuring time x Measuring point		Average±SD		
		Total number of bacteria	Gram-negative bacteria	Mannitol-positive staphylococci
Before opening	Treatment room	580ab*±18	27a±0	826b±817
	Room with cages	526a±82	14a±6	491a±331
	Waiting room	452a±125	111a±6	323a±232
Five hours after opening	Treatment room	699ab±25	208a±269	935b±335
	Room with cages	1003b±19	18a±13	500a±430
	Waiting room	415a±225	27a±13	495a±212
After work	Treatment room	1012b±157	18a±13	160a±13
	Room with cages	628ab±25	5a±6	354a±161
	Waiting room	562ab±231	36a±25	469a±88

* averages marked with the same letters are not significantly different by Tukey's test (α = 0.05)

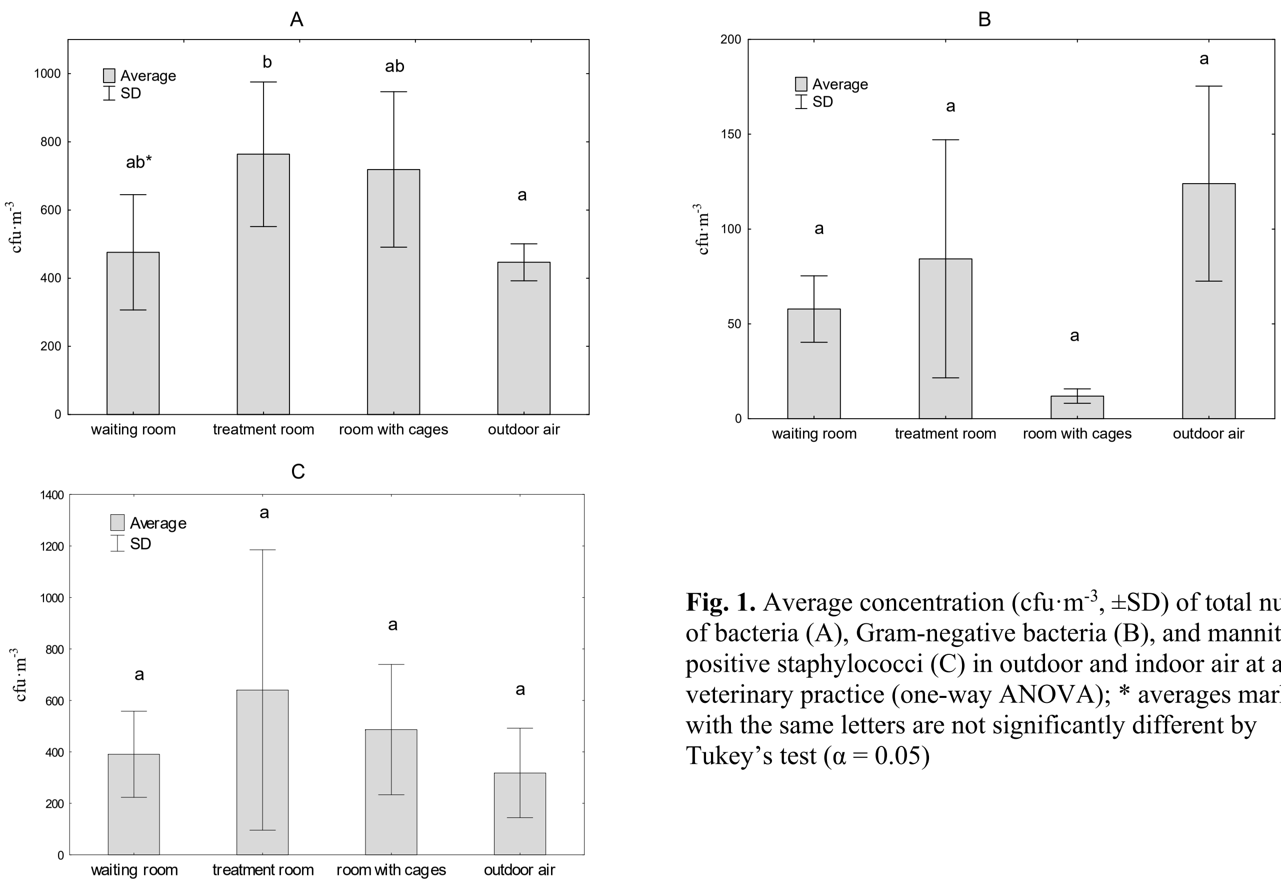


Fig. 1. Average concentration (cfu·m^{-3}, ±SD) of total number of bacteria (A), Gram-negative bacteria (B), and mannitol-positive staphylococci (C) in outdoor and indoor air at animal veterinary practice (one-way ANOVA); * averages marked with the same letters are not significantly different by Tukey's test ($\alpha = 0.05$)

Concentrations of mannitol-positive staphylococci in the studied premises ranged from 15 to 1404 cfu·m^{-3}. The results showed that the highest average concentration value of mannitol-positive staphylococci was observed in the treatment room and the lowest concentration was observed in the waiting room. The concentrations of mannitol-positive staphylococci aerosol were higher in the indoor air than in the outdoor air, but the analysis (one-way ANOVA) showed a non-significant differences in the concentrations of staphylococci between indoor and outdoor air (Tukey's test: $p > 0.05$). The analysis of two-way ANOVA showed that the higher concentration of mannitol-positive staphylococci in the studied rooms was observed in the treatment room five hours after opening and the lowest concentration was observed also in treatment room but after practice work. The analysis showed that the concentrations of mannitol-positive staphylococci in treatment room before opening and five hours after opening were significantly higher than concentrations in treatment room after veterinary practice work (Tukey's test: $p < 0.05$).

Microclimate conditions may affect the number of microorganisms and their spread in the air (Katial et al. 1997). Results of microclimate parameters measurments are presented in Table 3. Analysis of the impact of the temperature and relative humidity on the observed bacterial aerosol showed a significant correlation between the concentration of total number of bacteria and temperature ($R = 0.45$, $p < 0.05$) and relative humidity ($R = 0.37$, $p < 0.05$). There were no significant correlations between the concentrations of Gram-negative bacteria or mannitol-positive staphylococci and studied microclimate parameters ($p > 0.05$).

Table 3. Temperature and relative humidity of indoor and outdoor air at animal veterinary practice

Environment		Temperature [°C]		Relative humidity [%]	
		Range	Median	Range	Median
Indoor air	Treatment room	22.5-24.1	23.6	52.5-64.5	60.7
	Room with cages	22.7-22.9	22.7	54.5-62.3	60.9
	Waiting room	22.5-25.7	23.2	49.2-59.1	57
Outdoor air		20.2-21.8	20.7	50.3-62.6	58.2

By using a 6-stage Andersen's air sampler, it was possibile to get information about the size distribution of air bacterial biota in the investigated measuring points at the small animal veterinary practice (Figure 2 A-C). Based on the analysis of bioaerosol particle size distribution it was observed that in the treatment room the bacteria concentration had a maximum value in a range of diameters 2.1-3.3 µm. It shows that these microorganisms were present in the air as single cells and small aggregates and can be deposited in the human respiratory tract in primary bronchi. In the treatment room, Gram-negative bacteria concentration had a maximum value in a range of diameters 0.65-1.1 μm, so these microorganisms were present in the air as a single cells (and can be deposited in the human respiratory tract in secondary bronchi and brionchioles). Mannitol-positive staphylococci concentration had a maximum value in a range of diameters 4.7-7.0 μm (medium aggregates), so they can be deposited in the human respiratory tract in throat and trachea (Owen & Ensor 1992, Wlazło et al. 2008). In room with cages for animals, the total number of bacteria and Gram-negative bacteria concentration had a maximum value in a range of diameters 1.1-2.1 μm. Mannitol-positive staphylococci concentration had a maximum value in a range of diameters 4.7-7.0 μm. The analysis showed that in the waiting room the total number of bacteria concentration had a maximum value in a range of diameters 4.7-7.0 μm, Gram-negative in a range of diameters 1.1-2.1 μm and the mannitol-positive staphylococci concentration had a maximum value in a range of diameters 3.3-4.7 μm.

The percentage shares of identified bacteria in the examined veterinary practice are presented in Figure 3 (A-B). A total of 11 species of bacteria have been identified. In the indoor air, the predominant groups of microorganisms were rods of the *Bacillus* genus and Gram-positive cocci from the *Micrococcus* and *Staphylococcus* genus. *Bacillus thuringiensis*, *Staphylococcus saprophyticus*, *Micrococcus luteus*, *Staphylococcus Arletta*, *Bacillus jeotgali*, *Bacillus pumilus*, *Bacillus vallismortis*, *Paenibacillus amylolyticus*, *Lysinibacillus fusiformis*, *Enterococcus faecium* and *Pseudomonas putida* were isolated. From the outdoor air only 3 bacterial species were isolated (*Bacillus thuringiensis*, *Micrococcus luteus* and *Pseudomonas putida*).

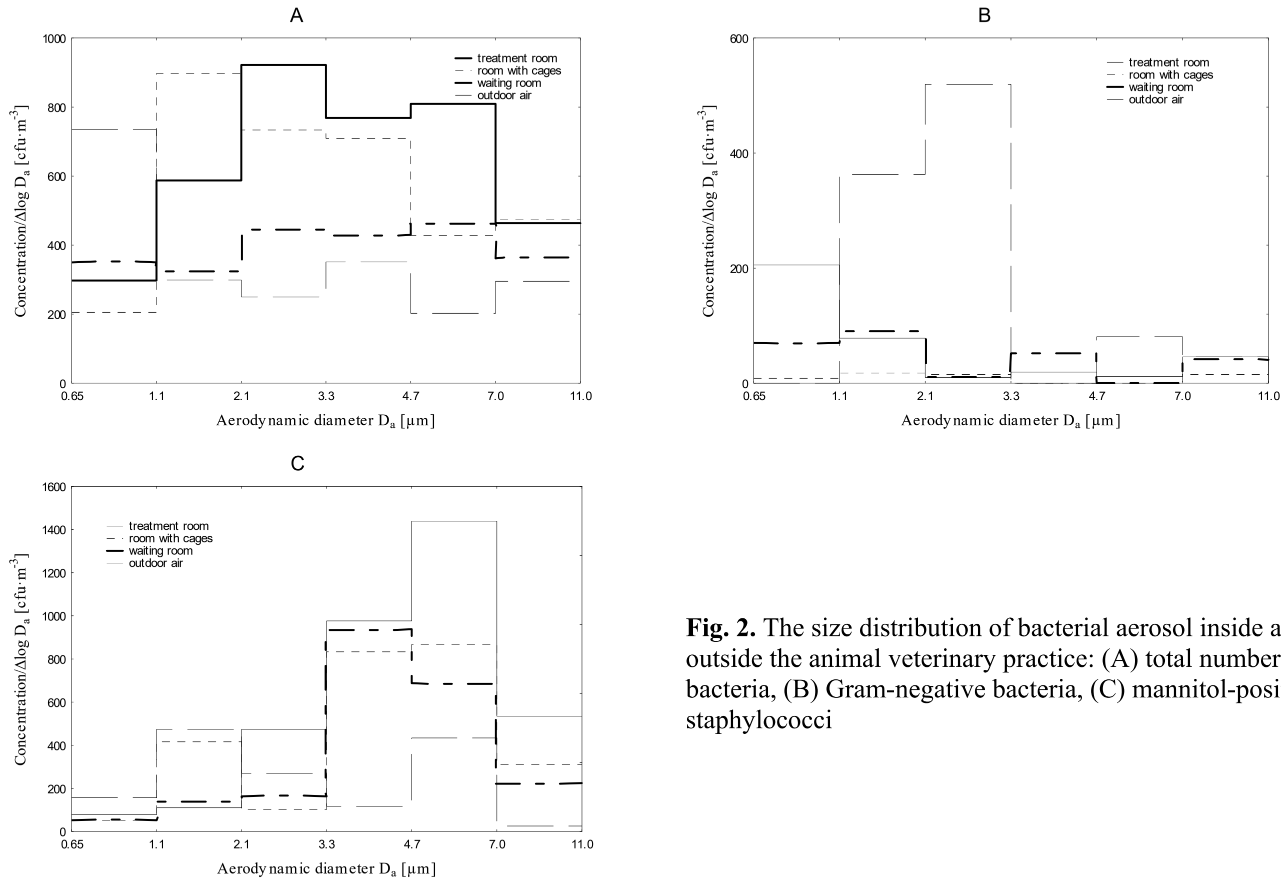
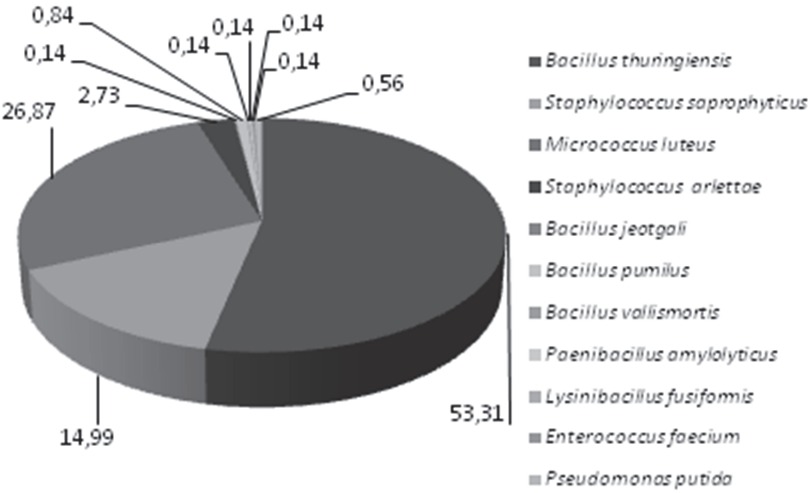


Fig. 2. The size distribution of bacterial aerosol inside and outside the animal veterinary practice: (A) total number of bacteria, (B) Gram-negative bacteria, (C) mannitol-positive staphylococci

A



B

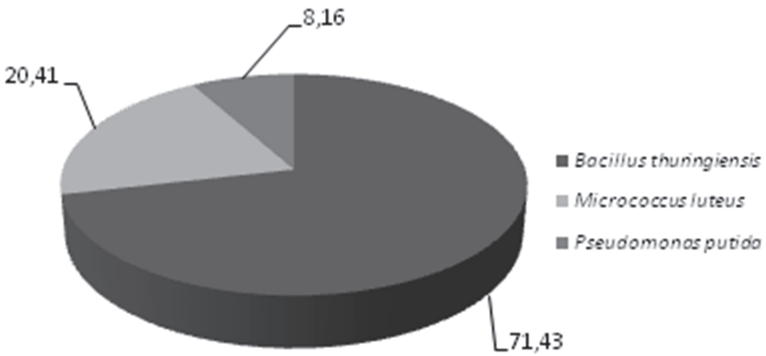


Fig. 3. The results of the identification of bacteria (%) isolated from the air at the studied animal veterinary practice: (A) indoor air, (B) outdoor air

4. Discussion

Occupational exposure to zoonotic diseases is an ingerent risk in veterinary medicine (Weese et al. 2002). In these studies an assessment of the microbiological quality of air in a small animal veterinary practice was made. Concentrations of total number of bacteria in the studied premises ranged from 256 to 1123 cfu·m^{-3}. The obtained results of indoor measurements of bioaerosol concentrations were compared with the Polish proposals for threshold limit values, which are $5 \cdot 10^3$ cfu·m^{-3} for bacteria in indoor and outdoor environments. It was found that the average concentrations of total number of bacteria obtained in this study were lower than reference values for total number of bacteria in residential and public buildings recommended by the Polish Panel of Experts of Biological Factors (Górny 2010). Low bioaerosol concentrations and similar results were obtained in studies in small animals veterinary hospitals (Harper et al. 2013). The inhalation of airborne Gram-negative bacteria can cause respiratory diseases (for example a chronic lungfunction impairment) (Zucker et al. 2000). In indoor air, the highest concentration of Gram-negative bacteria was observed in treatment room. The average concentrations of these microorganisms were also lower than reference values for Gram-negative bacteria in residential and public buildings ($2 \cdot 10^2$ cfu·m^{-3}) (Górny 2010). Because exsposure to endotoxins is associated with respiratory and systemic pathologies, endotoxin measurements should be carried out in future research (Samadi et al. 2010, Dequenne et al. 2013). In the indoor air, one of the predominant groups of microorganisms were Gram-positive cocci from the *Micrococcus* and *Staphylococcus* genus. It confirms the results obtained in bioaerosol studies in veterinary teaching hospitals in Taiwan (Chen et al. 2017). *Staphylococcus* was the third most frequently isolated genus from the air. It should be emphasized that the environment, such as small animal veterinary practice, may be an important source of MRSA infection (Hanselman et al. 2008). Some of the isolated bacteria such as *Pseudomonas putida* or *Staphylococcus arlettae* can be potentially pathogenic for human (Yang et al. 1996, Dinakaran et al. 2012). In the indoor and outdoor air the dominant bacterial species was *Bacillus thuringiensis*. Bacteria of the genus Bacillus occurs mainly in the external environment (eg soil, plants) and can be transmitted by people into the interior of the rooms (eg on clothes or footwear) (Wlazło et al. 2008). Statistical analysis showed significantly higher airborne microbial contamination in different measuring points at different measuring times of the day. Taking into account the normal size of one of the dominant group of bacteria (Gram-positive cocci), with aerodynamic diameters in the 1.1-2.1 μm range, it was found that the analysis of bioaerosol particle size distribution indicates additional emission of Gram-positive cocci from their main reservoir, which is the human body (increased emission during intense breathing and abrasion of the epidermis during work). Based on the results of this study it was found that the largest "load" of bacteria, isolated from the air, can reach (in the human respiratory system) to the region of the nasal and oral cavity, throat and trachea, as well as bronchioles (Owen & Ensor 1992). This information is very important for the assessment of the effects of biological aerosols on the human body (the place of deposition of a harmful factor usually determines the type of adverse health response). Analysis of the impact of the temperature and relative humidity on the observed bacterial aerosol showed that the increase in temperature and relative humidity affects the increase in concentration of bacteria in tested air at small animal veterinary practice, which is consistent with the observations of other authors (Li & Kendrick 1995).

5. Conclusions

Concentrations of bacterial aerosol between the internal studied rooms at the veterinary practice were not significantly different and were always lower than 1123 cfu·m^{-3}. The highest concentrations of total number of bacteria in the studied rooms was observed in the treatment room after veterinary practice work. However, the results of this study showed the possible biological risks for the veterinary workers or clients of small animal veterinary practice. Although the concentrations of bacterial aerosol were not exceed the proposals of limit values, it was found that among the detected bacteria pathogenic species as: *Pseudomonas putida* and *Staphylococcus arlettae* were present. To protect people from occupational injuries it is recommended to maintenance proper disinfection and sterilization procedures in workplaces with health education to the animal care workers. Therefore, there should be introduced a high-performance mechanical ventilation or air conditioning system, providing the appropriate microbiological quality of air in rooms where animals need adequate medical care.

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Abstract

Due to the nature of the work (animal treatment and care of animals) the environment of small animal veterinary practice can be contaminated by microorganisms. Therefore, veterinary practices or hospitals are facilities, where veterinarians, clients and animals can be exposed to biological agents. The objective of the study was to characterize the bacteriological quality of air in small animal veterinary practice in Krakow. Bioaerosol measurements were performed during the summer season of 2017. The samples of outdoor and indoor air at small animal veterinary practice were analyzed, using a 6-stage Andersen`s air sampler. The highest concentration of bacterial aerosol was observed in the treatment room. There were statistically significant differences in the concentrations of bacterial aerosol between indoor and outdoor air. Also, the analysis showed that there were significantly higher airborne microbial loads in different rooms at different measuring times of the day. Based on the analysis of bioaerosol particle size distribution it was found that the largest "load" of bacteria, isolated form the air, can reach (in the human respiratory system) to the region of the nasal and oral cavity, throat and trachea, as well as bronchioles. In the indoor air, the predominant groups of microorganisms were rods of the *Bacillus* genus and Gram-positive cocci from the *Micrococcus* and *Staphylococcus* genus. The study confirmed that the small animal veterinary practice can be a workplace related to exposure to microbial agents.

Keywords:
bioaerosol, bacteria, air, animal veterinary practice

Bakteriologiczna jakość powietrza w gabinecie weterynaryjnym

Streszczenie

Ze względu na specyfikę pracy (leczenie oraz opieka nad zwierzętami) środowisko gabinetu weterynaryjnego może być zanieczyszczone mikrobiologicznie. Gabinety czy szpitale weterynaryjne są placówkami, w których weterynarze, klienci i zwierzęta mogą być narażeni na działanie czynników biologicznych. Celem badań była charakterystyka bakteriologicznej jakości powietrza w gabinecie weterynaryjnym w Krakowie. Pomiary bioaerozolu wykonano w okresie lata w 2017 r. Próbki powietrza zewnętrznego oraz wewnętrznego w gabinecie weterynaryjnym pobierano przy pomocy 6-stopniowego impaktora Andersena. Najwyższe stężenie aerozolu bakteryjnego obserwowano w pokoju zabiegowym. Odnotowano istotne statystycznie różnice w stężeniach aerozolu bakteryjnego pomiędzy powietrzem wewnętrznym, a tłem zewnętrznym. Analiza wykazała również istotnie wyższe stężenia mikroorganizmów w zależności od punktu pomiarowego i pory dnia. Analizując rozkłady ziarnowe bioaerozolu stwierdzono, że najwyższy „ładunek” bakterii może dotrzeć (w układzie oddechowym człowieka) do rejonu jamy nosowej i jamy ustnej, gardła i tchawicy, a także oskrzelików. W powietrzu wewnętrznym dominującymi grupami mikroorganizmów były laseczki z rodzaju *Bacillus* i Gram-dodatnie ziarniaki z rodzaju *Micrococcus* i *Staphylococcus*. Badanie potwierdziło, że gabinet weterynaryjny może być miejscem pracy związanym z narażeniem na czynniki mikrobiologiczne.

Słowa kluczowe:
bioaerozol, bakterie, powietrze, gabinet weterynaryjny

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Thermal Decomposition of Asbestos Fiber from Asbestos Cement Wastes

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1. Introduction

Asbestos was widely used as a result of the industrial revolution of the last 100 years. Most of it was used for the production of asbestos cement products (Maciołek et al. 2012). Chrysotile asbestos constitutes from 90% to 95% of all asbestos used all over the world (Frank & Joshi 2014). It was added about 15% by weight to the total weight of cement-asbestos slates (Kusiorowski et al. 2014). The theoretical composition of chrysotile is: 13% H_2O, 33.65% MgO, 43.55% SiO_2 (Bolewski & Manecki 1993). Despite the fact that asbestos has been widely used in our everyday life, studies have shown for many years that it is not indifferent to human health. The greatest risk is release of fibers from products containing asbestos, as they penetrate the respiratory system, causing various diseases. Asbestosis, lung cancer, larynx, ovaries, mesothelioma (Więcek 2004) are some of the diseases that are caused by asbestosis. The World Health Organization (WHO) and the Agency for Research on Cancer (IARC) recommend phasing out asbestos due to its carcinogenic effects. It is estimated that occupational exposure to asbestos causes an estimated 107,000 deaths of people worldwide each year (Takahashi & Landigran 2016). As a result, a ban on the use, production and marketing of asbestos products has been introduced or is in the implementation process in many countries. Since 2005, the ban on asbestos has been in force in all EU countries (Commission Directive 1999/77/EC). Asbestos is banned in 60 countries around the world. Unfortunately, there are still countries where asbestos products are on the market. According to data published by the United States Geological Survey (USGS), asbestos production worldwide in 2015 was approximately 1.4 million Mg. The largest percentages were Russia, China, Brazil and Kazakhstan. In addition, asbestos products are still sold or used in many countries, including India, Indonesia, Bangladesh, Kyrgyzstan, Colombia (Kazan-Allen 2017). Currently, India is the world's largest importer of asbestos (Minerals.usgs.gov 2018).

Due to the harmfulness of asbestos, it is important to control its disposal and use in various products. Asbestos products should also be safely disposed, and the waste containing asbestos should be neutralized.

Currently, the dominant method of managing asbestos waste in the world is its storage or the use of solidification, which involves covering asbestos waste with a protective layer. These methods do not lead to the complete neutralization of hazardous fibers contained in asbestos waste, which can still be released into the environment. The European Parliament in its resolution on asbestos of 14 March 2013. (2012/2065(INI)) points out that asbestos is the preferred method of inertising when disposing of asbestos rather than storing it. Therefore, it is very important to look for and study technologies that would permanently eliminate the problem of fibrous structure of the asbestos. There are several dozen patented ways of disposing asbestos. These processes can also be divided into two groups: thermal, chemical and mechanochemical treatment.

Among thermal methods, the so-called vitrification is used at temperatures above 1000°C, where in various furnaces an inert silica material without fibers is obtained. Then, thermal methods based on the melting process, here at temperatures of 1350-1550°C, serpentine fibers are converted into silicate minerals and glass. Additionally, e.g. kaolin clay can be used in these processes in order to lower the melting point and obtain construction materials after the process (Belardi et al. 1998, Paolini et al. 2018, Poniatowska 2008). Attempts have been made in Germany and Italy to dispose of asbestos waste using a cement kiln. As a result of the process, glassy, amorphous clinker balls were obtained, and no harmful chrysotile asbestos fibers were found (Ambrosius et. al. 1996, Italcementi 1992, Paolini et al. 2018). Thermal disposal of asbestos-containing waste can also be carried out in plasma-based furnaces. As a result of neutralization in the plasma oven, a black, amorphous mass is formed, similar to glass, which can be reused in road construction and soil improvement (Klimas 1998, Paolini et al. 2018). In Poland, a technology using microwaves to neutralize asbestos has been developed. This process consists in heating the asbestos waste, which was previously crushed in a hermetic crusher, and then soaking it with additives, which improve wave absorption and reduce the temperature of the process up to 900-1000°C. Asbestos fibers are destroyed during processing (Paolini et al. 2018, Pawluk 2010).

Chemical methods use chemical reactions to convert asbestos into harmless compounds. Among others, strong acids, alkaline solutions, reducing factors such as metals in the elementary state are used. An interesting solution here is the technology using whey from the dairy industry, at high temperature and pressure, in the presence of a chelating agent, such as oxalic acid, lactic acid (Balducci et al. 2012, Paolini et al. 2018).

In case of mechanochemical methods, fibers are destroyed by mechanical grinding. There are used various mills in which crystalline networks and molecular bonds present in asbestos are destroyed. High energy milling is also based on this process (Deng et al. 2009, Paolini et al. 2018).

On the basis of available literature, it can be concluded that only methods affecting the transformation of asbestos fibers, e.g. chemical, thermal, cause that the waste produced as a result of their use is processed and inert for health. Therefore, these methods should be regarded as preferable for the disposal of asbestos waste.

2. Materials and methods

The aim of this paper was to evaluate the influence of temperature and time on asbestos decomposition and determine if the asbestos fiber structure is damaged at high temperatures.

The following test methods were used to achieve the study objective:

- Thermal analysis using a high-sensitivity balance, a furnace for heating the sample and a system for dosing the sample washed gases (derivatograph);
- Thermal treatment of waste in the furnace with electronically programmable temperature regulator;
- Observation of samples after calcination with the use of scanning electron microscope with EDS probe (Energy Dispersive Spectrometry) for analysis of qualitative composition of materials;
- Analysis of phase composition on X-ray diffractometer.

Tested samples of asbestos cement waste with a weight of 510 mg was heated at a rate of 7.5°C/min, from 20 to 1400°C for about 190 minutes in an air atmosphere using a 1500 D derivatograph, MOM Budapest.

Thermal treatment of asbestos cement waste was carried out by calcination in a Nabertherm furnace with electronically programmable temperature regulator, increasing the temperature at 10°C/min to 1000-1500°C, for 30 and 120 minutes.

In order to identify asbestos fibers in asbestos cement waste, a scanning electron microscope LEO type 1430 with EDS microanalyzer by Oxford Analytical type ISIS 300 was used to analyze the chemical composition in the micro-area.

Phase analysis was conducted on Philips X' Pert PW 3020 X-ray diffractometer for samples after calcination at 1250 and 1400°C for 120 minutes.

3. Research results and discussion

Figure 1 shows thermal analysis of cement-asbestos slates samples, DTA curve (thermal differential analysis) and DTG/TG curves (thermogravimetry) were obtained. Three effects correlated with specimen weight loss are visible in the obtained record on DTG curve. The first effect at a temperature of 120-160°C was related to the loss of adsorbed water and decomposition of gypsum being a slight admixture of cement slurry. The second maximum at the temperature of about 480-520°C is related to the dehydroxylation processes of chrysotile and hydrated silicates and aluminosilicates of calcium. The third maximum at the temperature of about 820°C is the effect of both the final dehydroxylation phases of the components of cement slurry and chrysotile (Paolini et al. 2018). The record of TG curve indicates a loss in mass of the sample equal to 33% in the range up to 500°C and 58% up to 820°C. It can be assumed that up to 820°C the main decrease in mass of the whole sample occurs, because the subsequent changes are already very small, there is a 5% decrease in mass. A total loss in mass was 61%. Therefore, the loss in mass of sample is related to water removal processes associated with Portland cement components. The image of changes in TG and DTG curves is also reflected in DTA curve. Effects on DTA curve are endothermal peaks associated with weight loss. At about 120-160°C this is associated with decomposition of the gypsum structure ($CaSO_4 \cdot 2H_2O$) which is an additive (retardant bond), a cement from which asbestos cement was made, leading to the formation of anhydrite ($CaSO_4$). The endothermal effect at a temperature of about 480-520°C results from chrysotile structure breakdown and initial phases of calcium silicates crystallization. The endothermal effect with a maximum of about 820°C results from calcite decomposition (Kusiorowski et al. 2015). At about 1320°C another endothermal effect is recorded, related to decomposition of calcium carbonates and polymorphic transformation of dicalcium silicate (belite) of γ to β (Bielankin et al. 1957).

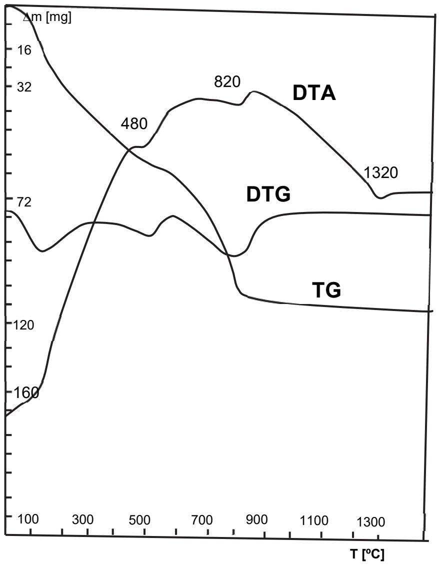
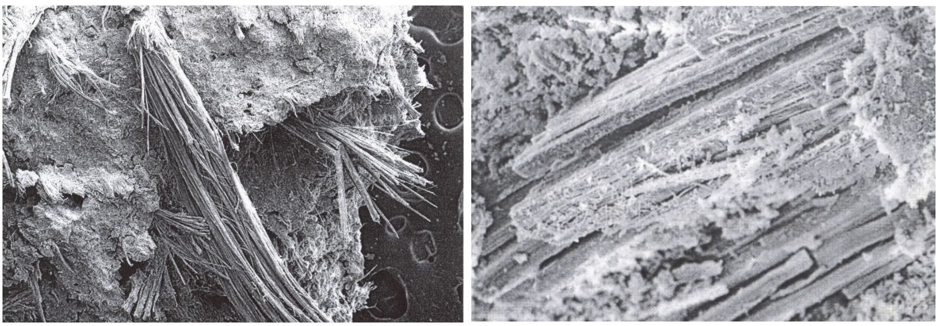


Fig. 1. DTA, DTG, TG curves of cement-asbestos slates after calcination at 1400°C forl190 minutes (Poniatowska 2008)

Tests conducted on a scanning electron microscope for raw samples show characteristic beams of chrysotile asbestos fibers. Cement minerals inlay asbestos fibers as a result of mixing with cement mass (Fig. 2a).

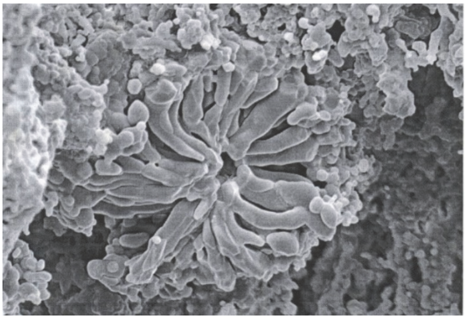


a) b)

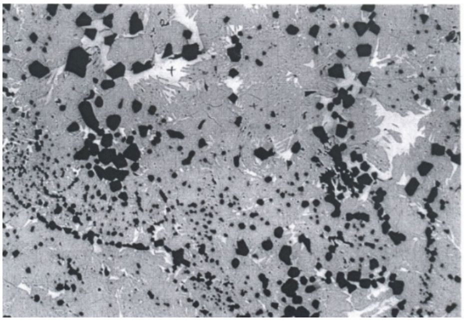
Fig. 2. SEM images of the sample of cement-asbestos slates a) and sample of cement-asbestos slates, in temperature of 1000°C for 30 minutes b) (Poniatowska 2008)

In case of samples after calcination at 1000°C, for 30 minutes (Fig. 2b), the first changes of asbestos in cement-asbestos slates are visible. Numerous packets and individual asbestos fibers are visible. Asbestos melting is at an early stages, and the packets are still prone to split into individual fibers.

Figures of samples after calcination at 1250°C for 120 minutes show the progress of calcination process in a form of increasing size of neogenic silicates contained in the cement binder, as well as their recrystallization along the asbestos fibers, which leads to their agglomeration and chemical transformation. Calcinated packet of chrysotile asbestos fibers creates characteristic rosettes. The number of visible fibrous packets in relation to samples after calcination at lower temperatures significantly decreases with the use of scanning electron microscope (Fig. 3a), and in the visible asbestos fibers are wrapped by calcium-magnesium silicates and the change of structure to granular.



a)



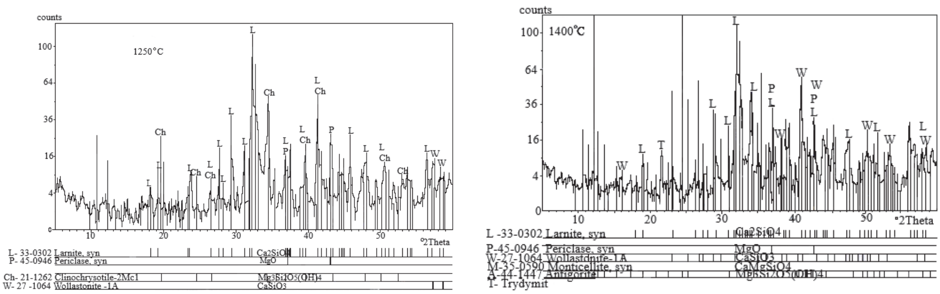
b)

Fig. 3. SEM images of sample of cement-asbestos slates in temperature of: a) 1250°C for 120 minutes, b) 1400°C for 120 minutes (Poniatowska 2008)

As a result of calcination process carried out for a longer period, an increase in the dimensions of crystallites of all components is obtained (Fig. 3b). Asbestos packets are completely transformed and converted into calcium silicates and magnesium oxide (periclase). Figure shows total calcination of asbestos in the sample. Black fields correspond to magnesium oxides, while light poles and needles are silicates and calcium aluminosilicates.

This is also confirmed by X-ray phase analysis (Fig. 4a), where in case of the sample after calcination at 1250°C for 2 hours, the presence of larnite and periclase as the main components, small amounts of wollastonite and trace amounts of chrysotile was observed. This type of composition indicates a significant sample transformation. As a result of dehydration of components, the tobermorite diminishes, a part of which is transformed into larnite (Kusiorowski et al.

2015). Larnite is also produced as a result of the synthesis reaction of calcium oxide and silica – components resulting from decomposition of calcite, as well as antigorite and chrysotile. Periclase is produced during decomposition of antigorite and chrysotile. Due to the excess of calcium over magnesium at 1250°C, the formation of calcium silicates will be the preferred process, and therefore magnesium oxide is present in the sample as a periclase.



a) b)

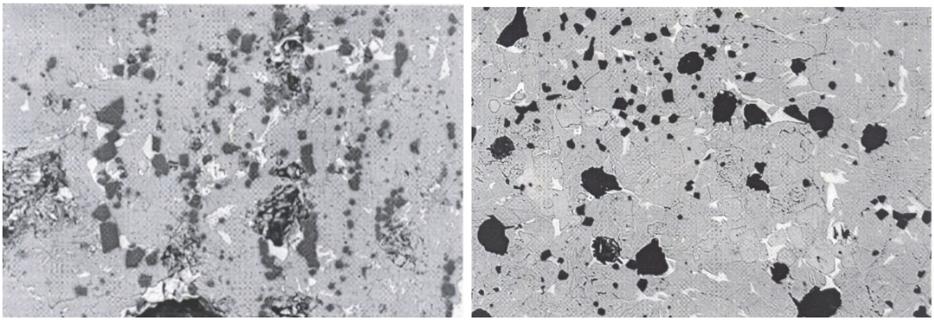
Fig. 4. X-ray diffraction patterns of cement-asbestos slates after calcination at: a) 1250°C for 120 minutes, b) 1400°C for 120 minutes (Poniatowska 2008)

In case of sample after calcination at 1400°C (Fig. 4b), larnite, periclase is dominant, wollastonite is likely, and monticellite and tridymite, antigorite and chrysotile were not found. The presence of tridymite should be associated with a far-reaching decomposition of antigorite and chrysotile. Monticellite is the effect of synthesis of calcium silicates with magnesium oxides. This type of composition confirms the process of asbestos disintegration from the serpentine group (antigorite and chrysotile).

Fig. 5a for samples after calcination at 1500°C for 30 minutes shows that the original structure of sample is transformed, barren silicates and calcium aluminates are formed and as a result of decomposition of chrysotile asbestos, magnesium oxides and di-calcium silicate are formed.

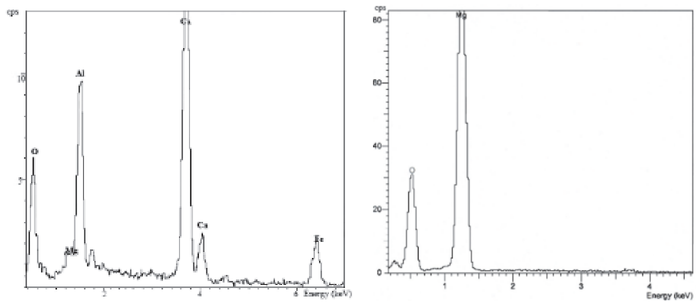
Heating the sample at 1500°C for 2 hours completely eliminates asbestos from cement-asbestos slates (Fig. 5b). The process of chemical transformation due to high temperatures led to the formation of coarse-crystalline calcium silicates, while the magnesium contained in chrysotile asbestos was transformed into an oxide phase in the form of periclase.

Three types of analytical spectra were obtained for this sample during the composition studies in the micro-area: for periclase (Fig. 6b), i.e. magnesium oxide, calcium silicates (Fig. 6c) and calcium-iron aluminates (Fig. 6a), formed as a result of calcination of asbestos cement components.

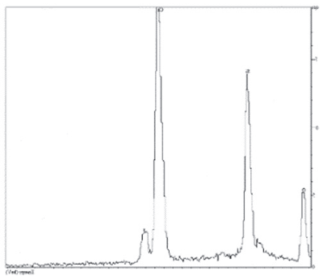


a) b)

Fig. 5. SEM images of sample of cement-asbestos slates in temperature of: a) 1500°C for 30 minutes, b) 1500°C for 120 minutes (Poniatowska 2008)



a) b)



c)

Fig. 6. Analytical spectrums of cement-asbestos slates, in temperature of 1500°C for 120 minutes, a) calcium and iron clay, b) periclase, c) calcium silicates (Poniatowska 2008)

Decomposition of chrysotile causes the release of silica, which leads to a preferential bonding with calcium oxide (resulting from the decarboxylation of $CaCO_3$ present in the old cement), resulting in the formation of dicalcium silicate, i.e. larnite. The calcination process leads to secondary clinkerisation, the main component of which is larnite, in cement terminology called belite and periclase resulting from the decomposition of chrysotile asbestos.

4. Conclusion

Based on the conducted research it can be established that thermal treatment of asbestos containing waste causes changes in the fibrous structure of the material. With the increase in temperature asbestos is transforming into neomorphic crystalline structures. In samples sintered in the temperature of 1250°C for 120 minutes trace amounts of chrysotile were found. When the temperature was increased to 1400°C, based on X-ray diffraction patterns, there were no traces of chrysotile. In this sample a significant recrystallization of alloy components and the beginning of periclase crystallization occurred, which is confirmed by photos of scanning electron microscope, analysis of the sample composition in the micro-area and the results of the phase composition analysis. When the temperature was increased to 1500°C, chrysotile contained in asbestos tile releases silica during decomposition, which binds to the calcium oxide from the cement phase. This produces dicalcium silicate (larnite), brownmillerite and periclase as a product of chrysotile decomposition. In this way, periclase is produced, magnesium oxide does not bind in silicate as excess calcium has a preference for secondary silicate formation. The calcination process leads to a second clinkerisation of the sinter components, the main components of which are larnite and periclase resulting from the decomposition of chrysotile asbestos. This composition confirms disintegration of asbestos in tested material and the formation of completely new, harmless phases. In case of samples sintered in the temperature of 1500°C for 30 minutes, phase composition studies were not carried out and thus it cannot be unequivocally stated that chrysotile asbestos has been eliminated. However, SEM image shows that the structure of the sample has transformed. Dark asbestos fiber residues are visible, which are probably magnesium oxides and dicalcium silicate. Extension of sintering time from 30 to 120 minutes for a temperature of 1500°C significantly changed the image of the SEM sample: there are no traces of asbestos fiber residue. Coarse crystalline calcium silicates and periclases are visible. To sum up, on the basis of thermal decomposition of cement-asbestos slates, it can be concluded that sintering of cement-asbestos slates at a temperature of 1400-1500°C causes a remold of the fibrous structure of chrysotile asbestos it contains. With the use of a method enabling such temperatures to eliminate the emission of asbestos fibers into the air (e.g. during cement production), subjecting it to heat treatment, we permanently change its structure and thus it becomes a mineral neutral to human health. Moreover, the material obtained gives potential uses for cement production (Witek et. al. 2012). This paper may provide a basis for further research on the possibility of thermal processing of asbestos-containing waste, in which the addition of fluxes to the process may also be considered, which reduce the decomposition asbestos temperature in asbestos cement (Poniatowska 2008).

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Abstract

Negative impact of products including asbestos and asbestos wastes on human health comes from asbestos' needle-like, fibrous structure. To terminate its negative influence on the environment, including human health, processes aimed at its destruction should be conducted. Basing on available literature one can ascertain that only chemical and thermal methods of asbestos fibers translation cause the ensuing waste to be health neutral. The aim of this paper was to evaluate the influence of temperature and time on asbestos decomposition and determine if the asbestos fiber structure is damaged at high temperatures. In the first stage of heating cement-asbestos slates, the physicochemical processes occurring in the material under investigation will involve dewatering, i.e. removal of adsorptive, constitutional and crystallizing water, followed by breaking down the chrysotile structure and destruction of its brucate layers, finally crystallization of the forsterite and later its disintegration into silica and periclase. During the sintering of asbestos cement we have an excess of calcium oxide coming from cement components. Chrisotile contained in asbestos cement exorcises during its dissolution silica which merges with calcium oxide from the cement phase. Thus arises bicalcium silicate (larnite), brownmillerite and periclase as a product of chrisotile dissolution. Periclase is therefore formed, magnesium oxide does not bind in silicate because the excess of calcium has the preference for the secondary formation of silicates. The process of sintering causes its contents to clinkering again, the main component of which is larnite and periclase resulting from the decay of chrysotile asbestos. It causes potential possibilities of using the products of this method to produce cement.

During the tests, in the temperature rises to 1400°C, there is a significant recrystallization of components and the beginning of the crystallization of periclase, which is confirmed by scanning tests, analysis of sample composition in the micro-area and results of phase composition analysis. To sum up, based on the conducted studies of the thermal decomposition of cement-asbestos slates, it can be concluded that sintering it at a temperature of 1400-1500°C leads to the transformation of the fibrous structure of the chrysotile asbestos contained therein. With the use of a method that allows the operation of such temperatures, eliminating the emission of asbestos fibers into the air, subjecting it to thermal treatment, we permanently change its structure and in this way it becomes a mineral indifferent to human health. In addition, the obtained material gives the potential to use products of this method of neutralizing cement-asbestos slates, e.g. in construction. This paper might be the basis for further research of the possibilities of thermal processing of asbestos-containing waste, in which the addition of fluxes to the process, affecting the decomposition temperature of asbestos in cement-asbestos slates can also be considered.

Keywords:
asbestos, asbestos wastes, asbestos cement, thermal decomposition of chrysotile asbestos

Termiczny rozkład włókien azbestu występującego w odpadach eternitu

Streszczenie

Negatywny wpływ wyrobów i odpadów zawierających azbest na zdrowie ludzkie wynika z igłowej, cienko włóknistej struktury azbestu. Dlatego w celu zlikwidowania jego negatywnego oddziaływania na środowisko, w tym zdrowie ludzi, należy prowadzić procesy prowadzące do zniszczenia jego struktury. Na podstawie dostępnej literatury można stwierdzić, że jedynie metody chemiczne i termiczne, mające wpływ na przekształcenie włókien azbestowych powodują, że powstały w wyniku ich zastosowania odpad jest obojętny dla zdrowia. Celem niniejszej pracy była ocena wpływu temperatury i czasu na rozkład azbestu i określenie, czy włóknista struktura azbestu ulega zniszczeniu w wysokich temperaturach. W pierwszym etapie ogrzewania eternitu procesy fizykochemiczne zachodzące w badanym materiale wiązały się z odwadnianiem, czyli usuwaniem wody adsorpcyjnej, konstytucyjnej i krystalizacyjnej, a następnie z rozbijaniem struktury chryzotylu i niszczeniem jego warstw brucytowych, w końcu krystalizacją, powstałego w trakcie narastania temperatury, forsterytu oraz późniejszym jego rozpadem na krzemionkę i peryklaz. W procesie spiekania eternitu mamy do czynienia z nadmiarem tlenku wapnia pochodzącego ze składników cementu. Chryzotyl zawarty w eternicie uwalnia podczas rozpadu krzemionkę, która łączy się z tlenkiem wapnia z fazy cementowej. W ten sposób powstaje krzemian dwuwapniowy (larnit), brownmilleryt, a także peryklaz, jako produkt rozpadu chryzotylu. Peryklaz powstaje w związku z tym, tlenek magnezu nie wiąże się w krzemian, ponieważ nadmiar wapnia posiada preferencje, przy wtórnym tworzeniu krzemianów. Proces spiekania prowadzi do powtórnej klinkieryzacji składników spieku, której głównym składnikiem jest larnit oraz peryklaz powstający z rozpadu azbestu chryzotylowego. Taki skład potwierdza dezintegrację azbestu w badanym materiale i powstanie całkiem nowych, nieszkodliwych dla środowiska faz. Stwarza to potencjalne możliwości wykorzystania produktów tej metody unieszkodliwiania eternitu do produkcji cementu. Jak stwierdzono w trakcie badań, dopiero przy wzroście temperatury do 1400°C następuje znacząca rekrystalizacja składników stopu i początek krystalizacji peryklazu, co potwierdzają badania skaningowe, analiza składu próbek w mikroobszarze oraz wyniki analizy składu fazowego. Reasumując na podstawie przeprowadzonych badań termicznego rozkładu eternitu można stwierdzić, że spiekanie go w temperaturze 1400-1500°C prowadzi do przekształcenia

struktury włóknistej zawartego w nim azbestu chryzotylowego. Przy zastosowaniu metody umożliwiającej działanie takich temperatur, eliminującej emisję włókien azbestowych do powietrza, poddając go obróbce termicznej trwale zmieniamy jego budowę i w ten sposób staje się on minerałem obojętnym dla zdrowia ludzkiego. Ponadto uzyskany materiał, daje potencjalne możliwości wykorzystania produktów tej metody unieszkodliwiania eternitu np. w budownictwie. Niniejsza praca może być podstawą do dalszych badań nad możliwością termicznego przetwarzania odpadów zawierających azbest, w których można rozważyć także dodawanie topników do procesu, wpływających na obniżanie temperatury rozkładu azbestu w eternicie.

Słowa kluczowe:
azbest, odpady azbestowe, eternit, termiczny rozkład azbestu chryzotylowego

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Implementation of ISO 14001 Standard in the European Union Countries

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1. Introduction

The turn of the 20th and 21st has been an increased pressure from both internal and external stakeholders to implement quality management systems that pose a challenge and are one of organization's predominant activities. Quality has become the basis of reflection on the development of quality management systems improvement methods for contemporary business use. Attention for quality matters by the use of knowledge, skills and competences of the employees, began to form a unified whole, i.e. a quality management mechanism that enables, inter alia, appropriate supervision, planning, improvement, documentation, modification, etc. This means a holistic change in the organization's management directed towards increasing its value by undertaking the following measures:

- production (technical and technological change, logistics, etc.),
- human resources (improvement of qualifications through training, shaping the appropriate structure of employment, etc.),
- leadership – management (integration of knowledge with experience, strategic initiatives, more transparent and effective motivation, etc.),
- computerization (proper means of communication, implementation of ICT-based solutions, etc.),
- environmental protection (formulation of pro-ecological policy as part of sustainable development, etc.).

The quality management system (QMS) defined as a tool of interrelate do interacting elements for establishing policy (Kanglong & Wei 2019; Paulrau & Jong 2011) and objectives, as well as a method to achieve these objectives (Peszko 2002), is used to manage and supervise an organization in relation to quality (Vidovic 2019). This means that organizations, through systemic measures, should constantly implement a specified quality strategy (Krawiec 2011; Searcy i in. 2012, Pirju 2019) to achieve significant long term development. It should be remembered, however, that the application of management system standards may be: obligatory (required and used in accordance with the specifics – nature of an activity or legal requirements) or optional (used voluntarily to obtain advantages (Urbaniak 2006), i.e. to increase competitiveness, improve the functioning of an organization, development, minimization of costs, etc.) (Myszewski 2009; Psomas et al. 2011; Bober et al. 2017).

It is worth pointing out that the use of management systems, within the framework of responsible management that efficiently uses quality instruments, provides organizations with the ability to develop and compete on both domestic and international markets, as well as to facilitate tasks and achieve quality objectives (Henrykowski 2008; Chiarini 2013; Pacana et al. 2017; Olkiewicz & Wolniak 2018; Andrei et al. 2019).

In the field of environmental protection, the environmental management system in accordance with the PN-EN ISO 14001: 2015-9 standard is a part of organisation's management system used to implement environmental policy and manage its environmental aspects (PN-EN 14001). This system identifies potential environmental threats that relate to its activity and the courses of action in the event of such threats were to occur. (Maletic i in. 2015; Pacana & Ulewicz 2017).

In other words: a system that operates in the framework of the system management model is a tool for the creation, maintenance and improvement of the quality of work, which indicates the directions for the improvement of organization's activities that are in line with the company's policy (Qi et al. 2013; Malindžák et al. 2017; Olkiewicz 2018). It is worth underlining that itis also a tool to support and activate top management to act and create the future. The main objectives of the environmental management system PN-EN ISO 14001: 2015-9 include:

- a proper environmental policy of an entity, adequate to the objectives of the organization's development strategy,
- a full identification of ecological issues and problems that are important for the company, while taking into account previous and planned environmental impacts,
- defining legal and normative requirements,
- setting priorities and environmental aims and objectives,
- implementation of programmes for the execution of tasks and analysis of their effects,
- proper operational control of processes affecting the state of the environment and, if necessary, making appropriate adjustments to an on-going basis,
- flexible response to signals and changes in the environment.

The system in accordance with the ISO 14001 standard is, therefore, designed to provide an organization with elements of effective environmental management, consisting in the organization and unification of activities for the purpose of environmental protection (Vires et al. 2012; Searcy et al. 2012) whilst achieving organization's objectives based on processes of continuous improvement in each element of the entity's activity. The use of this management system (Gebczyńska & Wolniak 2018) brings organizations closer to environmental globalization, i.e. entities that manage processes in the area of environmental protection in the framework of their activities (Pacana 2017). The main areas of activities of environmental globalization include:

- realism (real impact on production processes, the use of innovativeness, minimization of the greenhouse effect, etc.),
- correlation (interdependence and cooperation between entities minimizing geographical, legal, cultural and religious barriers),
- coordination (development of proper pro-ecological policy - its financing, monitoring and execution mechanisms),
- awareness (shaping of pro-ecological attitudes as an important element of a modern socio-economic life, quality and development of life),
- credibility (material, political, cultural, technological, legal, etc. responsibility for the creation, dissemination and promotion of pro-environmental behavior and activities).

Proper ecological management contributes to the incensement in the profitability of an organization through, among others: the effectiveness of the use of natural resources (reduction of the negative effects humans have on the environment whilst strengthening the economy's resistance to environmental pressure) (Szpor & Śniegocki 2012; Koukaou et al. 2013), creation of ecological products (Carley & Sapens 2000), modernization or creation of new technological processes (Woźniak et al. 2010), implementation of quality standards (Wolniak & Sędek 2009; Olkiewicz et al. 2015). Furthermore, this allows to conduct appropriate marketing policy (Oslo Manual 2005) as an organization that promotes pro-ecological behavior. Such a strategic direction in the era of "healthy lifestyle" will allow for a sustainable development of the organization and to gain competitive advantage in a particular economic sector and the area of business activity.

2. Methodology

This publication addresses the analysis of the implementation of the ISO 14001 standard in the European Union countries. Data on the number of implemented ISO 14001 certificates in individual countries were used to carry out this research (for the purpose of conducting research, only these countries where the number of certificates exceeded 100 were chosen - Malta and Luxemburg where, therefore, left out). The number of ISO 14001 certificates for each individual country were adopted as ISO Survey 2018. Appropriate data was collected in Table 1.

Table 1. ISO 14001 certificates, population and the GDP per capita in the EU countries

No	Country	ISO 14001	Population [mln]	PKB per capita [$]
1	Austria	1079	8.85	54085
2	Belgium	1012	11.46	49705
3	Bulgaria	1946	7.00	24577
4	Czech Republic	4266	10.64	39337
5	Croatia	1024	4.07	27664
6	Cyprus	216	0.87	41572
7	Denmark	1012	5.81	54564
8	Estonia	520	1.32	35346
9	Finland	1467	5.51	48221
10	France	6084	67.03	47113
11	Germany	8028	83.02	54984
12	Greece	1415	10.72	30522
13	Hungary	2391	9.80	33409
14	Ireland	957	4.90	81686
15	Italy	15118	60.36	40737
16	Netherlands	2181	17.28	59105
17	Latvia	336	1.92	31215
18	Lithuania	914	2.80	37162
19	Poland	2921	37.97	33409
20	Portugal	1382	10.28	33409
21	Romania	4553	19.40	27753
22	Slovakia	1687	5.45	37268
23	Slovenia	432	2.08	38841
24	Spain	12198	46.93	42120
25	Sweden	3598	10.23	54474
26	United Kingdom	11201	66.647	47042

Source: own work on basis of data from: ISO Survey 2018

The analysis also uses author's own indicator for the widespread of environmental certificates expressed in the number of certificates per million inhabitants for each country. Data on the population of the European Union countries was used (Eurostat 2019) for its calculation (Table 1). The indicator for the saturation with the ISO 14001 environmental certificates in the EU countries is shown in Table 2. Additionally, the GDP per capita was used in the analysis for each country. The GDP was calculated in accordance with the purchasing power parity method and is presented in Table 2. The GDP indicator was based on the Eurostat data for the year 2019.

Table 2. The saturation with the ISO 14001 environmental certificates in the EU countries

No	Country	ISO 14001 certificates per one million population
1	Austria	121.92
2	Belgium	88.31
3	Bulgaria	278.00
4	Czech Republic	400.94
5	Croatia	251.60
6	Cyprus	248.28
7	Denmark	174.18
8	Estonia	393.94
9	Finland	266.24
10	France	90.77
11	Germany	96.70
12	Greece	132.00
13	Hungary	243.98
14	Ireland	195.31
15	Italy	250.46
16	Netherlands	126.22
17	Latvia	175.00
18	Lithuania	326.43
19	Poland	76.93
20	Portugal	134.44
21	Romania	234.69
22	Slovakia	309.54

Table 2. cont.

No	Country	ISO 14001 certificates per one million population
23	Slovenia	207.69
24	Spain	259.92
25	Sweden	351.71
26	United Kingdom	168.06

Source: authors own work

3. Research results and discussion

Taking into account absolute numbers, the largest quantity of organizations having an environmental management system in accordance with the requirements of ISO 14001 occurs in the largest European Union countries, in particular: Italy 15118 certificates, Spain 12198 certificates, United Kingdom 11201 certificates, Germany 8028 certificates, France 6084 certificates. Due to the fact that European Union countries vary in size, there is no point in comparing the absolute numbers of certificates because, understandably, the larger the country the more certificates implemented. Therefore, it was considered that in order to eliminate the impact that the size of the country has on the obtained results, the number of ISO 10014 certificates per one million inhabitants should be used instead. This indicator is called "country saturation with certificates".

Figure 1 presents a summary of saturation with the ISO 14001 environmental certificates in the European Union countries. The analysis of the data shows that the highest level of saturation with certificates is in the Czech Republic (400,94), Estonia (393,94) Sweden (351,71), Lithuania (326,43) and Slovakia (309,54). The data indicates that ISO 14001 certificates are implemented to a greater extend in countries that joined the European Union after the year 2000.

These are the countries with lower levels of economic development compared to the countries of the "old" Union and the implementation of various types of management systems that have established reputation on international markets is a way to improve the functioning of economy and provide opportunity to enter larger markets. This becomes particularly evident when one takes into account the developed countries, e.g. Germany (96,7) or France (90,77), where levels of saturation with the ISO 14001 certificates are the lowest among the European Union countries.

Poland is lagging behind in the implementation of environmental management standards. With the level of saturation with certificates at 76,93, Poland takes the lowest place among the surveyed European Union countries. This is particularly a poor result in comparison with the neighboring countries that joined the European Union in a similar period of time. These countries have a significantly higher level of saturation, often by several times, with the ISO 14011 certificates. On this basis it can be concluded that there is limited interest with the environmental issues in Poland.

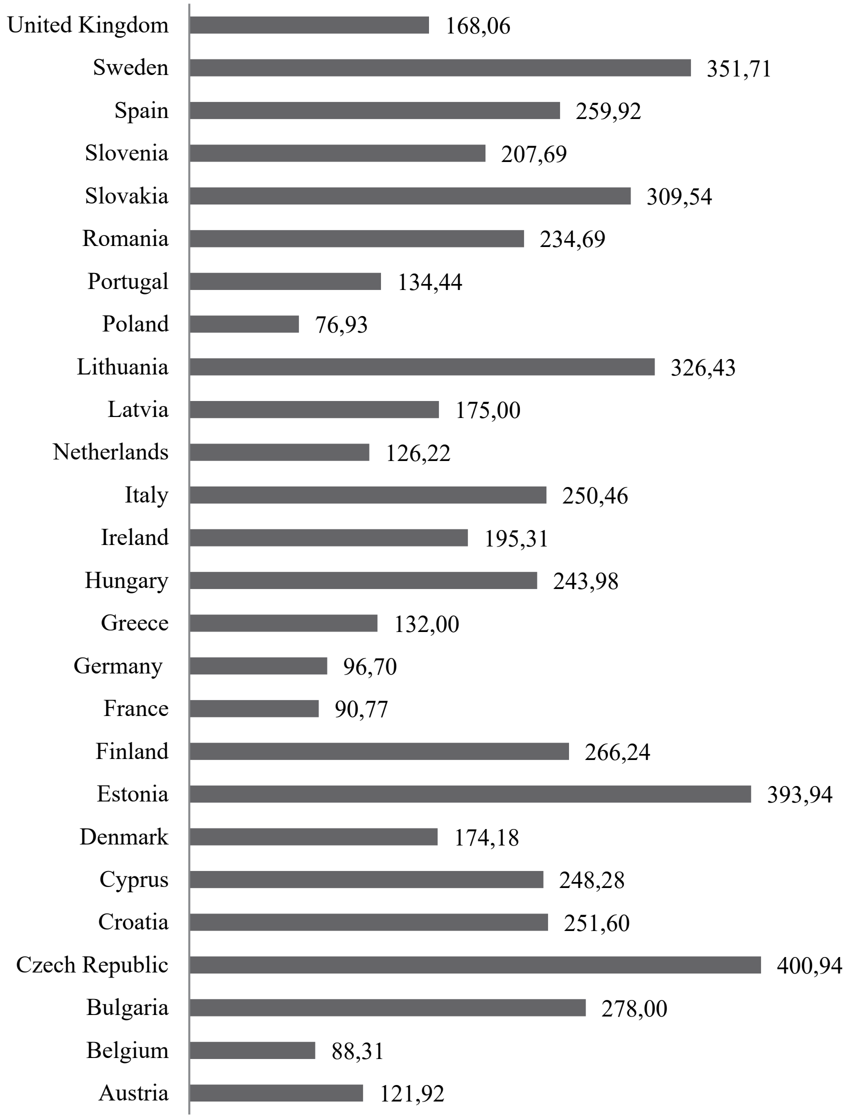

Fig. 1. ISO 14001 certificates per one million inhabitants in the EU countries

Figure 2 shows the analysis of the spread rate between the studied countries on the basis of two variables – the saturation with ISO 14001 certificates and the GDP per capita (numbers in the figure indicate the numbering of countries in accordance to Table 1 and Table 2).

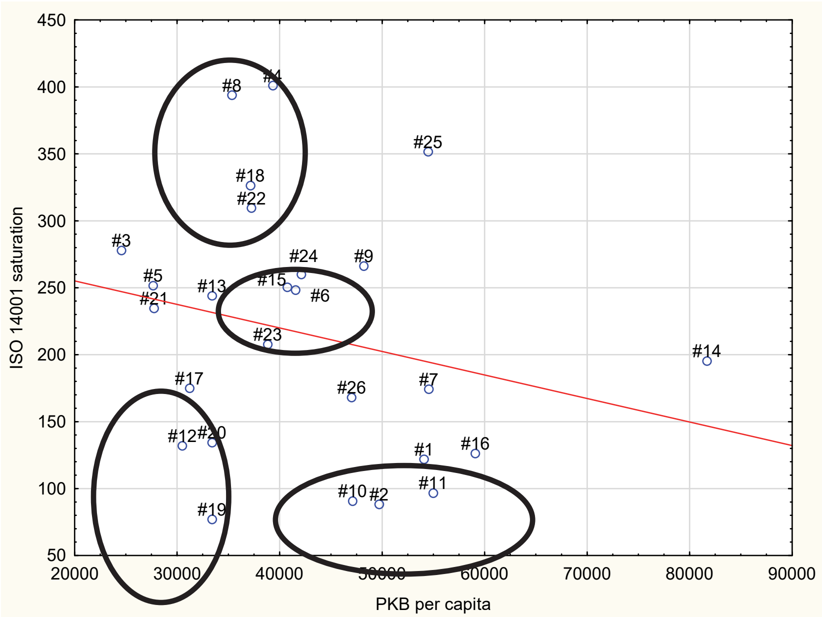

Fig. 2. The saturation level with the ISO 14001 and the GDP per capita

The statistical analysis of data at the α = 0.05 significance level has shown no existence of positive correlation between the variables. Nevertheless, it can be seen from the figure that the average indicator for the widespread of certificates is falling together with the prosperity of a country. This confirms the previous statement that in many cases environmental standards are a means to cope with the economic backwardness and to obtain a better marketing position for a given country, particularly in the international market. Other analyses indicate that a similar situation occurs with ISO 9001 quality management standards.

Several coherent country groups can be distinguished in Figure 2:

- Countries with a high level of saturation with certificates and an average GDP level per capita. These may include in particular: the Czech Republic, Estonia, Lithuania and Slovakia. These countries located in Central and Eastern Europe joined the EU in 2004 and, as was mentioned previously, are all strongly involved in the implementation of ISO 14001 to overcome the economic backwardness and not to lag behind the leading European Union countries. Simultaneously, these are the countries where the importance of environmental issues is notices because, as the example of Poland shows, the geographical location and economic conditions or even the year of accession to the European Union, does not determine the attitude towards the implementation of environmental management systems. Poland, despite the fact that in all mentioned areas is analogous to the discussed group of countries, is still situated on the completely opposite side of the chart – placed the lowest among other EU countries.

- The second group consists of countries with an average level of economic development and moderately higher level of saturation with ISO 14001 certificates than would result from their prosperity. Four countries can be included in this group: Cyprus, Finland, Italy and Spain. Outside Finland, these are all Mediterranean countries. In the case of Spain and Italy, the frequent implementation of environmental certificates is most likely due to reasons similar to the frequent implementation of ISO 9001 quality management certificates in these countries. It serves as a method to reduce corruption, bureaucracy and problems concerning the organization of work in these countries.
- The third group enlists countries with a low GDP level and a minimum involvement in the implementation of ISO14001 environmental certificates. This group includes: Lithuania, Greece, Portugal and Poland. In these countries there is no importance attached to environmental issues in business.
- The fourth group consists of relatively prosperous countries (medium and high level of GDP per capita) that are implementing relatively few ISO 14001 certificates. This group includes: Austria, Belgium, France, Germany and the Netherlands. Organizations in these countries have a firm position on the international market, so even though they do not have appropriate standards, they find clients. As a consequence, there is no market pressure in these countries to implement environmental standards.

Distinguished groups are coherent and are connected with ISO 14001 saturation and PKB per capita. Especially interesting is the second group, because on this example, we see the important role of management systems certification to counteract the economic backwardness to achieve competitiveness on the global market.

4. Conclusions

The analysis presented in this publication demonstrated that there is a negative relationship between the GDP per capita and the saturation with ISO

14001 certificates in the European Union countries. It has been noted that ISO 14001 certificates are particularly often implemented in countries that joined the EU in 2004: the Czech Republic, Estonia, Lithuania and Slovakia. Similar to the ISO 9001 quality management systems, ISO 14001 environmental certification occurs in countries with medium economic backwardness in comparison to highly developed countries. Organizations in these countries want to enter international markets and perceive certificates as a convenient way to prove that they operate in accordance with the modern environmental policy. Market pressure is a very important factor in the implementation of ISO 14001 environmental standards by organizations. They implement these standards when it enables them to expand into new, in particular international markets.

Apart from objective facts, the attitude of citizens of given countries towards the environmental issues also plays a very important role. This can be seen in the case of Poland, which has the lowest saturation level with ISO 14001 certificates in the European Union, despite having similar economic conditions and market pressure. This can be resolved by carrying out activities that increase awareness towards the importance of environmental issues in a given country.

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Abstract

The uptake of various types of norms on management around the world resulted in the creation of a range of certificates that have been accepted by organizations and are improving their marketing position on the international market. In the area of environmental management, the ISO 14001 norm is the type of certificate that is widely used. This norm is implemented by many industrial and, ever more often, service organizations around the world.

This publication presents an analysis of the state of implementation of the ISO 14001 standard in European Union countries. To carry out the analysis, saturation of ISO 14001 indicator was introduced, which is discussed in detail in the later part of the publication. The article aims to examine saturation with the ISO 14001 certificates of European Union countries and determine whether there exists a relation between the saturation of ISO 14001 certificates and the wealth of individual countries measured by GDP per capita.

Keywords:
environmental management, quality, ISO 14001, certificate

Implementacja normy ISO 14001 w krajach Unii Europejskich

Streszczenie

Powszechne rozpowszechnienie rożnego rodzaju norm dotyczących zarządzania na świecie powoduje, że powstało wiele tego rodzaju certyfikatów, znajdujących uznanie organizacji i poprawiających ich pozycje marketingową na rynku międzynarodowym. W obszarze zarządzania środowiskowego tego rodzaju certyfikatem, powszechnie stosowanym na świecie, jest norma ISO 14001. Jest ona stosowana na całym świecie przez wiele organizacji zarówno przemysłowych jak i coraz częściej usługowych.

W niniejszej publikacji przedstawiono analizę stanu implementacji normy ISO 14001 w krajach Unii Europejskiej. Aby wykonać tego rodzaju analizę posłużono się wprowadzonym wskaźnikiem nasycenia certyfikatami ISO 14001, który został szczegółowo omówiony w dalszej części publikacji. Celem artykułu jest zbadanie nasycenia certyfikatami ISO 14001 krajów Unii Europejskiej i określenie czy istnieje związek między nasyceniem certyfikatami ISO 14001 a zamożnością poszczególnych krajów mierzonym PKB per capita.

Słowa kluczowe:
zarządzanie środowiskowe, jakość, ISO 14001, certyfikat

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Energy Efficiency of High-temperature Installations and Method of Determining Thermal Properties of Pipe Insulation Materials

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1. Introduction

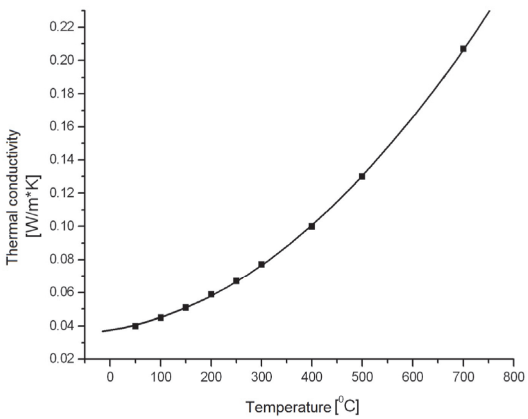
It is estimated that the potential energy savings that can be generated in production plants in Poland connected with thermal modernisation of industrial installations shall amount to 27 PJ and carbon dioxide emissions can be reduced by 2.2 million tonnes of CO_2 annually. The potential annual savings shall exceed the energy consumption of more than 400,000 households or the reduction of CO_2 emissions by 1.1 million mid-range cars each with a mileage of 12,500 km per year (Gürtler A. 2014).

One of the most important elements which influences the improvement of energy efficiency of high-temperature industrial installations is the proper selection of materials which hinder the escape of heat from the installation. The fundamental issue is the choice of an appropriate material/product to carry out the thermal modernization investment, whose parameter determining the insulation properties is the thermal conductivity coefficient (λ, [W/m·K]) in a given temperature at which the material/product will operate. Thanks to such information, it is possible to properly and correctly design a thermal modernization of a high-temperature installation, which should include an optimal solution taking into account the costs and the rate of return on the investment. The above issues were the subject of Cammerer's work (Cammerer J.S. 1967), where problems related to the calculation and application of insulation in industry, as well as measurement techniques in high and low temperature technical and industrial installations were considered.

What constitutes a problem prevailing on the Polish market is the limited possibility to determine the thermal properties of materials/products for thermal insulation at high temperatures (above 100°C to 800°C), including pipe materials. This article aims at presenting a method of determining the heat conductivity coefficient for this type of materials; it also specifies the necessary requirements for apparatus for this type of tests and describes the investment losses related to improper determination of thermal parameters.

2. Legal requirements for determining the thermal properties of materials for thermal insulation of industrial installations

The basic standard specifying the manner of presenting thermal properties of insulation materials at temperatures other than those used for general construction (in general construction materials are characterized by the determination of thermal conductivity coefficient in only one temperature, in 10°C) is EN ISO 13787:2003 "Thermal insulation products for building equipment and industrial installations – Determination of declared thermal conductivity." It applies to both flat products (Miros A. 2012) and pipe products. The requirement of the above mentioned standard is for the producer to present the dependence of thermal conductivity coefficient on the average temperature in the form of a curve or a table (Fig. 1).



Temperature [°C]	Thermal conductivity [W/m·K]
50	0.040
100	0.045
150	0.051
200	0.059
250	0.067
300	0.077
400	0.100
500	0.130
700	0.207

Fig. 1. Declared thermal conductivity curve and table for mineral wool sample

Applying EN ISO 13787:2003 results directly from the standards for thermal insulation products for building equipment and industrial installations, i.e. a package of standards in the range from EN 14303 to EN 14320 as well as EN 15599 and EN 13055. However, if the determination of thermal properties concerns products for high-temperature applications, i.e. temperatures at which thermally insulating organic materials cannot be used (over the long-term influence at 180°C) (Miros A. 2016), then we talk only about such inorganic materials as: mineral wool (glass wool, rock wool), foamed glass, silicate products, expanded perlite, expanded clay, ceramic wool and aerogel mats (Table 1). For most products: mineral wool, silicate products, expanded perlite, expanded clay and foam glass, an appropriate standard specification has been prepared (EN 14303:2015, EN 14306:2015, EN 15599-1:2010); however, there are no appropriate standards developed for ceramic wool and aerogel mats as yet.

Table 1. High temperature thermal insulation materials together with their estimated maximum temperature of application and relevant document of reference

Thermal insulation product	Form of product	Estimated maximum temperature of application [°C]	Document of reference
mineral wool	mats/slabs	800	EN 14303:2015
foam glass	stiff slabs	430	EN 14305:2015
silicate products	stiff slabs	1000	EN 14306:2015
expanded perlite	granulate	800	EN 15599-1:2010
expanded clay	granulate	750	EN 13055:2016
ceramic wool	mats	1400	NTA/ETA*)
aerogel	mats	650	NTA /ETA*)

*) NTA – National Technical Assessments, ETA – European Technical Assessment

As aerogel mats are increasingly frequently used to insulate industrial installations, in the absence of an appropriate standard specification, the manufacturer (or authorised representative body) should, prior to launching the product's sale, obtain a special document that allows the product to be legally introduced to the market. Such a document may be a European or National Technical Assessment [until 31.12.2016, such a document was a technical approval, which was replaced by a National Technical Assessment (in accordance with Regulation of 17.11.2016, item 1968)]. The relevant documents (European technical assessment) issued hitherto for the European market do not, however, contain any determined thermal properties in the whole scope of application. For example, for a product whose scope of application is up to 200°C (http://www.core-prosystems.co.uk/thermal-insulation/aerogel-spaceloft-insulation) the thermal conductivity coefficient was determined only at one temperature, i.e. 10°C (ETA - 11/0471). The λ_{10} parameter does not provide information about thermal insulation at other temperatures (Furmański 2013) – Fig. 2, which may pose a considerable problem in the proper design of an investment project for the thermal modernisation of an industrial installation.

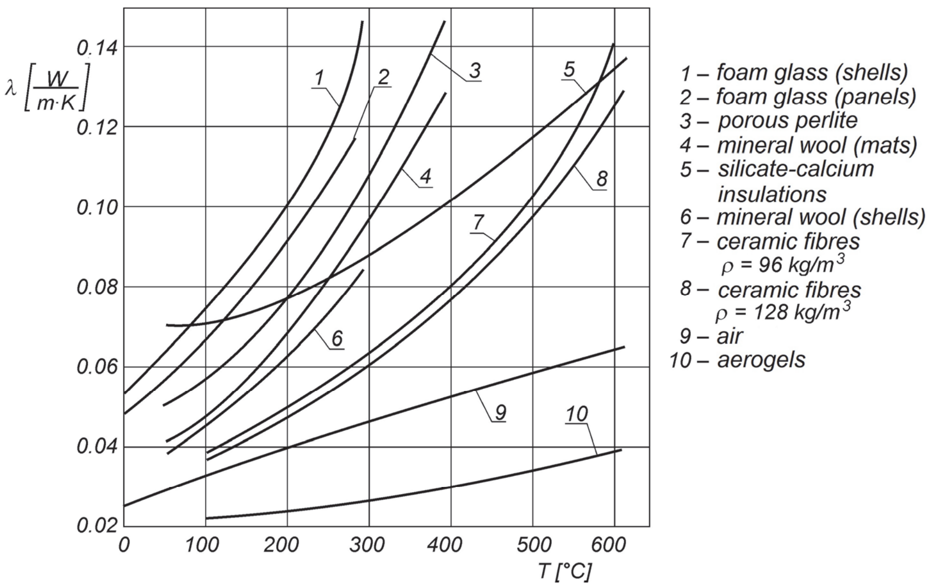


Fig. 2. Thermal conductivity change of different insulation materials vs. temperature (Furmański 2013)

The determination of thermal properties of materials at high temperatures may be hampered by costly and specialist requirements for measuring equipment and limited access to the appropriate accredited measuring methodology in Poland.

3. Requirements for apparatus measuring thermal conductivity coefficient

Thermal insulation products usually take the shape of an insulated surface. Usually insulated surfaces are flat surfaces (e.g. building walls, tank walls), convex surfaces (e.g. silos, curved-surface tanks) or pipes (e.g. heat pipes, elbows). For the most part, materials used for insulation, i.e. mats, slabs and pipe sections, come in such shapes. In the case of elastic materials, there is an additional option to adjust the insulation to surface irregularities, arches, curves, etc. without having to cut the material, which can result in thermal bridges. What constitutes an entirely different issue is insulation of valves due to irregular and non-standard dimensions and shapes (www.keafer.pl). When it comes to filling materials (granulates), the shape of the insulated surface is not important; however, it is crucial to protect the material against decrement during exploitation.

Determination of thermal conductivity coefficient value for thermally insulating products is performed applying the method in steady-state conditions on two types of apparatus, depending on the shape of the product, on the apparatus for flat-rolled (ISO 8302:1991) or pipe (EN ISO 8497:1996) products. It is not advisable to carry out only measurements of thermal conductivity coefficient for flat-rolled products due to a significant difference between internal structures of flat-rolled and pipe (cylindrical) products as well as due to the fact that thermal properties often depend on the direction of heat flow, which results in the fact that the measurement of unidirectional heat flow, as in the case of flat-rolled products, may not be representative (EN ISO 8497:1996). The measurement of the conductivity coefficient should be performed in apparatus constructed in accordance with the guidelines contained in the ISO 8302:1991 standard (ISO 8302:1991, EN 1946-2:1999) for flat-rolled products and (EN ISO 8497:1996) for pipe products (the issues connected with measuring thermal conductivity coefficient of flat-rolled products have been discussed in Miros. A 2013a).

The thermal conductivity test [W/(m·K)] for pipe sections is based on the measurement of the thermal flux flowing through a sample under the influence of the temperature gradient generated in the heat pipe (1) (EN ISO 8497:1996):

$$\lambda = \frac{\ln(D_2 - D_0)}{2\pi L} \cdot \frac{\Theta}{\left(T_0 - T_2\right)} \tag{1}$$

where:

Θ – the heat flux [W],
D – the pipe diameter [m],
T – the surface temperature [K],
L – the measurement length [m],
indices $_{0.2}$ – the internal and external surface.

Below there are presented issues related to the newly constructed two-chamber apparatus for measuring the thermal conductivity coefficient in the steady-state conditions for pipe products (pipe sections) with configuration:

1. Temperature range of the sample from the cold side: -50°C - 500°C.
2. Temperature range of the sample from the heat side: -30°C - 700°C.

3. Average temperature of measurement from -40°C (with ΔT: 20K) to 600°C (ΔT_{max}=200K).
4. The range of temperature differences (ΔT) between the cold side and the heat side of the sample:
   a. ΔT=20K in the range from -40°C to 500°C.
   b. ΔT_{max}=750K in $T_{average}$= 325°C (in the system when the temperature of test pipe T_{max}=700°C).
5. Measuring range of thermal conductivity coefficient value from 0.015 to 0.6 W/(m·K).
6. Minimum length of sample = 1 m.
7. Range of diameters of the measured sample: from 32 mm to 394 mm.
8. A set of test pipes with a diameter of 22 mm, 42 mm, 48 mm, 194 mm.
9. Number of thermocouples/sensors per one test pipe: 4.

Fig. 3. The two-chamber pipe apparatus for thermal conductivity tests within the temperature range from -40 to 600°C

When constructing a test apparatus for measuring the thermal conductivity coefficient of pipe products (pipe sections), the following issues connected with measurement uncertainties should be considered in order to obtain repeatable and reliable results:

- temperature imbalance between sections (measuring and guarding) of the heating pipe
- measuring section area,
- emission performance of test surfaces,
- edge heat losses at the ends of heat pipe,
- linearity of the apparatus.

The construction of the test pipe consists in independent control of the temperatures of the measuring section and the guarding section. Due to this design of the heat pipe, an **imbalance in temperature** between these sections may occur during the measurement. The occurrence of the imbalance causes heat flux, partly through the sample and partly through the gap that separates the sections. The narrower the gap, the greater the imbalance error. On the other hand, in the design of the apparatus, it is taken into account that increasing the gap width increases the uncertainty of determining the measurement area. In the case of measurements at high temperatures, the radiation impact increases by increasing the thermal flux through the gap (EN ISO 8497:1996, EN 1946-5:2000, Miros 2013b). This effect may be minimised by low thermal conductivity filling material (CEN/TS 15548-1:2011), but the unbalanced thermal flux through both the sample and the apparatus (both gaps) shall be less than 1 % of the thermal flux delivered to the sample through the centre of the test pipe (according to the recommendations in EN 1946-5:2002).

The aforementioned gap, which separates the heating and guarding sections, plays an important role in determining the **measuring section area**, which is defined as a field surrounded by a line delineating the centre of the gap (Fig. 3). This field is not equal under all test conditions to the actual measuring field of the sample, which is cut through by the heat flux supplied by the central part of the pipe (EN ISO 8497:1996).

In order to estimate the uncertainty error in defining the field through which a thermal flux of the size Θ passes, two extreme cases related to the minimum and maximum thickness of the tested sample should be considered.

In the case of a minimum thickness sample (5 mm), the field through which the heat flux supplied by the measuring section of test pipe passes approaches the field defined by the edges of the measuring section gap. The actual length of the measuring field shall then aspire to a value of 600 mm (the physical length of the test section).

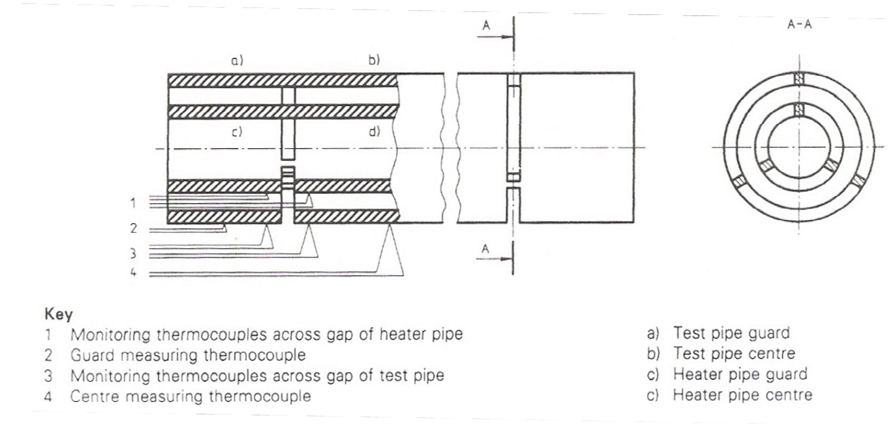


Fig. 4 Guarded end apparatus (EN ISO 8497:1996)

For the maximum thickness sample, in accordance with EN 1946-5:2000, if the thickness of the sample is much larger than the width of the gap (e.g. 10 times), the field boundary will be defined by lines passing through the centre of the gaps, i.e. twice as large (because there are two gaps) as half the width of the gap (in this case it is 6 mm for sample thicknesses from 60 mm to 100 mm). Therefore, the uncertainty caused by defining the measuring field through which the thermal flux of the size Θ passes can be determined through the difference between the extreme values of the length of the measuring section (600 and 606 mm), i.e. 1%.

The test surfaces of the apparatus shall have the highest possible heat dissipation capacity. Determination of **the emissivity of the test surface** consists in determining the density of the thermal flux passing through the air layer (in steady-state conditions, with no convection) at various temperature differences (ΔT).

The axial heat flux from the test section to the sample guarding section affects the maximum thickness of the sample - the uncertainty associated with **edge losses of heat at the ends of the pipe**. For an apparatus with no end insulation, the end temperature ratio is (2) (EN ISO 8497:1996):

$$e = \frac{(T_e - T_2)}{\left(T_1 - T_2\right)} \tag{2}$$

where:

T_e – temperature at the ends of the sample (assumed as uniform)

T_1 – temperature of the heat side of the sample

T_2 – temperature of the cold side of the sample

Table 2. Calculation of extreme cases (extreme diameters of test heat pipe and extreme possible thicknesses of sample) of the edge heat loss on the end of heat pipe

Diameter of test pipe [m] d_0	Sample thickness [m] d_2	Sample diameter [m] $d_0 + 2d_2$	Equivalent sample thickness [m] d_{eq}	End temperature ratio e	Heat losses at pipe ends [%] E_e
0.022	0.005	0.032	0.0060	0	**0.00**
0.022	0.1	0.222	0.2566	0	**1.93**
0.044	0.005	0.054	0.0055	0	**0.00**
0.044	0.1	0.244	0.2090	0	**0.70**
0.048	0.005	0.058	0.0055	0	**0.00**
0.048	0.1	0.248	0.2036	0	**0.61**
0.194	0.005	0.204	0.0051	0	**0.00**
0.194	0.1	0.394	0.1396	0	**0.05**
0.022	0.005	0.032	0.0060	1	**0.00**
0.022	0.1	0.222	0.2566	1	**-1.87**
0.044	0.005	0.054	0.0055	1	**0.00**
0.044	0.1	0.244	0.2090	1	**-0.69**
0.048	0.005	0.058	0.0055	1	**0.00**
0.048	0.1	0.248	0.2036	1	**-0.60**
0.194	0.005	0.204	0.0051	1	**0.00**
0.194	0.1	0.394	0.1396	1	**-0.05**

The above table presents some of the calculations for extreme cases (extreme diameters of the test pipe and extreme possible sample thicknesses). The uncertainty due to edge losses at the pipe ends is greater than 1% in only two cases where the test pipe has the smallest diameter (22 mm) and the thickness of the test sample is the largest (100 mm) as well as when the edge temperature of the test sample is practically equal to the temperature of the centre ($T_e = T_2$) or the edge temperature of the test sample is practically equal to the temperature of heater pipe ($T_e = T_1$).

One of the most important criteria for the assessment of systematic errors of the apparatus is the determination of its **linearity test**. It consists in recording possible changes in the thermal conductivity coefficient at a specific average test temperature, but with different temperature differences (ΔT). Generally, the test results of the thermal conductivity coefficient should not differ from each other.

The above measurements are carried out also in other average temperatures, which of course depend on the range of the test apparatus (ISO 8302:1991, EN ISO 8497:1996, EN 1946-5:2000).

Table 3. The results of linearity test of pipe apparatus for mineral wool sample

Thermal conductivity coefficient λ [W/m·K]	Average temperature 10°C	Average temperature 300°C	Average temperature 700°C
for ΔT=10°C	0.03874	0.08274	0.19387
for ΔT=20°C	0.03842	0.08237	0.19152
for ΔT=40°C	0.03820	0.08209	0.19447
average λ	0.03145	0.07224	0.19329
Standard deviation λ	2.727E-4	3.26E-4	1.56E-3
Coefficient of variation [%]	0.86709	0.4503	0.8071

4. Analysis of losses due to incorrect determination of the thermal conductivity coefficient

The following example shows how important it is to determine the correct value of the thermal conductivity coefficient of thermal insulation, which has been taken from Annex C of the standard EN ISO 12241:2008 (EN ISO 12241:2008) as an illustration for calculating the temperature drop over the pipe length.

The following input data have been specified in the standard:
- temperature of the medium (hot flux): t_m = 250 [°C]
- mass of the medium flux: m = 45000 [kg/h]
- specific heat: C_p = 2.233 [kJ/(kg·K)]
- ambient air temperature: t_{amb} =- 10 [°C]
- diameter of the pipe: D_i = 0.40 [m]
- length of the pipe: l = 2500 [m];
- thickness of the insulation: d = 0.12 [m]
- thermal conductivity at temperature of 120°C: λ_{120} = 0.061 [W/m·K]
- outer diameter of the pipe, $D_e = D_i + 2d$ = 0.64 [m]

Based on equation (3) (EN ISO 12241:2008), an approximate temperature drop along the length has been estimated [°C]:

$$\Delta t = \frac{(q_l \cdot l \cdot 3.6)}{(m \cdot C_p)} = 19.0 \tag{3}$$

where:
q_l – the linear density of the heat flux [W/m] is (4) (EN ISO 12241:2008):

$$q_l = \frac{(t_{amb} - t_m) \cdot 2\pi\lambda}{\left(\ln \frac{D_e}{D_i}\right)} = 212.02 \tag{4}$$

As the above formulae show, the thermal conductivity coefficient is directly proportional to the temperature drop; thus, if the measured thermal conductivity coefficient was higher by 10%, i.e. not λ_{120} = 0.0610 [W/m·K], but λ_{120} = 0.0671 [W/m·K], then the temperature drop would also be higher by 10 % (Δt = 20.89 [°C]), and thus so would the costs of delivering the medium would increase.

However, there is another error, the consequences of which are much more serious. The aforementioned situation of determining the thermal conductivity coefficient at only one temperature (λ_{10}) from the entire range of high-temperature insulation application results in much greater differences. Using this example and assuming that the change in the thermal conductivity coefficient is similar to the changes shown in Fig. 1, the difference between λ_{10} = 0.038 [W/m·K] and λ_{120} = 0.048 [W/m·K] would be more than 26 % of the difference between the designed and actual temperature of the medium along the length of the pipe. Such a thermal modernization investment would not make any sense in practical terms.

5. Conclusions

The key element when designing and investing in thermal modernization is a reliable and accurate determination of the insulation parameters of individual elements, in particular the materials constituting the basic thermal insulation. However, without proper equipment and appropriate technical background, it is not possible to determine the thermal conductivity coefficient of the material/product, and the consequence of improper selection of insulation parameters may result in long-term losses for the investor. Therefore, the thermal parameters of materials dedicated to industrial installations should be determined over the entire range of use (without extrapolation to higher temperatures), on a selected, proven apparatus for measuring the thermal conductivity coefficient and in accordance with the appropriate standard procedure.

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Abstract

The article describes a method of determining the thermal conductivity coefficient value of high temperature insulation materials (over 100°C up to 800°C), especially of pipe products. Necessary requirements for the pipe test apparatus together with results of pipe apparatus requirement tests have been shown here. Moreover, an example of investment losses related to improper determination of thermal parameters of an insulating material has been presented.

Keywords:
thermal conductivity coefficient, pipe apparatus, high temperature insulation

Efektywność energetyczna instalacji wysokotemperaturowych a metoda wyznaczania charakterystyki cieplnej rurowych materiałów termoizolacyjnych

Streszczenie

Artykuł przedstawia sposób określania współczynnika przewodzenia ciepła dla materiałów/wyrobów do izolacji cieplnej w wysokich temperaturach (powyżej 100°C do 800°C), w szczególności materiałów rurowych. Przedstawiono niezbędne wymagania dla aparatów do badań współczynnika przewodzenia ciepła wyrobów rurowych wraz z wynikami pomiarów właściwości użytkowych aparatu. Przedstawiono przykład strat inwestycyjnych związanymi z niewłaściwym określeniem parametrów cieplnych materiału izolacyjnego.

Słowa kluczowe:
współczynnik przewodzenia ciepła, aparat rurowy, wysokotemperaturowe izolacje

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The Influence of Soil Fertilization with Struvite on Water Efficiency – Lysymetric Columns

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1. Introduction

At the end of the twentieth century, among people involved in agricultural production, a discussion began on cultivation technologies for crops. It was found that the existing methods of fertilization do not fulfill their role, because the barrier of effectiveness of the doses of nutrients was achieved. The rapid physical and chemical degradation of the soil affected the physiological condition of the plants, resulting in a decrease in yields and their quality. First of all, you should take care of the right condition of the soil as the basic and only source of nutrients, water, and plant growth substances.

Soil additives, consisting of specific mixtures of mineral compounds, should affect the activation of cellular metabolism processes, soil microflora, best adapted to the environment. Applied proper fertilization stimulates the processes occurring in the humus in a gentle way. This triggers a number of reactions favoring the development of soil and plants, allowing to compensate for the degrading effect of intensive agricultural production. Works on fertilizers enriched with microelements, growth regulators or amino acids with extended release of biogenic elements have begun. An important element in the application of fertilizers is their dose, which is closely related to the previously determined soil parameters.

Due to the high rate of exploitation of phosphate rock, from which fertilizers are produced, other sources of this element are sought for. Therefore, there is growing interest in the field of effective recovery of nutrients from waste. The bioavailable forms in which we can recover phosphorus are calcium phosphates, as well as struvite – $(NH_4)Mg[PO_4] \cdot 6H_2O$ – containing 58% P_2O_5 (Doyle & Parsons 2002). Struvite is a mineral, inorganic chemical compound, having a crystalline form, quickly becoming weathered in the form of a white powder. Struvite crystals contain two important macroelements necessary for the growth and development of plants - phosphorus and nitrogen. Struvite is characterized by low solubility, thanks to which fertilizer components are released slowly, which reduces the need for frequent fertilization. Struvite can be used directly in agriculture as a mineral fertilizer (de Bashan & Bashan 2004). The phosphorus recycling from waste including sewage sludge is favored by the development of other more efficient wastewater treatment technologies. It is estimated that one inhabitant of Europe discharges about 2 g of phosphorus per day (on average) mainly in the form of sewage, from which subsequently in the purification process significant amounts of sludge containing various impurities, including biogenic compounds, are obtained. While biogenic compounds in the aquatic environment are part of its rapid eutrophication, in the case of field crops the presence of these components is a necessary soil component in order to obtain sufficiently high yields. The problem is that the waste containing these compounds also contain many other elements and undesirable components that prevent their direct use as a fertilizer. So in order to properly use the components contained in the waste and get a good fertilizer, it is necessary to isolate them. However, the problem of proper processing and waste management as well as recovery of valuable components is still waiting for a solution, not only in Poland but also in the world. At present, economically, struvite production is still unprofitable, but in the near future when fertilizer prices start to grow, the profitability of the process will become a reality. Struvite is an almost perfect fertilizer – in addition to containing two basic macroelements necessary for plant growth, it also exhibits correspondingly low solubility. So is the so-called organic fertilizer or in other words slow-acting fertilizer because it dissolves slowly in the soil and the plants themselves stimulate its intensity. In connection with the above, there is no leaching element for both its surface water and deeper soil layers, where it may become inaccessible to plants. As you can see, this mineral can significantly contribute to solving selected problems of environmental protection.

This work focuses on the analysis of the effect of struvite soil fertilization on the quality of effluent and the physical and chemical properties of soil.

2. Material and methods

The research was carried out in lysimeter columns, reflecting the top layer of the soil profile. The columns were filled with soil with appropriate doses of struvite. Struvite used in the tests was obtained in laboratory conditions.

2.1. Substrates for research

The soil for research according to the classification of Polish Society of Soil Science, the 2008 and USDA (United States Department of Agriculture) after drying to dry air and sieving through a 2 mm sieve, they were classified as loamy sand. The material was taken from the backyard garden. The effectiveness of fertilization on acidic soils is very low, therefore high pH soil was selected for testing.

This initial material was used to obtain 3 mixtures with different weight ratio, for 250 g of soil:

- mixture with content of 0.1 g struvite, denoted as M/0.1(53.2 kg/ha),
- mixture with content of 0.5 g struvite, denoted as M/0.5 (266.2 kg/ha),
- mixture with content of 1 g struvite, denoted as M/1.0 (533.5 kg/ha).

The control sample (soil without struvite addition) was denoted as M/0.0. Basic physical and chemical analyses were performed for samples of soil and soil mixtures (see Table 1).

Synthetic struvite was obtained from distilled water, the following ion concentrations were used: 100 mg PO_4^{3-}/L, 500 mg NH_4^+/L, 20 mg Mg^{2+}/L, and pH=10 (Worwąg 2018a; Worwąg 2018b; Worwąg & Kałwak 2018). The resulting sediments were analyzed using a X-ray diffractometer. The results of the analysis demonstrate that the sediments contain 99% of the mixture of struvite, its amorphous forms and trace contents of compounds used for synthesis of the compound, and NaOH used for correction of pH. Confirming the content of 58% P_2O_5 in the resulting sediments. Struwit contains 9.9% Mg, 12.62% P, 6.57% H, 5.71% N and 65.20% O. Amounts N introduced into the soil together with 0.1; 0.5; and 1 g struvite dose was 0.0057g, respectively; 0.02855g, 0.0571g. By contrast, the quantity P 0.01262 g for a dose of 0.1 g struvite; 0.0631 g for the 0.5 g dose and 0.1262 g for the 1 g dose.

2.2. Physical and chemical analysis

Analyses of soil material included:

- organic matter based on the EN 1997-2:2007 standard; Organic matter was determined by dry combustion (% OM determination): organic matter is burned in furnaces muffle furnace. First, the absolutely dry soil mass was determined, the soil sample was dried at 105°C and then, the sample was calcined in a mouflon oven at 500°C for 5 hours,
- pH in H_2O and 1M KCl for the soil was determined using the potentiometric method by means of a multiparameter meter (HANNA INSTRUMENTS HI 9828) according to ISO 10390:2005,
- total alkaline cations (Tac) were evaluated using the Kappen method (Karczewska & Kabała 2005),
- total carbon (TC) content was evaluated by means of the Multi N/C 2100 analyzer (Analytik Jena) according to PN-EN 15936:2013-02E,
- total phosphorus (TP) content was evaluated according to ISO 6878:2004,
- available phosphorus (AP) extraction by the Egner-Riehm method determined on a spectrophotometer (Riehm 1958),

- total nitrogen (TN) was determined by the Kjeldhal method (Horneck & Miller 1998) using the BÜCHI 435 mineralizer and the BÜCHI 355 distillation system.

Furthermore, pH, conductivity and TDS (Total Dissolved Solids) were determined in the leachates from lysimetric columns.

- electrical conductivity and TDS were determined directly in the leachate from lysimetric columns using a mulitparameter meter (HANNA INSTRUMENTS HI 9828),
- total phosphorus content was evaluated according to ISO 6878:2004.

Each evaluation was repeated for three times, and the analysis was based on mean values.

2.3. Research procedure – lysimeter test

The study used a lysimeters with a smooth inner wall made of acrylic glass with the length of 1.0 m and inner diameter of 5 cm. Each column was connected via a valve with a bottle in which the effluents formed were collected. Lysimeter examinations in the columns were carried out in 3 columns modeling 3 levels of soil washing (10, 20 and 30 cm) for each soil mixture with an appropriate dose of struvite and soil without struvite. Each experiment consisted of flushing water through a column filled with a mixture, with an amount modeling the average annual rainfall for the area from which the soil sample was taken, which was assumed at the level of 650 mm. Simulation of the rainfall was performed using deionized water, with its dose calculated according to annual rainfall levels in the area where soil sample was obtained, by converting to the surface of the column (0.001963 m^2).

The dose calculated in this way was divided into 12 portions corresponding to monthly precipitation, which were administered to the column for the next 12 days. Before the experiment began, the material in the columns was watered to similar water content (97.65%).

Leachates from the columns were collected every 2 days and designated as L1 (leachate after 2 days), L2 (leachate after 4 days), L3 (leachate after 6 days), L4 (leachate after 8 days), L5 (leachate after 10 days), L6 (leachate after 12 days). The research stand for the column experiments is shown in Figure 1.

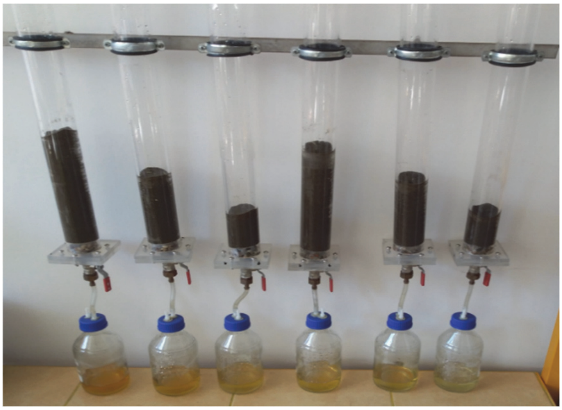

Fig. 1. Stand for column experiments

3. Results and discussion

3.1. Analysis of the soil before and after completion of the experiment

Table 1 presents overall characterization of soil and mixtures of soil with various doses of struvite before and after 12 days of running the experiment. After completion of the experiments, the soil was removed from the columns, averaged (3 columns with different height of soil profile were connected) for each combination and subjected to the analysis. Percentage of the organic fraction for the soil was 3.65%, whereas for the mixtures, it ranged from 3.30% to 3.35%. The content of organic matter after completion of the experiment was not significantly changed (OM: 3.18-3.32%)

Addition of struvite to soil led to the increase in the content of biogenic elements: total nitrogen and phosphorus, especially in the mixture of soil with 1g struvite. Total phosphorus content and available forms before experiment in the mixtures increased with the increasing struvite percentage. A noticeable increase in the content of available forms of phosphorus was observed for the mixtures with addition of 0.5 g and 1.0 g struvite. The total carbon content in the soil and mixtures was at a similar level, ranging from 15.01 to 15.2 mg/g. At the end of the experiment an increase in the tested parameter was observed for all combinations. A similar tendency was observed for total nitrogen.

Reducing the content of organic matter and at the same time increasing the content of total carbon in the soil after the experiment can be associated with the transformation of individual fractions included in the organic matter, the process of humification. In addition, some of the substance can be washed away and pass into the effluent. The high pH of the soil helps reduce the leaching of total carbon.

Table 1. Physical and chemical properties of test substrates: soil and soil mixtures (before and after experiment)

Parameters	Substrates			
	(M/0.0)	(M/0.1)	(M/0.5)	(M/1.0)
OM, %	3.65[b] 3.32[a]	3.30[b] 3.10[a]	3.33[b] 3.20[a]	3.35[b] 3.18[a]
pH, (-)	H_2O: 7.58[b] 7.80[a]	H_2O: 7.65b 7.75[a]	H_2O: 7.68[b] 7.84[a]	H_2O: 7.71[b] 7.81[a]
	KCl: 7.45[b] 7.38[a]	KCl: 7.42[b] 7.31[a]	KCl: 7.44b 7.30[a]	KCl: 7.48[b] 7.28[a]
Total alkaline cations, mmol (+) /100 g	0.20[b] 0.22[a]	0.22[b] 0.24[a]	0.23[b] 0.25[a]	0.23[b] 0.25[a]
Total carbon, mg/ g	15.01[b] 17.00[a]	15.18[b] 17.44[a]	15.20[b] 17.25[a]	15.17[b] 17.93[a]
Total phosphorus, mg P_2O_5/ 100 g soil	425.1[b] 401.4[a]	451.4[b] 421.0[a]	565.7[b] 510.1[a]	841.4[b] 675.5[a]
Available phosphorus, mg P/ kg	265.0[b] 228.0[a]	289.0[b] 274.0[a]	489.0[b] 417.0[a]	645.0[b] 488.0[a]
Total nitrogen, mg/g	0.79[b] 0.87[a]	0.80[b] 0.90[a]	0.89[b] 1.01[a]	1.01[b] 1.22[a]

b – before experiment
a – after experiment

Acidity is the basic indicator of soil fertility. It has a positive effect on the structure, determines the activity of microorganisms, the dynamics of the processes of mineralization and humification of organic matter, the absorption of macro- and microelements, and thus significantly affects the efficiency of fertilization. Optimal pH is the foundation of effective fertilization. The high pH of the studied soil had a beneficial effect on fertilization efficiency.

All the substrates were characterized by an alkaline reaction. Analysis of these parameters showed that the sample is alkaline mineral soil with high phosphorus content. After experiment, an insignificant reduction in the pH (KCl) value was found with the increase in struvite content in the soil. Availability of nutrients for plants depends on acidity of soil they grow in (Mocek 2015; Zawadzki 1999). According to Handzel, availability of some nutrients is reduced in acidic soils, eg. molybdenum, boron or phosphorus (Handzel et al. 2017).

3.2. Analysis of the leachate from lysimeter columns

Migration of phosphorus in the soil profile is connected with physico-chemical properties of the soil solution. The following parameters were evaluated to find changes in chemical composition of waters that wash the soil profile in eluates from lysimetric columns: reaction (pH), electrical conductivity (EC) and total dissolved solids (TDS), which is the indicator of water mineralization. Table 2 presents the results of the analysis of leachates from lysimetric columns sampled 6 times over the period of the experiment.

The first analyzed parameter was reaction of leachates from lysimetric columns. In all leachates from soil samples with addition of struvite, regardless of the sample height, a decline in pH was observed compared to pH of the leachate from the control sample (M/0.0 – soil without struvite addition). The highest differences were found for the 10 cm samples, with maximal decline in pH of 1.83 for addition of 1.0 g of struvite. For the samples with height of 20 and 30 cm, the reduction in the value was lower (max. 0.89). A general tendency for a gradual reduction in pH with the increase in struvite content in the sample was found, especially noticeable for the samples with height of 10 cm. This suggests that the most important changes occur in the upper part of the soil profile. Addition of struvite leads to an insignificant increase in acidity of leachates. However, pH determined for the soil samples and its mixtures after completion of the experiment (Table 2) confirms that they remain to have an alkaline character.

Electrical conductivity (EC) and TDS are the parameters which are closely correlated with each other and depend on each other. For most of the analyzed leachates, the increase in the content of struvite in the soil sample led to the increase in the value of both parameters. The biggest increase was found for the samples with content of struvite of 1.0 g, regardless of the sample height. They ranged from 143 $\mu S\ cm^{-1}$ and 0.07 ppb for the 10 cm samples to 404 $\mu S\ cm^{-1}$ and 0.2 ppb, and 597 $\mu S\ cm^{-1}$ and 0.3 ppb for the 20 cm and 30 cm samples, respectively. This means an increase at the level of 54.2-122.3% for EC and 53.8-183.3% for TDS. The increase in the content of struvite applied to the soil translated directly into mineralization of the soil solution. The analysis of the dynamics of soil profile leaching by consecutive doses that modelled the atmospheric precipitation showed a decline in salinity of the soil solution as a result of leaching the soluble forms, which is consistent with the commonly observed tendency (Roy 2017). Solutions with EC lower than 25,000 $\mu S\ cm^{-1}$ are considered as little saline. Therefore, the analyzed leachates belong to very little saline, whereas adding the used struvite doses did not lead to the increase in salination that would have a negative effect on plants by making it difficult to collect water or inhibiting root growth (Balemil & Negisho 2012).

Table 2. Analysis of the leachates from lysimetric columns

No leachate [1]	Parameters	Unit	Type of sample [2] – height of the soil profile, cm											
			M/0.0 –10	M/0.0 -20	M/0.0 -30	M/0.1 –10	M/0.1 -20	M/0.1 -30	M/0.5 –10	M/0.5 -20	M/0.5 -30	M/1.0 –10	M/1.0 -20	M/1.0 -30
L1	pH	(-)	8.25	8.19	*0	7.93	8.11	7.95	8.01	8.14	8.29	7.91	7.92	8.03
	COND	µS/cm	821	1842	*0	528	873	1301	575	1596	2491	694	2052	2238
	TDS	ppb	0.41	0.92	*0	0.26	0.44	0.65	0.29	0.80	1.20	0.35	1.03	1.22
L2	pH	(-)	8.16	8.18	7.97	7.63	7.64	7.73	7.80	8.02	8.05	7.26	7.71	7.82
	COND	µS/cm	331	505	1488	314	677	1008	357	581	899	418	909	1294
	TDS	ppb	0.16	0.25	0.74	0.16	0.34	0.50	0.18	0.29	0.44	0.21	0.45	0.64
L3	pH	(-)	8.39	8.14	8.11	8.49	8.02	7.85	7.55	7.60	7.76	7.02	7.45	7.68
	COND	µS/cm	193	285	488	332	410	550	194	360	680	276	590	1085
	TDS	ppb	0.10	0.14	0.24	0.16	0.21	0.28	0.1	0.18	0.34	0.14	0.29	0.54
L4	pH	(-)	8.33	8.24	8.21	7.43	7.26	7.43	7.51	7.49	7.64	7.14	7.35	7.37
	COND	µS/cm	264	241	482	223	351	223	262	289	545	407	414	692
	TDS	ppb	0.13	0.17	0.24	0.12	0.17	0.11	0.13	0.19	0.27	0.20	0.21	0.35
L5	pH	(-)	8.07	7.68	7.78	7.98	7.28	7.24	7.03	7.08	7.2	6.24	6.90	6.97
	COND	µS/cm	228	283	238	212	311	190	238	172	239	233	288	659
	TDS	ppb	0.11	0.14	0.12	0.11	0.16	0.10	0.12	0.09	0.12	0.12	0.14	0.34
L6	pH	(-)	8.25	8.09	8.05	7.56	7.29	7.42	7.52	7.51	7.49	6.82	7.73	7.71
	COND	µS/cm	127	145	210	139	164	196	111	154	206	111	241	367
	TDS	ppb	0.06	0.07	0.11	0.07	0.08	0.10	0.06	0.08	0.10	0.06	0.12	0.18

[1] designation as described in point 2.3.
[2] designation as described in point 2.1.
*0 – no leachate
COND – conductivity

Table 3. Analysis of phosphorus of the leachates from lysimetric columns

No leachates	mg P/L											
	Struvite dose g/250g soil											
	0 (control)			0,1			0,5			1,0		
	height of the soil profile (cm)											
	10	20	30	10	20	30	10	20	30	10	20	30
L1	0.62 ±0.08	1.00 ±0.01	0.39 ±0.01	2.32 ±1.02	2.49 ±1.15	1.79 ±1.25	10.55 ±0.16	11.66 ±0.0	11.20 ±0.11	18.75 ±5.71	24.95 ±4.23	13.11 ±2.15
L2	0.42 ±0.02	0.18 ±0.01	0.48 ±0.001	3.80 ±0.07	3.61 ±0.02	3.06 ±0.01	12.92 ±0.27	14.93 ±0.0	10.29 ±0.11	29.15 ±2.53	36.49 ±0.65	23.89 ±0.16
L3	0.35 ±0.02	0.20 ±0.02	0.47 ±0.002	3.49 ±0.09	3.85 ±0.03	3.62 ±0.07	10.32 ±0.05	12.55 ±0.18	10.32 ±0.05	28.27 ±0.11	37.91 ±1.02	39.62 ±0.11
L4	0.50 ±0,0	0.58 ±0.003	0.44 ±0.01	3.94 ±0.96	4.62 ±0.08	4.39 ±0.08	8.38 ±0.54	12.12 ±0.11	12.15 ±0.27	27.59 ±3.02	39.14 ±0.46	45.15 ±0.27
L5	0.82 ±0.04	0.69 ±0.01	0.40 ±0.01	3.92 ±0.001	4.60 ±0.0	3.93 ±0.13	8.27 ±0.05	11.66 ±0.11	13.11 ±0.43	26.71 ±0.16	41.26 ±1.56	57.99 ±0.54
L6	0.62 ±0.01	0.64 ±0.004	0.45 ±0.01	4.16 ±0.45	4.57 ±0.06	3.89 ±0.09	8.68 ±0.11	12.95 ±0.0	12.65 ±0.11	25.87 ±1.56	41.57 ±0.59	46.10 ±0.97

± standard deviation

3.3. Analysis of a phosphorus content in the leachate from columns lysimeter

Table 3 shows the content of P in the effluents registered for individual height of soil profiles in soil samples for subsequent leachate samples. Based on the obtained results, it was found that the mechanism of phosphorus release is similar, regardless of the dose of struvite used. However, the dose has a direct effect on the amount of leached phosphorus in the leachate. In addition, the relationship between pH and the content of leached phosphorus in leachate was confirmed (Busman et al. 2009). During the drop in pH (Table 2) an increase in the phosphorus content in the leachate was noted. Analyzing the phosphorus content in the leachate for individual doses and soil profiles, no regularity was observed. For each dose and individual profiles, the phosphorus leaching proceeded differently and with varying intensity and stability over time.

4. Conclusions

The amount of leached phosphorus is directly related to the dose of struvite in the mixture. As the dose increases, the content of leached into the phosphorus eluate increases. The highest levels of phosphorus concentrations per 20 cm of soil profile height are observed, for a 0.1 g struvite dose. For higher struvite doses, i.e. 1.0 the highest concentrations were recorded for the level of 30 cm. After the 6th intake of the eluate, which was the result of washing the soil profile with simulated annual precipitation, the concentration of leached phosphorus is decreased. It is to be expected that further washing of the bed will leach lower doses of soluble phosphorus until its soluble forms are exhausted.

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Abstract

The rapid physical and chemical degradation of the soil affected the physiological condition of the plants, resulting in a decrease in yields and their quality. Soil additives, consisting of specific mixtures of mineral compounds, should affect the activation of cellular metabolism processes, soil microflora, best adapted to the environment. An important element in the application of fertilizers is their dose, which is closely related to the previously determined soil parameters. This work focuses on the analysis of the impact of struvite soil fertilization on the quality of seepage water, the experiment was carried out in lysimeter columns. Different doses (0.1; 0.5; 1.0 g) of struvite obtained under laboratory conditions by chemical synthesis were used in the study. Three levels of soil wash (10, 20, 30 cm) were analyzed for each dose. For washing, distilled water was used in the amount corresponding to the average annual rainfall for the areas from which the soil was taken for testing. The experiment simulated the monthly precipitation each day, and the resulting effluents analyzed: phosphorus content, pH, conductivity, resistance and sum of dissolved substances Total Dissolved Solids (TDS).

Based on the obtained results, it was found that the amount of phosphorus leached is directly related to the dose of struvite in the mixture. The dependence between the amount of phosphorus in the leachate and the pH value was confirmed. Analyzing the effect of struvite fertilization on the soil, an increase in the content of biogenic elements with increasing doses, especially of available forms of phosphorus, has been noted. Despite the soil flushing, the phosphorus content in the soil was still high at the end of the experiment, confirming the low solubility of struvite and the slow release of the constituents.

Keywords:
struvite, soil, leachate waters, lysimeter, leaching

Wpływ nawożenia gleby struwitem na jakość wód odciekowych – kolumny lizymetryczne

Streszczenie

Postępująca szybko degradacja fizyczna i chemiczna gleby, wpłynęła na stan fizjologiczny roślin skutkując spadkiem plonów i ich jakości. Dodatki doglebowe, składające się z specyficznych mieszanin związków mineralnych powinny wpływać na aktywację procesów metabolizmu komórkowego, mikroflory gleby, najlepiej przystosowanej do środowiska. Istotnym elementem przy stosowaniu nawozów jest ich dawka, która ściśle powiązana jest z określonymi wcześniej parametrami gleby. Niniejsza praca skupiała się na analizie wpływu nawożenia gleby struwitem na jakość wód odciekowych, doświadczenie przeprowadzono w kolumnach lizymetrycznych. W badaniach zastosowano różne dawki (0.1; 0.5; 1.0 g) struwitu uzyskanego w warunkach laboratoryjnych na drodze syntezy chemicznej. Dla każdej dawki analizowano trzy poziomy przemywania gleby (10, 20, 30 cm). Do przemywania zastosowano wodę destylowaną w ilości odpowiadającej średnim rocznym opadom dla terenów z których pobrano glebę do badań. W eksperymencie symulowano miesięczny opad każdego dnia, a w powstających odciekach analizowano: zawartości fosforu, pH, przewodnictwo, oporność i suma substancji rozpuszczonych Total Dissolved Solids (TDS).

Na podstawie uzyskanych wyników stwierdzono, że ilość wyługowanego fosforu jest bezpośrednio związana z dawką struwitu w mieszaninie. Potwierdzono również zależność między ilością otrzymanego fosforu w odcieku a wartością pH. Analizując wpływ nawożenia struwitem na glebę, odnotowano wzrost zawartości pierwiastków biogennych wraz ze wzrostem dawki, zwłaszcza dostępnych form fosforu. Mimo przepłukiwania gleby, po zakończeniu doświadczenia zawartość fosforu w glebie była wciąż na wysokim poziomie, potwierdzając niską rozpuszczalność struwitu i powolne uwalnianie składników.

Słowa kluczowe:
struwit, gleba, wody odciekowe, lizymetr, ługowanie

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Evaluation of the Effectiveness of a Wastewater Treatment Plant with MBBR Technology

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1. Introduction

As environmental protection requirements have become more stringent in recent years, one consequence has been a search for more effective ways of treating wastewater biologically. Among the new solutions are ones based around the increased concentration of biomass in biological reactors as compared with conventional activated sludge. Examples of such solutions are:

- MBBR (Moving Bed Biofilm Reactor) technology, in which the reactor additionally contains carriers, e.g. of plastic, on which biofilm may form,
- AGS (Aerobic Granular Sludge) technology, in which microorganisms are concentrated in a compact spherical biomass resistant to variable loads of pollution,
- MBR (Membrane Biological Reactor) technology, in which membrane separation of treated wastewater from activated sludge is applied (Czarnota et al. 2016, Gromiec 2016).

The development of the MBBR process was based on the idea of bringing together, within a single system, the best characteristics of the activated sludge and biofilm processes, with the undesirable characteristics of each process eliminated (Barwal & Chaudhary 2014, Bassin & Dezotti 2018). The resultant technology is compact and easy to operate, and is often used as a retrofit of existing activated sludge tanks, in order to increase capacity in an existing system (Barwal & Chaudhary 2014). With biomass immobilised on free-support media, the retention of solids in the biological reactor is enhanced (Bassin & Dezotti 2018). The advantages of this technology as compared with activated-sludge systems are: a higher effective sludge retention time (SRT) that favours nitrification, more limited production of sludge, more limited requirements as regards area, and resilience to toxic shock. Moreover, this technology does not need recirculation of sludge, which is the case with activated-sludge systems, so process performance is independent of a secondary clarifier (Burton et al. 2013). It is concluded that MBBR is efficient in removing from municipal wastewater 60-90% of COD, 75-97% of BOD_5, 40-85% of TKN and other nutrients up to a certain extent (Barwal & Chaudhary 2014). A process based on a biofilm and activated sludge in the same tank favours nitrification, since the issue of the retention time for solids becomes partly uncoupled from the hydraulic retention time. This is particularly important where a WWTP is operating at low temperatures, as under these conditions, the sludge age needed to support nitrification is relatively great, due to the low growth rates achieved by nitrifying bacteria (Bassin & Dezotti 2018).

Regardless of the technology deployed, the stability and efficiency of any wastewater treatment plant are affected by factors over which the operator has no influence, has limited influence or has full control. Among the factors on which an operator has only limited influence is the quantitative and qualitative variability of the effluent flowing into the treatment plant. Quantitative and qualitative changes in wastewater are due to the specificity of the catchment area, the presence of industrial plants, the season, the day of the week or even the hours of the day. A detailed analysis of the quality and quantity of raw sewage allows the operator to select appropriate parameters to ensure proper operation of a facility (Piaskowski & Kołacz 2011, Bugajski et al. 2016, Krupicz & Masłoń 2016).

The aim of the article is to evaluate the work of the wastewater treatment plant in Nowa Wieś operating in the MBBR technology in the aspect of effective wastewater treatment. Due to the low stability of biogenic compounds removal from wastewater in the MBBR system, an analysis was made of the impact of wastewater temperature and the quality of raw wastewater and water drained from the lagoon on nitrification, denitrification and biological dephosphatation processes.

2. Characteristics of the Nowa Wieś WWTP

The mechanical-biological wastewater treatment plant in Nowa Wieś was commissioned in 1997. While the facility was extended and modernised in the 2003-2005 period the biological wastewater treatment technology based on the Bardenpho method emerged over time as no longer effective. This necessitated further modernisation of the plant between 2013 and 2015. The target capacity of the extended wastewater treatment plant is now of 2800 $m^3 \cdot d^{-1}$, while the population equivalent is 21000. The receiving water for treated wastewater is the Mrowla stream at km 2+700 along its length, and the discharge of the treated wastewater is regulated by a permit dated 28 June 2013 (Decyzja... 2013) issued on the basis of the 2017 Water Law Act. The quality requirements for treated wastewater specified in this document (in line with the applicable law), are as presented in Table 1. The technological system of the WWTP consists of an expansion chamber, sieve, grit chamber, separation chamber 1, two Moving Bed Biofilm Reactors, separation chamber 2 and two secondary settling tanks. The system is as presented in Fig. 1.

Table 1. Minimum percentage reduction in pollution[1] (Decyzja… 2013 & RMŚ 2014)

Highest permissible concentrations of pollutants in treated wastewater	Parameter				
	BOD_5 [%]	COD_{Cr} [%]	TSS [%]	TN [%]	TP [%]
Water Law permit	90.0	75.0	90.0	80.0	85.0
Regulation of the Minister for Environment	90.0	75.0	90.0	70.0-80.0	80.0

[1] the minimum percentage reduction of pollution levels is determined in relation to the pollutant load in the influent

Wastewater inflowing into the WWTP is discharged through pressure collectors to the expansion chamber (KRP), from where it flows to the Mechanical Treatment Building via a gravitational channel. The mechanical part of the plant is equipped with a sieve and a grit chamber. The sieve cooperates with the press to dewater screenings. The grit chamber, which is integrated with the sieve, works together with a sand separator. Following mechanical treatment, wastewater flows through the gravity channel to separation chamber 1 (KR1), from where it is directed for biological wastewater treatment along with the recirculated sludge flowing from the pre-denitrification sludge chamber (KPDN).

The processes removing compounds of carbon, nitrogen and phosphorus take place with the participation of activated sludge and MBBR technology, in two independent sequences. In the biological part of the treatment plant, wastewater in turn flows through:

- a denitrification chamber (BIO-DN) with submersible agitator, measuring sludge density, temperature, pH and oxygen (total chambers volume is 1123 m^3),
- a dephosphatation chamber (BIO-P) filled with EvU-Perl carrier (Fig. 2) (target filling at the level of 72 m^3), with submersible agitators and a deposit agitation grid (total volume 288.4 m^3),
- a nitrification chamber (BIO-N) equipped with an aeration grate, internal recirculation system (RW), agitators of the "mill wheel" type, and filling with EvU-Perl carrier (target filling of 114 m^3), a system to retain elements of this filling and a system to measure levels of dissolved oxygen (total chambers volume 1628 m^3).

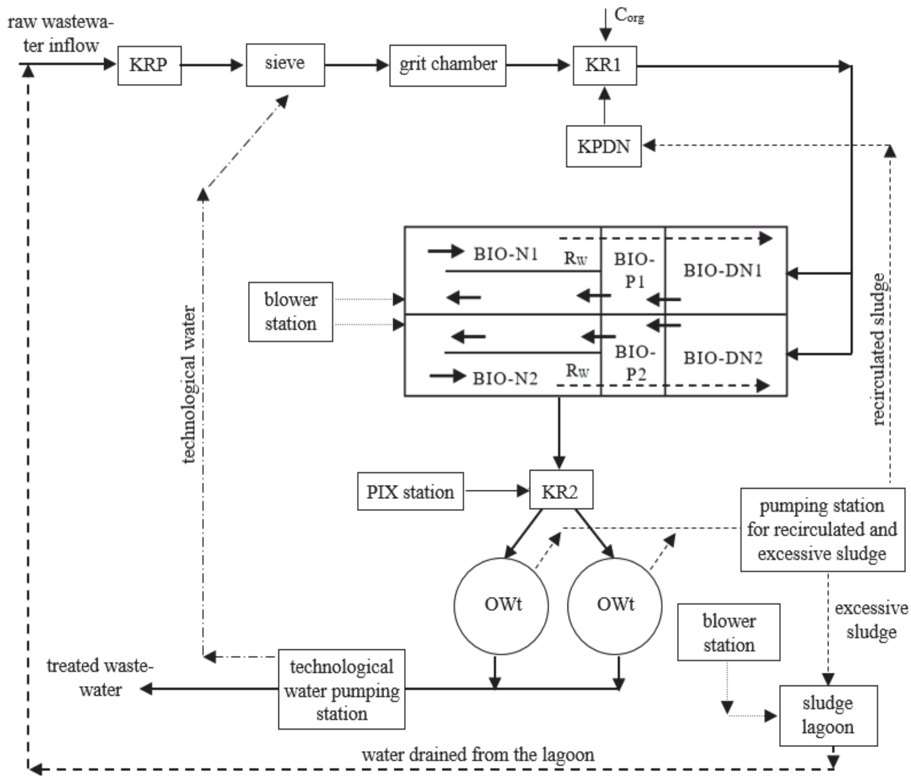

Fig. 1. Scheme presenting the technology used by the wastewater treatment plant in Nowa Wieś: KRP – expansion chamber, KR1 and KR2 – separation chamber 1 and 2, KPDN – pre-denitrification sludge chamber, BIO-DN – denitrification chamber, BIO-P – dephosphatation chamber, BIO-N – denitrification chamber, OWt – secondary settling tank

Fig. 2. The carrier EvU-Perl from Nowa Wieś WWTP (without and with biomass) (own photography)

The project assumes the following sludge technological parameters: sludge concentration – 3.7 kg·m^{-3}, sludge age – 20 days, and organic load – 0.0625 kg BOD_5·kg MLVSS^{-1}·d^{-1}. The volume load of the activated sludge chamber was assumed to be 0.231 kg BOD_5·m^{-3}·d^{-1}. The BOD_5 load on the surface of the deposit is 2.50 g BOD_5·m^{-3}·d^{-1}, for the specific surface of 700 m^2·m^{-3} and with a 14% volumetric share of carrier in the biological reactor. Moreover, it was assumed that if the ratio of TN/BOD_5 in the inflowing wastewater were to be unfavourable, an external source of organic compounds would be used. From the biological reactor, wastewater is discharged into separation chamber 2 (KR2), from where it flows into two radial settling tanks (OWt), where it is separated from biomass. PIX 122 coagulant is dosed into separation chamber 2, before the secondary settling tanks. From the latter, treated sewage flows through the chamber serving in monitoring and measurement prior to its being discharged to the receiving water.

Excessive sludge produced during biological wastewater treatment is directed to a sludge lagoon of cubic capacity 6329 m^3, which takes the form of an earth tank lined with PEHD film. In the balance of excessive sludge an increase in amount at the level of 0.8 kg MLVSS·kg BOD_5^{-1} was taken into account. At current loading of the Nowa Wieś WWTP, retention time for sludge in the lagoon is of 2 years and 3 months. The sludge in the lagoon is aerated using tubular fine-bubble diffusers. Periodic emptying of the lagoon of its accumulated sludge is carried out by means of a mobile press. Water drained from the lagoon is directed to the beginning of the purification system.

The study includes an analysis of the efficiency of operation of the Nowa Wieś WWTP in the 2016-2018 period. The assessment of the plant's efficiency was based on values for pollution indicators in raw and treated sewage made available by the plant operator (i.e. in relation to BOD_5, COD, TSS, TN and TP), as well as on the calculated efficiency of removal of particular pollutants. Chemical analyses for biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total nitrogen (TN), total phosphorus (TP), and total suspended solids (TSS) entailed measurement methods in line with Polish Standard Methods. Basic descriptive statistics such as minimum, maximum, average and median, along with standard deviation and coefficient of variation, were all determined for the aforementioned indicators.

3. Results and discussion

3.1. Hydraulic load of the WWTP

In the period under consideration, the Nowa Wieś WWTP operated under variable hydraulic conditions (Table 2, Fig. 3). Values for average daily flow ranged between 1482.0 $m^3 \cdot d^{-1}$ and 3617.0 $m^3 \cdot d^{-1}$. Both minimum and maximum flows were recorded in 2017. The mean daily flow in the three consecutive years was of 1965.9 $m^3 \cdot d^{-1}$, 1907.1 $m^3 \cdot d^{-1}$ and 1895.9 $m^3 \cdot d^{-1}$.

Table 2. Quantitative characteristics of wastewater flowing into the Nowa Wieś WWTP in 2016-2018

$Q_{av\ d}$ $[m^3 \cdot d^{-1}]$	Average	Median	Minimum	Maxi-mum	Standard deviation	Percentile 15%	Percentile 85%	Mean range
2016	1965.9	1905.0	1488.0	3235.0	265.4	1730.8	2222.5	1747.0
2017	1907.1	1859.0	1482.0	3617.0	239.7	1694.2	2145.2	2135.0
2018	1895.9	1848.5	1543.0	2857.0	213.1	1711.3	2109.0	1314.0

The mean hydraulic load in relation to the design hydraulic load of the treatment plant (2800.0 $m^3 \cdot d^{-1}$) was thus of about 70.0%, 68.0% and 67.7%, respectively. However, at different times over the analysed period, the amount of wastewater entering the plant oscillated between 53% and 129% of design capacity. Nevertheless, higher-than-planned flows were only noted 8 times, involving just 0.73% of all observations. They were a consequence of snowmelt and/or intensive precipitation (Fig. 3).

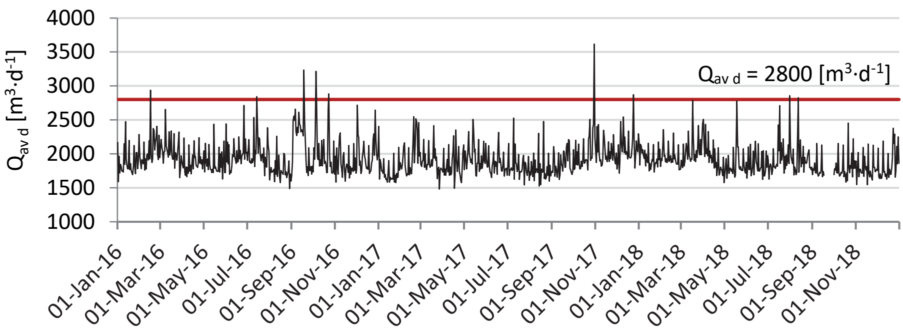

Fig. 3. Average daily flow into the WWTP, 2016-2018

The percentile of 85% of the recorded daily flows for each year is lower than the design flow. This indicates a reserve of hydraulic capacity of the plant at a level of about 640 $m^3 \cdot d^{-1}$. The total monthly flow varied from 53462 to 65745 $m^3 \cdot month^{-1}$. The months with the lowest and highest flows in the analysed period were November 2018 and September 2016 respectively.

3.2. Quality of raw wastewater

There were significant differences in the quality of wastewater flowing into the Nowa Wieś WWTP and the loads of individual pollutants (Table 3). Furthermore, significant change from year to year was to be noted in the content of pollutants in raw wastewater. The highest noted concentrations of organic compounds, as determined by BOD_5 and COD indices, and of total nitrogen, occurred in 2018 and were of 726.0 mg $O_2 \cdot dm^{-3}$, 1778.0 mg $O_2 \cdot dm^{-3}$ and 146.0 mg $TN \cdot dm^{-3}$ respectively.

Table 3. Values of selected descriptive statistics for concentrations and loads of individual pollutants noted in the 2016-2018 period

Parameter	Year	Pollution concentration [$mg \cdot dm^{-3}$]	Pollution load [$kg \cdot d^{-1}$]
		$\frac{\text{minimum} - \text{average} - \text{maximum}}{\text{standard deviation} - \text{coefficient of variation}}$	
BOD_5	2016	$\frac{296.0 - 387.3 - 513.0}{55.2 - 0.14}$	$\frac{580.2 - 742.6 - 913.7}{105.6 - 0.14}$
	2017	$\frac{339.0 - 408.5 - 490.0}{52.2 - 0.13}$	$\frac{616.0 - 767.9 - 983.4}{109.0 - 0.14}$
	2018	$\frac{296.0 - 459.8 - 726.0}{123.0 - 0.27}$	$\frac{529.5 - 876.3 - 1395.3}{252.0 - 0.29}$
COD	2016	$\frac{642.0 - 938.9 - 1293.0}{168.9 - 0.18}$	$\frac{1268.0 - 1810.0 - 2632.5}{391.3 - 0.22}$
	2017	$\frac{613.0 - 868.9 - 1061.0}{141.0 - 0.16}$	$\frac{1318.8 - 1627.4 - 1986.6}{244.4 - 0.15}$
	2018	$\frac{725.0 - 1068.9 - 1778.0}{275.6 - 0.26}$	$\frac{1286.2 - 2030.0 - 3134.6}{509.3 - 0.25}$
Total suspended solids	2016	$\frac{259.0 - 395.0 - 720.0}{128.5 - 0.33}$	$\frac{409.5 - 782.5 - 1758.2}{360.5 - 0.46}$
	2017	$\frac{146.0 - 307.4 - 470.0}{104.8 - 0.34}$	$\frac{246.6 - 573.4 - 859.6}{183.5 - 0.32}$
	2018	$\frac{183.0 - 475.3 - 920.0}{233.4 - 0.49}$	$\frac{324.6 - 904.0 - 1713.6}{437.0 - 0.48}$
Total nitrogen	2016	$\frac{72.1 - 93.8 - 121.0}{16.0 - 0.17}$	$\frac{128.7 - 180.1 - 227.1}{31.7 - 0.18}$
	2017	$\frac{72.9 - 98.3 - 123.0}{13.4 - 0.14}$	$\frac{149.6 - 184.0 - 217.7}{20.7 - 0.11}$
	2018	$\frac{70.5 - 98.2 - 146.0}{19.0 - 0.19}$	$\frac{150.7 - 188.1 - 312.7}{49.1 - 0.26}$
Total phosphorus	2016	$\frac{7.3 - 15.9 - 32.5}{8.2 - 0.52}$	$\frac{15.7 - 31.4 - 79.4}{19.6 - 0.62}$
	2017	$\frac{10.4 - 18.9 - 47.8}{10.2 - 0.54}$	$\frac{19.4 - 34.9 - 82.1}{17.1 - 0.49}$
	2018	$\frac{8.8 - 16.6 - 35.6}{7.1 - 0.43}$	$\frac{15.1 - 32.4 - 76.3}{16.5 - 0.51}$

The lowest values were in turn the 296.0 mg $O_2 \cdot dm^{-3}$ noted for BOD_5 (in 2016 and 2018), 613.0 mg $O_2 \cdot dm^{-3}$ for COD (2017) and 70.5 mg $TN \cdot dm^{-3}$ for total nitrogen (2018). In the case of total phosphorus, the highest concentration was the 47.8 mg $TP \cdot dm^{-3}$ recorded in 2017, while the lowest characterised 2016 (7.3 mg $TP \cdot dm^{-3}$). Higher concentrations of organic compounds, total nitrogen and total phosphorus in raw wastewater were to be observed in the April-June periods of each year, as a consequence of the introduction of water drained from the sludge lagoon, the quality of which changed in line with both ambient temperature and lagoon mixing.

The determination of BOD_5/COD, BOD_5/TN, COD/TN, BOD_5/TP and COD/TP ratios is important in assessing the susceptibility of wastewater inflow to a WWTP, e.g. to denitrification and biological dephosphatation processes (Cyganecka et al. 2008, Klaczyński 2012, Mazurkiewicz 2012, Klaczyński 2013, Młyńska et al. 2017, Sytek-Szmeichel et al. 2016). The BOD_5/COD value for example indicates susceptibility or resistance to biological decomposition on the part of organic compounds present in wastewater. In the period in question, 63.9% of the observations corresponded to average susceptibility of organic compounds to biochemical decomposition. The results indicating the presence of easily degradable organic compounds in wastewater are 19.4% (Fig. 4a). On the other hand, the most frequent BOD_5/TN ratios in raw wastewater were of between 3 and 5 (in 72.2% of cases), with this indicating a favourable influence of raw wastewater on the effectiveness of the denitrification process and numbers of nitrifying bacteria in activated sludge. BOD_5/TN values below 3 in turn indicate that the nitrification process may dominate in a reactor, but were noted in just 2.3% of observations (Fig. 4b). In the case of the COD/TN ratio, values above 8 (Cyganecka et al. 2008) and above 9 (Klaczyński 2012) were noted in 88.9 and 63.9% of cases respectively. In the case of the BOD_5/TP ratio, over 72% of cases involved values greater than 20 (Fig. 4c). On the other hand, almost 78% of COD/TP values were higher than the minimum recommended value, i.e. 40, indicating the most favourable conditions for effective phosphorus removal by way of the biological phosphorus-removal process.

Changes in the amount of wastewater flowing into the wastewater treatment plant and different concentrations of particular pollutants translate into pollutant loads in the years analysed. The distribution of organic pollutant loads expressed as BOD_5 and COD indexes oscillated in the 529.5-1395.3 kg $O_2 \cdot d^{-1}$ range, and between 1268.0 and 3134.6 kg $O_2 \cdot d^{-1}$ respectively. The load of biogenic compounds was from 128.7 to 312.7 kg $TN \cdot d^{-1}$ and from 15.1 to 82.1 kg $TP \cdot d^{-1}$. The load of total suspended solids was in turn between 246.6 and 1758.2 $kg \cdot d^{-1}$.

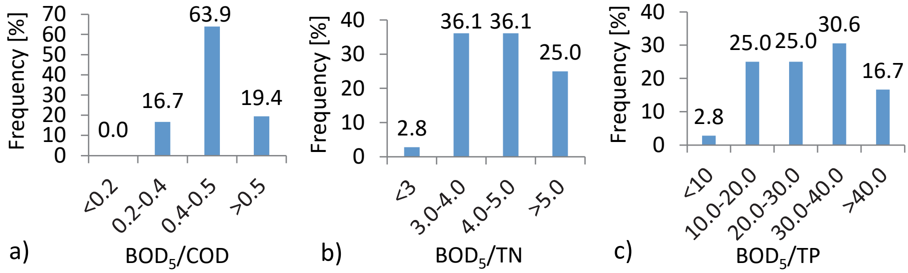

Fig. 4. Frequency of occurrence of specific values of selected ratios

3.3. Efficiency of wastewater treatment

The criterion for evaluation the efficiency of the wastewater treatment plant in Nowa Wieś form the percentage reduction of organic compounds, biogenic compounds and suspension. Selected descriptive statistics on the effectiveness of removal of particular pollutants from wastewater and the quality of treated wastewater are presented in Tab. 4.

The analysis of the results shows that the percentage of reduction of organic compounds and total suspended solids in the wastewater treatment plant in question was higher than the minimum percentage of reduction of pollution specified in the water-rights permit. The effectiveness of organic compounds removal for BOD_5 and COD ranged from 96.9 to 99.7% and from 90.1 to 98.9%, respectively. The concentration of organic compounds in treated wastewater oscillated between 1.2 and 10.4 mg $O_2 \cdot dm^{-3}$ and between 10.0 and 76.0 mg $O_2 \cdot dm^{-3}$, respectively for BOD_5 and COD (Table 4, Fig. 5a and b).

The efficiency of reduction of total suspended solids from wastewater was from 91.5 to 99.8%, as a result the concentration of the suspended solids in the outflow varied in the range of 2.0-18.4 $mg \cdot dm^{-3}$ (Table 4, Fig. 5c).

In the analysed period of operation of the WWTP, reductions in levels of biogenic compounds proved to be insufficient. The efficiency of total nitrogen removal ranged from 8.4 to 93.8%, and the concentration of this pollutant in the outflow from the wastewater treatment plant ranged from 6.3 to 83.7 mg $TN \cdot dm^{-3}$ (Table 4, Fig. 5d). The efficiency of TN removal below the required reduction efficiency specified in the water-rights permit (80.0%) was recorded 13 times within 3 years. Insufficient removal of nitrogen compounds in each of the analysed years was observed in the period from January to April (in 2017 year also in May). Both the lowest and the highest reduction of nitrogen compounds was recorded in 2017 year.

Table 4. Values of selected descriptive statistics for the concentration and efficiency of removal of individual pollutants in the years 2016-2018

Parameter	Year	Pollution concentration [mg·dm^{-3}]	Efficiency [%]
		$\frac{\text{minimum} - \text{average} - \text{maximum}}{\text{standard deviation} - \text{coefficient of variation}}$	
BOD_5	2016	$\frac{1.8 - 3.4 - 5.5}{1.3 - 0.38}$	$\frac{98.2 - 99.1 - 99.6}{0.4 - 0.00}$
	2017	$\frac{1.2 - 4.2 - 10.4}{2.7 - 0.63}$	$\frac{96.9 - 98.9 - 99.7}{0.7 - 0.01}$
	2018	$\frac{1.9 - 5.2 - 7.3}{1.9 - 0.36}$	$\frac{97.7 - 98.7 - 99.7}{0.6 - 0.01}$
COD	2016	$\frac{10.0 - 39.7 - 60.0}{16.9 - 0.43}$	$\frac{91.0 - 95.7 - 98.9}{2.1 - 0.02}$
	2017	$\frac{17.0 - 46.9 - 76.0}{22.2 - 0.47}$	$\frac{90.1 - 94.6 - 98.1}{2.6 - 0.03}$
	2018	$\frac{29.0 - 43.3 - 56.0}{9.1 - 0.21}$	$\frac{92.9 - 95.6 - 98.3}{1.5 - 0.02}$
Total suspended solids	2016	$\frac{3.8 - 8.3 - 15.4}{3.1 - 0.38}$	$\frac{96.0 - 97.8 - 98.8}{1.0 - 0.01}$
	2017	$\frac{3.0 - 7.6 - 16.8}{4.2 - 0.55}$	$\frac{91.5 - 97.3 - 98.9}{2.0 - 0.02}$
	2018	$\frac{2.0 - 9.0 - 18.4}{5.5 - 0.61}$	$\frac{95.6 - 97.7 - 99.8}{1.4 - 0.01}$
Total nitrogen	2016	$\frac{7.52 - 20.8 - 49.7}{17.8 - 0.85}$	$\frac{41.5 - 78.7 - 91.3}{17.5 - 0.22}$
	2017	$\frac{6.3 - 34.0 - 83.7}{32.6 - 0.96}$	$\frac{8.4 - 65.6 - 93.8}{33.1 - 0.50}$
	2018	$\frac{7.0 - 21.3 - 59.9}{19.8 - 0.93}$	$\frac{29.9 - 76.7 - 93.1}{22.9 - 0.30}$
Total phosphorus	2016	$\frac{0.21 - 2.1 - 9.2}{2.7 - 1.27}$	$\frac{70.0 - 89.4 - 97.3}{9.7 - 0.11}$
	2017	$\frac{0.1 - 3.4 - 14.8}{4.2 - 1.23}$	$\frac{69.0 - 85.6 - 99.1}{11.8 - 0.14}$
	2018	$\frac{0.32 - 2.1 - 7.31}{2.0 - 0.95}$	$\frac{56.5 - 87.2 - 97.3}{11.5 - 0.13}$

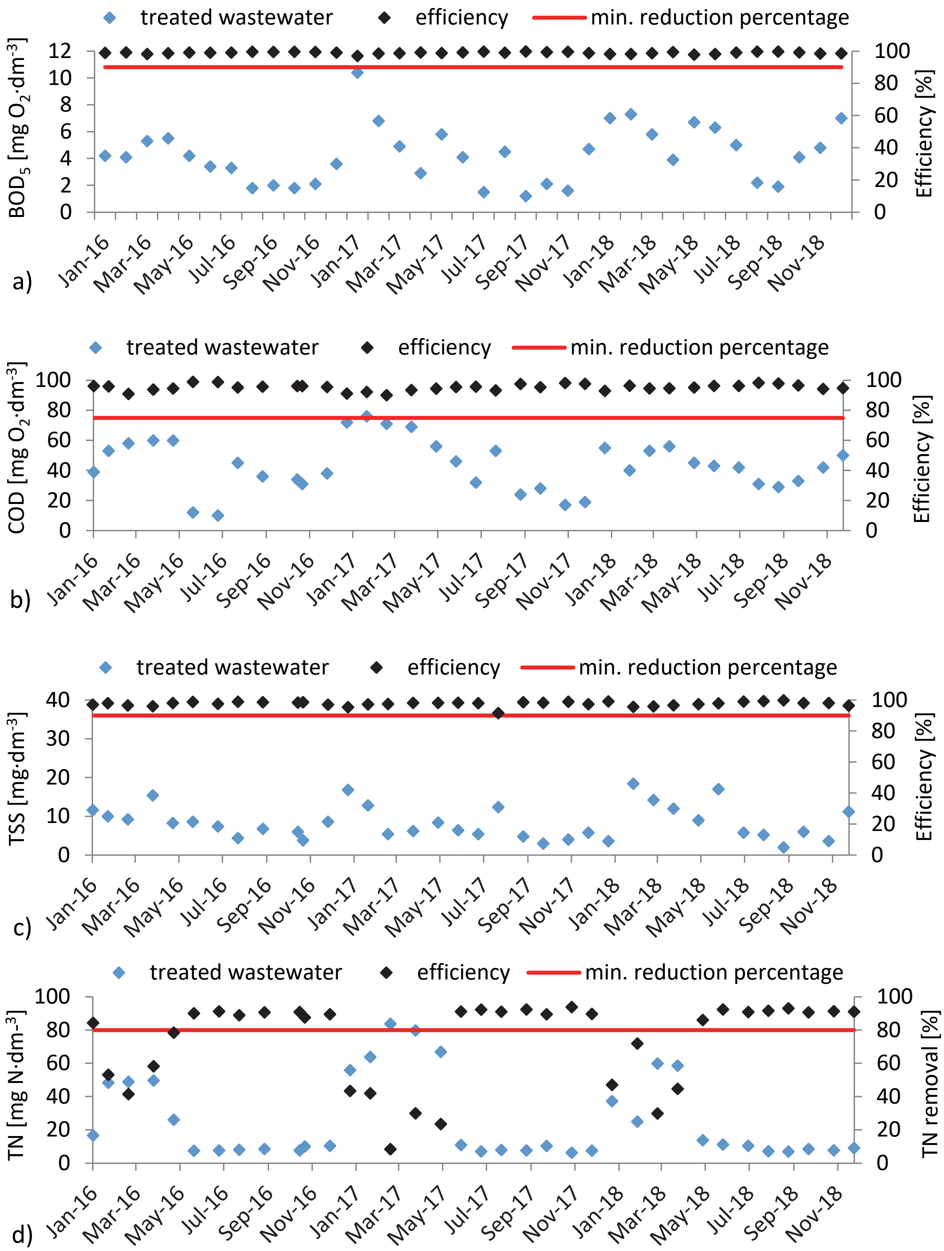

Fig. 5. The quality of treated wastewater and removal efficiency of individual pollutants

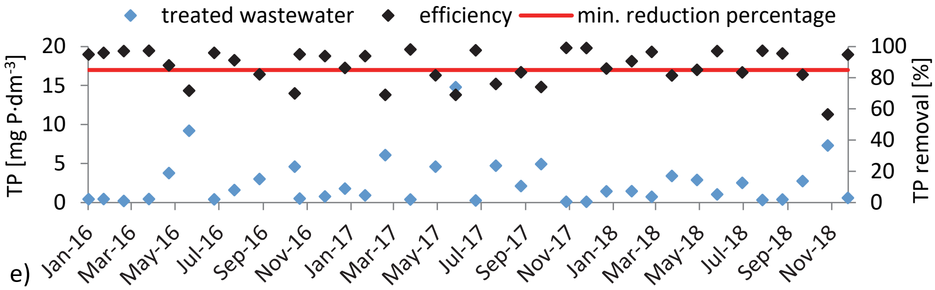

Fig. 5. cont.

The results of biochemical tests from the winter period (January 2018) showed a decrease in nitrification rate between two dates, both by the biomass of the activated sludge (by approx. 79.4%) and biomass on the carrier (by approx. 60.0%). In addition, the highest percentage of nitrification conducted by the biofilm was only 17.7%. Also in the assessment of the denitrification rate, between successive dates, a decrease of about 43.0% for active sludge and about 68.0% for biomass on a carrier was observed.

On the other hand, the efficiency of removing total phosphorus from wastewater was from 56.5 to 99.1%, while the average efficiency in subsequent years was 89.4±9.7%, 85.6±11.8% and 87.2±11.5%. The concentration of this pollutant in treated wastewater varied from 0.1 to 14.8 mg TP·dm^{-3} (Table 4, Fig. 5e). The achieved efficiency of total phosphorus removal resulted not only from biological phosphorus removal but also from chemical phosphorus precipitation. The efficiency of TP removal below the required reduction efficiency specified in the water-rights permit (85.0%) was also recorded 13 times within 3 years. However, it was not observed that the decrease of efficiency was in the same months in the subsequent years. Only October was the month in which the decrease in phosphorus reduction observed in all years. Moreover, twice (2016 and 2017) such a dependency was observed in June and September.

According to the literature, there are different levels of efficiency of removal of organic and biogenic compounds using MBBR technology. Chu & Wang (2011) applied MBBR technology to remove organics and nitrogen from wastewater with a low C/N ratio, achieving levels of 90.0 and 65.0% respectively in so doing. Shrestha (2013) reported, that carrier filling rate in a MBBR is important to the removal of organic compounds. In research carried out at 10, 20, 30 and 40% filling rates, the average levels of COD removal efficiency reported were 75.7, 91.1, 85.5 and 79.6% respectively. Ahmadi et al. (2014) reported that the efficiency of an MBBR system as regards COD removal exceeded 80%. In turn, Wang et al. (2006) reported that efficiency of removal of COD from domestic wastewater was in the 71.3-77.1% range. Gani et al. (2016) found levels of removal of total phosphorus and suspended solids ranging from 84.0 to 98.0% and 85.0 to 94.0%, where influent concentrations were 3.3-7.1 mg TP·dm^{-3} and 74.0-356.0 mg·dm^{-3}, respectively. In an MBBR with suspended plastic carriers (AnoxKaldnes K5), and a 50% filling ratio, average phosphorus and total nitrogen removal efficiencies were respectively of 76.8% and 70.0% (almost complete nitrification, with average ammonium removal efficiency equal to 82%) (Mudhaffar et al. 2015). By using a moving bed biofilm process in conditions that were anaerobic or anoxic, or aerobic, total nitrogen and phosphorus removal efficiencies obtained were of 84.6 and 95.8% respectively (Kermani et al. 2008).

The wastewater treatment plant in Nowa Wieś is obliged to remove biogenic compounds, however, the results presented in Table 4 and Fig. 5 confirm the operational problems of the facility in this scope. The data made available by the operator show that the sludge age in these years was maintained at the range of about 5 to 25 days. The concentration of biomass varied from approx. 2.0 to 5.8 kg MLVSS·m^{-3}, while the biomass loading of BOD_5 ranged from 0.04 to 0.11 kg BOD_5·kg MLVSS^{-1}·d^{-1}. The degree of external recirculation was also kept within the recommended limits with the average value of approx. 0.8. In turn, the degree of internal recirculation allowed to maintain the nitrate concentration at the level of 6.0 mg·dm^{-3}.

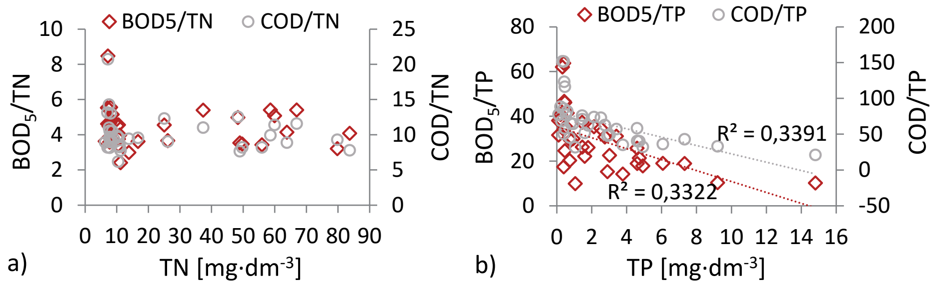

Fig. 6. Relationship between selected ratios and TN or TP concentrations in treated wastewater

The recognizing of the effect of BOD_5/TN and COD/TN ratio of raw wastewater did not show any significant dependencies between these ratios and the degree reduction of total nitrogen and total nitrogen concentration in treated wastewater. However, it can be observed (Fig. 6a) that the concentration of total nitrogen in treated wastewater below 10.0 mg TN·dm^{-3} was most frequently observed at BOD_5/TN values ranging from 3.60 to 5.0. In turn, a high correlation was observed between BOD_5/TP and COD/TP ratio and total phosphorus concentration in treated wastewater (r = 0.5764 and r = 0.5823) (Fig. 6b). The lowest

TP concentrations in treated wastewater, at the level of up to 1.0 mg P·dm^{-3}, were observed for BOD_5/TP ratio values above 30.

Over the whole 2016-2018 period, the temperatures in the BIO-DN1 and BIO-DN2 chambers were in the range 7.5-20.5°C. Assessment of the dependent relationship between TN concentration in outflow and efficiency of removal as set against temperature (Fig. 7) showed a high level of correlation (r = 0.7665 and 0.7647 respectively).

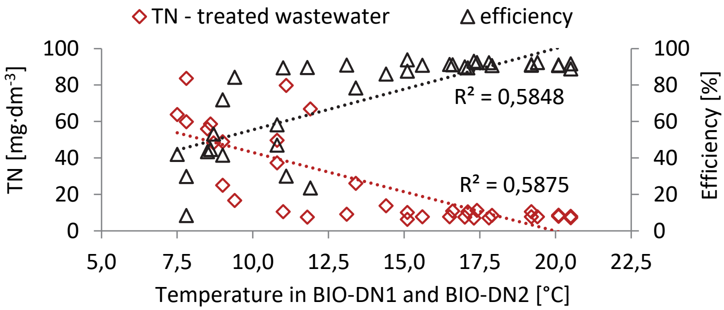

Fig. 7. Relationship between TN concentration in outflow or TN removal efficiency and temperature in the denitrification chamber

Periods of low temperature were indeed associated with increased concentrations of total nitrogen in treated wastewater (typically to about 50.0 mg·dm^{-3} in 2016, 84.0 mg·dm^{-3} in 2017 and 60.0 mg·dm^{-3} in 2018). In addition, WWTP employees report very high winter concentrations of ammonium compounds in outflow, indicative of low efficiency (i.e. inhibition) of the nitrification process. There nevertheless remain points not accounted for readily by reference to this relationship, which may indicate the presence of a further factor influencing nitrification.

Over the analysed period, water drained from the sludge lagoon was also introduced into the technological process of wastewater treatment. This represents an additional load of biogenic compounds also capable of impacting upon treatment efficiency. Values for TN and TP loads in raw wastewater and water drained from the sludge lagoon on selected dates were as presented in Fig. 8.

The nitrogen load introduced with water drained from the sludge lagoon was in the range 6.9-30.8 kg TN·d^{-1}, in this way accounting for between 3.0 and 20.0% of the load in raw wastewater (Fig. 8a). Total nitrogen concentrations varied from 67.8 to 145.0 mg TN·dm^{-3} in the case of raw wastewater, from 38.0 to 197.5 mg TN·dm^{-3} in water draining from sludge lagoon and from 11.0 to 92.0 mg TN·dm^{-3} in treated wastewater. However, it should be emphasised further that on days when a high concentration of TN in water draining from sludge lagoon was observed and the ambient temperature was propitious, the TN concentration in treated wastewater was low. This suggests that temperature was indeed the main factor limiting effective removal of nitrogen compounds.

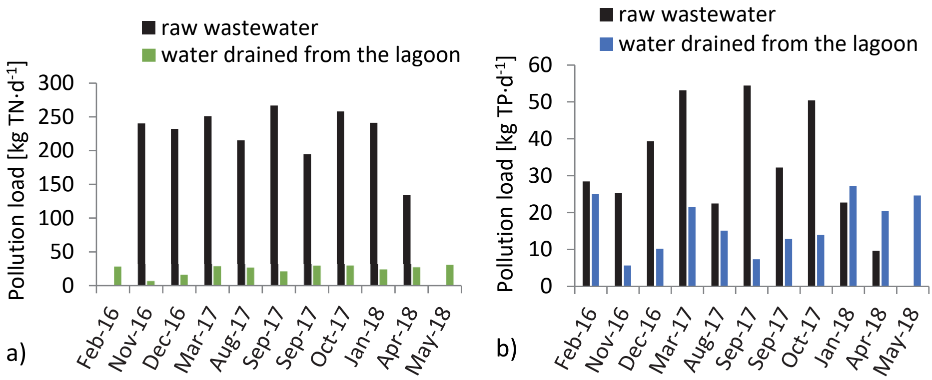

Fig. 8. Values for loads of biogenic pollutants in raw wastewater and water drained from the sludge lagoon

On the other hand, the total phosphorus load varied from 5.6 to 27.2 kg TP·d^{-1} and made up from 13.5% to 210.0% load of raw wastewater (Fig. 8b). Phosphorus concentration ranged from 4.9 to 29.6 mg TP·dm^{-3} – raw wastewater; from 31.0 to 158.0 mg TP·dm^{-3} – water drained from sludge lagoon and from 1.0 to 10.7 mg TP·dm^{-3} – treated wastewater. It should be emphasized that in the sludge lagoon anaerobic conditions prevail, which causes the release of phosphorus embedded in the biomass in the biological part of the treatment plant. Therefore, the primarily removed phosphorus is released back and returned with water drained from sludge lagoon to the wastewater part. It is worth emphasizing that on the days when very high concentrations of TP in water drained from sludge lagoon were observed, the concentration in the effluent from WWTP was usually above 5.0 mg TP·dm^{-3}. Thus, it was one of the causes of increased phosphorus concentration in the effluent from the wastewater treatment plant.

4. Conclusions

The hydraulic load of the wastewater treatment plant in Nowa Wieś is 68.6% of the planned load, which is 2800.0 m^3-d^{-1}. The hydraulic capacity reserve of the plant, estimated by reference to the percentile value of 85% of recorded daily flows, is approximately 640 m^3·d^{-1}. The interpretation of the plant's efficiency in relation to the requirements set out in the permit issued under the Water

Law Act indicates correct operation of the facility in terms of the removal of organic compounds and elimination of total suspended solids.

The average level of efficiency determined for the removal of organic compounds from sewage was 98.9±0.6% for BOD_5 and 95.3±2.1% for COD, denoting that the average concentration of these compounds in outflow was of 4.3±2.1 and 43.3±16.7 mg $O_2 \cdot dm^{-3}$ respectively. The average value for the efficiency of removal of total suspended solids was in turn 97.6±1.5%, with the average concentration on discharge equal to 8.3±4.3 mg$\cdot$dm^{-3}. Unfortunately, in the analysed years, a dozen or so times (in about 36% of the results) the reduction of biogenic compounds proving achievable was below the level laid down by the permit, i.e. 80.0% for TN and 85.0% for TP. The average efficiencies of removal of nitrogen and phosphorus compounds from wastewater in the analysed period were in fact of 73.7±25.3% and 87.4±10.8% respectively. This denotes that the average concentration of biogenic compounds in treated wastewater was 25.4±24.4 mg TN$\cdot$dm^{-3} and 2.5±3.1 mg TP$\cdot$dm^{-3}. The evaluation of raw wastewater quality showed that values for the BOD_5/TN, COD/TN, BOD_5/TP and COD/TP ratios are invariably within the range recommended for the proper course of denitrification and nitrification processes. This leaves the typical cause of problems relating to insufficient removal of total nitrogen as low temperature, which is found to restrict nitrification. In addition, it is possible to conclude that water drained from the sludge lagoon may have contained substances also acting to curb the nitrification process. In the case of insufficient reduction of phosphorus compounds, the problem results from additional loading of this pollutant.

If the efficiency of nutrient removal in the Nowa Wieś WTTP is to be raised, sludge management will need to be organised better. It may also be necessary to adapt the nitrification chambers to low winter temperatures by increasing their volume, or by replacing the biofilm carrier. It is also worthwhile assessing the quality of wastewater treated mechanically, with attention paid to the of BOD_5/TN, COD/TN, BOD_5/TP and COD/TP ratios, with a view to noting if these are definitely favourable to biological wastewater treatment processes.

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Abstract

The MBBR technology base on the idea of bringing together, within a single system, the best characteristics of the activated sludge and biofilm processes. With biomass immobilised on free-support media, the retention of solids in the biological reactor is enhanced. The advantages of this technology as compared with activated-sludge systems are: a higher effective sludge retention time (SRT) that favours nitrification, more limited production of sludge, more limited requirements as regards area, and resilience to toxic shock. The MMBR technology does not need recirculation of sludge, which is the case with activated-sludge systems, so process performance is independent of a secondary clarifier. Wastewater treatment based on the MBBR process in the same tank favours nitrification, since the issue of the retention time for solids becomes partly uncoupled from the hydraulic retention time. This is particularly important where a WWTP is operating at low temperatures, as under these conditions, the sludge age needed to support nitrification is relatively great, due to the low growth rates achieved by nitrifying bacteria.

The aim of the paper is the evaluation of the effectiveness of a wastewater treatment plant in Nowa Wieś (Poland). The technological system of the Nowa Wieś WWTP consists of an sieve, grit chamber, two reactors with moving bed biofilm (MBBR reactors with the EvU-Perl carriers) and two secondary settling tanks. The study includes an analysis of the efficiency of operation of the Nowa Wieś WWTP in the 2016-2018 period. The assessment of the plant's efficiency was based on values for pollution indicators in raw and treated sewage made available by the plant operator (i.e. in relation to BOD_5, COD, TSS, TN and TP), as well as on the calculated efficiency of removal of particular pollutants.

The average level of efficiency determined for the removal of organic compounds from sewage was 98.9±0.6% (BOD_5) and 95.3±2.1% (COD), denoting that the average concentration of these compounds in outflow was of 4.3±2.1 and 43.3±16.7 mg $O_2 \cdot dm^{-3}$ respectively. The average value for the efficiency of removal of total suspended solids was in turn 97.6±1.5%, with the average concentration on discharge equal to 8.3±4.3 $mg \cdot dm^{-3}$. Unfortunately, in the analysed years, a dozen or so times (in about 36% of the results) the reduction of biogenic compounds proving achievable was below the level laid down by the permit, i.e. 80.0% for TN and 85.0% for TP. The average efficiencies of removal of nitrogen and phosphorus compounds from wastewater in the analysed period were in fact of 73.7±25.3% and 87.4±10.8% respectively. This denotes that the average concentration of biogenic compounds in treated wastewater was 25.4±24.4 mg TN·dm^{-3} and 2.5±3.1 mg TP·dm^{-3}.

Keywords:
MBBR technology, activated sludge, EvU-Perl carrier material, organic compounds, biogenic compounds

Ocena efektywności działania oczyszczalni ścieków z technologią MBBR

Streszczenie

Technologia złoża ruchomego (MBBR) opiera się na idei połączenia w ramach jednego systemu najlepszych cech osadu czynnego i błony biologicznej. W wyniku unieruchomienia mikroorganizmów na ruchomych nośnikach, retencja biomasy w reaktorze biologicznym jest zwiększona. Zaletami tej technologii w porównaniu do klasycznego osadu czynnego są: wyższy efektywny wiek osadu, który intensyfikuje proces nitryfikacji, mniejszy przyrost osadu nadmiernego oraz odporność układu na dopływ substancji toksycznych. Technologia MBBR nie wymaga recyrkulacji osadu czynnego, co ma miejsce w przypadku systemów osadu czynnego, więc wydajność procesu jest niezależna od osadnika wtórnego. Oczyszczanie ścieków w oparciu o proces MBBR sprzyja nitryfikacji, ponieważ kwestia czasu retencji biomasy zostaje częściowo niezależna od hydraulicznego czasu retencji. Jest to szczególnie ważne, gdy oczyszczalnia ścieków działa w niskich temperaturach, ponieważ w tych warunkach wiek osadu potrzebny do podtrzymania nitryfikacji jest stosunkowo duży, ze względu na niskie tempo wzrostu osiągane przez bakterie nitryfikacyjne.

Celem pracy jest ocena efektywności oczyszczalni ścieków w Nowej Wsi (Polska). Układ technologiczny oczyszczalni w Nowej Wsi składa się z sita i piaskownika, dwóch reaktorów z osadem czynnym i złożem ruchomym w postaci kształtek EvU-Perl oraz dwóch osadników wtórnych. Opracowanie obejmuje analizę efektywności działania oczyszczalni ścieków w Nowej Wsi w latach 2016-2018. Ocenę efektywności przedmiotowej oczyszczalni dokonano w oparciu o wartości wskaźników zanieczyszczeń w ściekach surowych i oczyszczonych udostępnionych przez eksploatatora oczyszczalni (BZT_5, ChZT, zawiesina ogólna, azot ogólny, fosfor ogólny), a także obliczonej efektywności usuwania poszczególnych zanieczyszczeń.

Średnia efektywność usunięcia ze ścieków związków organicznych wyniosła 98.9±0.6% (BZT_5) oraz 95.3±2.1% (ChZT), efektem czego średnie stężenie tych związków w odpływie wynosiło odpowiednio 4.3±2.1 mg O_2·dm^{-3} oraz 43.3±16.7 mg O_2·dm^{-3}. Wartość średnia efektywności usuwania zawiesiny ogólnej była na poziomie 97.6±1.5%, przy średnim stężeniu równym 8.3±4.3 mg·dm^{-3}. Niestety w analizowanych latach kilkanaście razy (ok. 36% wyników) odnotowano niższy stopień redukcji związków biogennych, niż ten określony pozwoleniem wodno-prawnym tj. 80.0% dla N_{og} i 85.0% dla P_{og}.

Wyznaczona średnia efektywność usunięcia związków azotu i fosforu ze ścieków w rozpatrywanym okresie wyniosła odpowiednio 73.7±25.3% oraz 87.4±10.8%. Średnia wartość stężenia związków biogennych w ściekach oczyszczonych była równa 25.4±24.4 mg N·dm^{-3} oraz 2.5±3.1 mg P·dm^{-3}.

Słowa kluczowe:
technologia MBBR, osad czynny, złoże biologiczne EvU-Perl, związki organiczne, związki biogenne

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An Analysis of Bioelements in the Source Waters of Sanok District on the Border of the Eastern and Western Carpathians and their Impact on the Functioning of the Human Body

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1. Introduction

The cradle of contemporary balneotherapy and physical therapy were the peoples inhabiting the lands of the Mediterranean basin. Ancient Egyptians, Greeks and Romans discovered the healing values of the surrounding nature. Hippocrates (460-380 BC) and Asklepiades (120-56 BC) were considered the precursors of medical art in ancient times, who mainly used the benefits of sunlight and water (Rak 2011). Wojciech Oczko (1537-1599), the court physician of Stefan Batory and Zygmunt III (Tchórzewska-Cieślak and Rak 2005) is considered to be the father of Polish balneology. An important concept of balneology is crenotherapy. Crenotherapy is a drinking therapy with mineral waters. The following types of mineral waters are distinguished:

Natural spring water is water originating from documented underground resources, extracted with one or more natural or drilled holes, originally pure chemically and microbiologically, not differing in properties and mineral composition from water intended for human consumption, specified in the provisions on collective supply in water (Tchórzewska-Cieślak and Rak 2006).

Natural mineral water is water originating from documented resources of groundwater, extracted with one or more natural or drilled holes, originally pure chemically, microbiologically, characterized by stable mineral composition and properties of physiological significance, resulting in beneficial effects on human health, according to specific requirements (Tchórzewska-Cieślak and Rak 2005, Tchórzewska-Cieślak and Rak 2006, Rozporządzenie 2011).

Bottled medicated water is water intended for sale in unit packaging, originally clean, untreated underground water from one deposit, whose chemical composition and physical properties determine a specific therapeutic effect, confirmed by the results of pharmacological research (Tchórzewska-Cieślak and Rak 2006, PN-Z- 11001-1).

Pharmacodynamic factors are the minimum content of selected chemical components (so-called specific components) or the minimum value of the physical properties of water that causes their therapeutic effect (Rozporządzenie 2016, Michalski 2006). The basic components of mineral waters whose content in water determines its degree of mineralization include: anions: chloride, bicarbonate and sulphate, and cations: sodium, potassium, calcium and magnesium (Tchórzewska-Cieślak and Rak 2006). It is worth remembering that natural mineral waters not only supplement water losses, but also shortages of some of the bio-elements that are essential for the proper functioning of the body. Essential for the body bioelements taken from mineral water are bioactive and easily digestible (Błaszczyk and Tuszyński 2007).

The basic process conditioning the existence of Earth's Shell - called the biosphere – is photosynthesis, taking place in green parts of plants with the participation of chlorophyll, using solar energy, in the presence of minerals. The role and share of individual bioelements in biochemical processes occurring in living organisms are largely determined by the atom's structure (Gertig and Przysławski 2006).

Taking a quantitative criterion of difference in the occurrence in the body and the ranges of recommended intake, these bioelements are divided into macroelements and microelements. You can also distinguish a three-level division, which also takes into account the so-called ultra-trace elements (Gertig and Przysławski 2006).

Macroelements – elements whose content in the body on a dry matter basis is greater than 0.01%, and safe or recommended intake is greater than 100 mg/day. These include calcium (Ca), phosphorus (P), magnesium (Mg), sodium (Na), potassium (K), sulfur (S), chlorine (Cl), as well as carbon (C), hydrogen (H), oxygen (O), nitrogen (N) (taking into account only the content criterion in the body).

Microelements – elements whose content in the body in terms of dry mass is less than 0.01%, and safe and recommended consumption is less than 100 mg/day. Includes iron (Fe), zinc (Zn), copper (Cu), iodine (I), selenium (Se), fluorine (F), chromium (Cr), manganese (Mn), molybdenum (Mo), boron (B), cobalt (Co), nickel (Ni), silicon (Si), tin (Sn), vanadium (V).These elements are often referred to as "trace".

Ultra trace elements – are elements whose content in the body in terms of dry mass is less than 0.00001%. These include silver (Ag), gold (Au), rad (Ra), and some elements from the group of microelements (according to different authors) (Gertig and Przysławski 2006), eg selenium, vanadium and strontium.

The aim of the article was EXPERIMENTAL IDENTIFICATION of sodium (Na), chlorine (Cl), calcium (Ca), sulfur (S) and iron (Fe), boron (B) and strontium (Sr) occurring in elevated concentrations in the source waters of Sanok District. It was necessary to experimentally demonstrate a high content of macroelements (Na, Cl, Ca, S), microelements (Fe, B) and ultra-trace element strontium (Sr) in the selected 6 sources.

The aim of the work was to characterize the above-mentioned bioelements in chemical terms, functions in the human body and the role and occurrence in groundwaters. In addition, it was recommended to present the results and interpretations of the analyzed source waters, including trace elements (bioelements) (selenium, molybdenum). The content of these elements in spring waters was determined by the most advanced analytical methods of modern chemistry.

2. Research area

All researched sources occur in the Sanok Poviat, whose area in terms of geology and structure belongs to the outer (flysch) Carpathians. In addition, all sources are located on the border of the Eastern and Western Carpathians (Fig. 1).

The outer (flysch) Carpathians, which are the outermost unit of the Carpathians, are built of sedimentary rocks formed in the geosynclinical reservoir. These are different varieties of sandstone and slate; along with minor marls, keratoses and limestones. The lithological diversity of Jurassic-Cretaceous-Paleogene-Neogene sediments and the style of disturbances allow to distinguish external tectonic-facies units in the Carpathians: Magura, Dukla, Grybów, Pre-Magura, Silesia, Podlasie and Skole (Paczyński and Sadurski 2007). There are tectonic units in the Sanok Poviat: Silesia, Podlasie and Skolska (Międzybródź-Mrzygłód-Tyrawa Solna) (Rajchel 2016a).

In the region of the external Carpathians, there is considerable potential for the intake of mineralized waters, both deeper parts of flysch formations and their subsoil. These waters, often found in areas with physiographic conditions particularly favorable for the development of spa treatment, should be used as curative (Paczyński and Sadurski 2007).

The Jasielsko-Ustrzycki subregion also including the Sanok Poviat abounds in chloride, iodide and chloride-bicarbonate waters, iodide often accompanying oil deposits (Tyrawa Solna) (Rajchel 2016a). Such waters were encountered in a large number of oil wells, the largest of which are located in the anticlonal zones of the central Carpathian synclinorium (Porowski 2006). The possibilities of using these waters for medicinal purposes, apart from three spas (Iwonicz Zdrój, Rymanów Zdrój, Polańczyk), are practically unlimited.

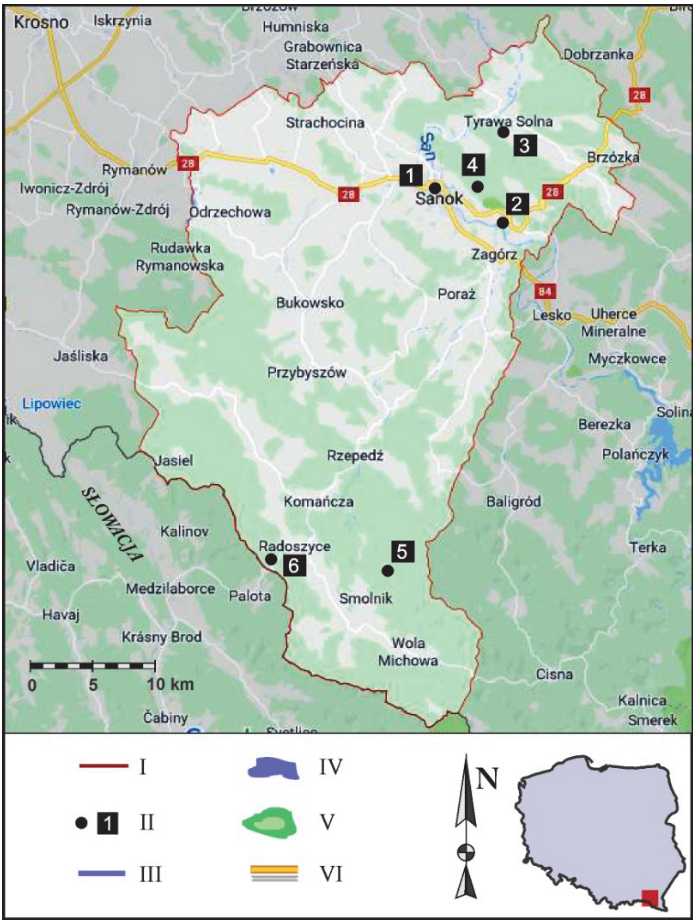

Fig. 1. Localisation of test points, I – the borders of the Sanocki poviat; II – test point with code number: 1 – Sanok Chopin source, 2 – Bykowce San, 3 – Tyrawa Solna, 4 – Liszna, 5 – Mików, 6 – Radoszyce; III – rivers, streams; IV – lakes, water reservoirs; V – forests; VI – national, local roads
Source: Author's own studies based on cartographic materials supplied by the Google maps

Table 1. Identification of the water sample

Place	Position Sample	Code	GPS N	GPS E	Altitude [m]	Water source	Minerals [$mg \cdot dm^{-3}$]	Type of water
SANOK The Source of Chopin	1	PCH	49°33.765'	22°11.929'	329	spring	Calcium Ca > 150 Sod Na < 20	„Natural mineral water, containing calcium” „Natural mineral water, low-Sodium”
BYKOWCE SAN	2	BYK	49°32.180'	22°16.434'	293	spring	Iron Fe >10	„Specific healing iron water”
TYRAWA SOLNA	3	TRS	49°36.280'	22°16.843'	274	spring	HBO_2 metabolic acid > 10 Sodium Na > 1000 Chlorine Cl > 2000 Calcium Ca > 150 Strontium Sr > 10	„Specific therapeutic boron water” „Natural mineral water, containing chloride sodium and calcium”
LISZNA	4	LIS	49°34.214'	22°14.753'	365	spring	Sulphides $S^{2-} > 3$ Molybdenum Mo = 0.0005	„Specific curative sulphide water”
MIKÓW	5	MIK	49°17.311'	22°08.380'	546	spring	–	„Natural spring water from Bieszczady Mountains”
RADO-SZYCE	6	RAD	49°17.790'	22°01.554'	575	spring	General hardness. = 10° dH Low-mineral water <500	„The Miraculous Spring” „soft water” „Natural spring water from Bieszczady Mountains”

In many locations, it is possible to utilize the already closed petroleum wells often requiring reconstruction. Drilling new holes, which can be successful, is recommended in points especially climatically suited for developing spa treatment in them (Paczyński and Sadurski 2007).

Of all the sources studied, four of them are located in Sanok, Bykowce, Tyrawa Solna and Liszna in the Sanok commune, while the other two flow out in Mików and Radoszyce belonging to the Komańcza commune (Table 1). None of the sources researched by the authors are currently used for economic or spa purposes.

3. Methodology

An analysis of water from six sources from the eastern and southern parts of the Sanok poviat was conducted (Fig. 1). Each sample was marked with a three-letter code and a number of the station from which water was collected (1-6) was assigned. Geographical coordinates were determined for each position. The source that is at the place of religious cult was called „The Miraculous Spring" (Chowaniec 2007). Basic physico-chemical parameters of water samples were measured, ie pH, redox potential ORP (Oxidation Reduction Potential) oxidation-reduction potential (Horne and Goldman 1994), conductivity, EC (Electrical Conductivity), electroconductivity, temperature. There were portable instruments for measuring pH, ORP, EC potential and temperature (all quantities depend on temperature) (Łach 2011).

The "Macroelements" are included the determinaton results of calcium, magnesium, sodium and potassium using atomic absorption spectrometry (ASA) (Atomic Absorption Spectrometry) (Szczepaniak 2002). The "macro elements" also include phosphorus and sulfur, which were determined using ICP-OES (Inductively Coupled Plasma - Optial Emission Spectroscopy) optical inductively coupled plasma emission spectroscopy. In contrast, chlorine was analyzed argentometrically (PWSZ 2018).

Microelements (1 + 2), including iron, zinc, heavy metals, copper, chromium, nickel, manganese (Barycka and Skudlarski 2001) were determined using the ASA method. In addition, the amount of non-metals such as iodine, fluorine in the analyzed samples was determined using Ion Chromatography (Ion Chromatography) ion chromatography (fluorine WSSE 2019). Other non-metals, ie. silicon, boron and important element of molybdenum were analyzed using ICP-OES. It should be remembered that the information about "traces" at Microelements (1 + 2) refers to the criterion of the division of bioelements presented in the INTRODUCTION of this work. One should not confuse "trace" quantities of bioelements found in living organisms, with "trace" amounts of elements found in groundwater (spring). Boron and silicon, for example, are micronutrients present in trace amounts (< 0.01%) in organisms, whereas, in the studied groundwaters (source), their amount is considerable (even a dozen or so milligrams in cubic decimeter). The same phenomenon applies to strontium (ultra-small elements). The ICP-OES method was designated for vanadium (ultra element).

As for the methodology, this can be seen two interesting cases. The first one concerns the analysis of strontium, which was carried out using the ICP-MS method (PETROGEO 2019). The second case is selenium analysis performed by three different methods (ASA, ICP-OES, ICP-MS), ICP-MS (Inductively Coupled Plasma) mass spectrometry with ionisation in inductively coupled plasma. Most often (this is not the rule) metals are determined using the ICP-OES method, and nonmetals using the ICP-MS method. This applies in particular to methods using plasma light sources (ICP) and fluorescent lamps that allow high-energy transitions, and thus excitation of non-metals. Therefore, the first of these methods is designated bar (metal). Strontium (ultra element) and bar occur in relatively large quantities after calcium and magnesium in groundwater. Therefore, the content of these elements was included in the calculation of the amount (sum) of cations [mg · dm^{-3}], in the investigated waters. The last cation from this table is the lithium already traditionally marked by the "plasma" method.

To prepare data for analysis of alkaline earth metals (calcium, magnesium) for water sample (6), the formula for calculating water hardness (Chorostyński and others 2018) was used:

$$\mathrm{Two} = \sum_{i=1}^{k} c_i m_i$$

where:
Two – general hardness of water [mmol · dm^{-3}],
c – concentration of metal cation [mg · dm^{-3}],
m – multiplier of metal cation [mmol · mg $^{-1}$].
Ca multiplier = 0.02495 mmol · mg^{-1}
Mg multiplier = 0.04114 mmol · mg^{-1}

With the water hardness (6) expressed in millimols in cubic decimeter, it is easy to calculate the hardness of this water in German degrees (° dH) and determine the type of hardness based on tabular data eg soft water (Krause 1993).

When we have the silicon concentration in the tested samples, the concentration of orthosilicic acid can be calculated. Based on the boron content, the concentration of metaboric acid can be calculated.

Classical analysis of anions: chlorides – argentometry (PWSZ 2018), sulphates (VI) – turbidimetry (WSSE 2019), bicarbonates – alkacimetry (PWSZ 2018), allowed to calculate mineralization (cations + anions + undissociated substances) [mg · dm^{-3}] and specify its type.

4. Results

The physicochemical parameter, measured using a pH meter, was the hydrogen ion exponent (ph). The reaction was determined for 6 spring waters (1-6), two waters showed an alkaline pH > 8 (3.4). At the source, the ORP parameter was measured for all tested waters, for two waters (2.4) it assumed a negative value, which indicates the reducing properties of these waters. Water (2) showed the potential of ORP (-110 mV) and water (4) (-123 mV). The electroconductive (EC) indicator (conductivity) in $\mu S \cdot cm^{-1}$ was the highest for water (3) and it was EC > 5000, in other samples it did not exceed 950. In contrast, for water (6) it was the lowest (340 $\mu S \cdot cm^{-1}$), which indicates low salinity (mineralization) (Table 2). Table 3 presents the determination results of alkali metals (sodium, potassium) and alkaline earth metals (calcium, magnesium). A significant amount of sodium had water (3), more than 1000 $mg \cdot dm^{-3}$, the same water contained calcium > 150 $mg \cdot dm^{-3}$. Water (1) also shares this inequality for calcium. Table 3 contains the results of analyzes for phosphorus, chlorine and sulfur. Of these three non-metals, the most interesting result is the chlorine content in water (3), which exceeded 2,000 $mg \cdot dm^{-3}$. It should be remembered that Table 3 includes macroelements, i.e. those that occur in living organisms in large quantities, while one of the non-metals (phosphorus) in spring waters, as it results from the analysis, is less than 0.10 $mg \cdot dm^{-3}$. Similarly, very low sodium content was demonstrated in water (1) with high calcium content (Table 3).

Microelements 1 (bioelements found in trace amounts in living organisms) (Table 4) are metals (iron), heavy metals (zinc, copper) and non-metals (iodine, fluorine, silicon). An interesting fact is the content of iron in water (2) above 10 $mg \cdot dm^{-3}$. The quantities of other bioelements are standard for groundwater (zinc) and copper < 0.01 $mg \cdot dm^{-3}$, iodine < 0.3 $mg \cdot dm^{-3}$, fluorine < 0.1 $mg \cdot dm^{-3}$. The silicon content is also average for spring waters and amounts to several or several mg.

Microelements 2 (bioelements found in trace amounts in living organisms) (Table 5), are metals (important biometal) molybdenum, heavy metals, chromium, nickel, manganese (noble metal) and nonmetal boron. The heavy metals chromium and nickel are found in the tested (source) waters in quantities lower than 5 $\mu g \cdot dm^{-3}$. For water (2), the concentration of manganese exceeded 1000 $\mu g \cdot dm^{-3}$, and the boron concentration for water (3) reached about 3000 $\mu g \cdot dm^{-3}$. Molybdenum is a bio-element determined in the smallest quantities, below 1 $\mu g \cdot dm^{-3}$, two waters (5, 6) showed the molybdenum concentration so low that the result (< LOQ) was below the limit of quantification.

Table 2. Physicochemical parameters

Parameter	pH	±%	ORP	±%	conductivity EC	±%	Temperature
Unit	unitless	-	[mV]	-	[$\mu S \cdot cm^{-1}$]	-	[°C]
Method / Sample	potentiometry	RSD	potentiometry	RSD	conductometry	RSD	Thermometer
1	7.70	6.70	+131	4.10	920	3.50	9
2	7.55	4.20	-110	5.30	818	3.40	9
3	8.07	7.80	+170	6.80	5750	6.70	10
4	8.03	5.30	-123	4.70	820	4.20	15
5	7.72	6.10	+70	4.30	500	5.50	12
6	7.56	6.40	+60	4.80	340	3.10	10

% RSD – relative standard deviation expressed in percentage, significance level p = 0.95 n = 3

Table 3. Macroelements

Element [$mg \cdot dm^{-3}$]	Calcium Ca	±%	Phosphorus P	±%	Magnesium Mg	±%	Sodium Na	±%	Chlorine Cl	±%	Potassium K	±%	Sulfur S	±%
Method / Sample	ASA	RSD	ICP-OES	RSD	ASA	RSD	ASA	RSD	Argento-metry	RSD	ASA	RSD	ICP-OES	RSD
1	154	2.7	0.07	4.2	7	1.1	2.3	2.6	9	6.4	0.6	1.2	51	4.8
2	106	3.2	0.02	4.6	24	2.4	11.8	1.3	16	5.2	0.5	2.8	0.3	5.7
3	195	2.4	0.08	5.3	31	3.6	1012.1	3.8	2025	8.4	17.0	3.4	5	4.2
4	89	1.3	0.03	2.7	10	2.5	65.0	2.4	34	5.7	2.2	1.4	20	1.3
5	73	4.7	0.01	5.4	21	3.4	8.7	1.7	6	4.2	0.7	1.3	6	3.8
6	63	1.2	0.04	5.6	4	2.5	8.4	1.8	5	6.8	1.3	1.8	4	2.8

Table 4. Microelements 1 (traces)

Element [mg·dm^{-3}]	Iron Fe	±%	Zinc Zn	Copper Cu	Iodine I	Fluorine F	Silicon Si	±%
Method / Sample	ASA	RSD	ASA	ASA	CHROMAT. ION.	CHROMAT. ION.	ICP-OES	RSD
1	0.02	7.4	< 0.01	< 0.01	< 0.3	< 0.10	11.35	4.1
2	11.60	2.3	< 0.01	< 0.01	< 0.3	< 0.10	12.76	3.9
3	0.20	6.2	< 0.01	< 0.01	< 0.3	< 0.10	10.66	4.8
4	0.07	7.8	< 0.01	< 0.01	< 0.3	< 0.10	8.83	2.7
5	0.03	5.9	< 0.01	< 0.01	< 0.3	< 0.10	6.82	3.3
6	0.02	6.4	< 0.01	< 0.01	< 0.3	< 0.10	7.07	3.4

Table 5. Microelements 2 (traces)

Element [µg·dm^{-3}]	Chrome Cr	Manganese Mn	±%	Molybdenum Mo	±%	Boron B	±%	Nickel Ni
Method / Sample	ASA	ASA	RSD	ICP-OES	RSD	ICP-OES	RSD	ASA
1	< 5	< 10	-	0.32	4.3	51	2.2	< 5
2	< 5	1120	7.2	0.24	5.4	18	1.7	< 5
3	< 5	50	3.8	0.35	3.2	2921	2.8	< 5
4	< 5	30	4.1	0.50	3.7	766	1.2	< 5
5	< 5	< 10	-	< LOQ	-	18	2.4	< 5
6	< 5	< 10	-	< LOQ	-	24	5.8	< 5

< LOQ – result below the limit of quantification

Table 6 includes selected ultra-elements, which include selenium, vanadium and strontium. Strontium is present in relatively large quantities in spring waters just after calcium and magnesium (Table 7). The concentration of strontium in water (3) exceeded 10 mg · dm^{-3}. For comparison purposes, three selenium analyzes in all samples were carried out using three different analytical methods to increase the accuracy and precision of the assay. The highest concentration of selenium did not exceed 20 µg · dm^{-3}. Vanadium is an ultra-element found in organisms in the amount of 10-5% (on a dry weight basis). The same element was marked in source waters (2-5) in the amount of 1.5 · 10^{-5} g · dm^{-3}. The two tested waters (1, 6) had a vanadium concentration below the limit of quantification (< LOQ).

Table 7 contains minerals already discussed earlier, with the exception of barium, which together with magnesium and strontium (the same group of the periodic table) is worth determining in underground (spring) water. Barium concentration in certain groundwaters may exceed 1 mg · dm^{-3}. This happened in the case of tested water (3), for which [Ba^{2+}] > 3 mg · dm^{-3}. Lithium concentration, similarly to the barium concentration, for the same water tested (3) exceeded 1 mg · dm^{-3}. Table 7 includes the sum of cations expressed in mg · dm^{-3}.

Table 8 contains minerals, which include anions found in spring waters.

The following anions were determined: chlorides, sulphates (VI) and bicarbonates (Table 8). The concentration of these ions is average as for groundwater, with two exceptions: water (3) contains chlorides in the amount of more than 2,000 mg · dm^{-3} (already mentioned in the discussion of table 3), the second exception is related to the concentration of bicarbonates in water (6), which is smaller than 220 mg · dm^{-3}. The concentration of bicarbonates has a significant influence on the size of mineralization. In Table 8 based on the amount of silicon and boron, the calculated concentrations of undissociated substances, including orthosilicic acid H_2SiO_3 and HBO_2 metaboric acid, are also included. Summing up the number of cations (Table 7), anions and undissociated substances (Table 8) for the analyzed spring waters (1-6), the mineralization (Table 8) was calculated in mg · dm^{-3}. Mineralization for water (3) looks very impressive, almost 3.7 g · dm^{-3}, while water (6) has a very low mineralization equal to 330 mg · dm^{-3}. Also noteworthy is a high level of the mentioned metaboric acid, which exceeded 10 mg · dm^{-3} in water (3).

It is worth adding that for all results excluding inequality (<), also excluding measurements below the limit of quantification (< LOQ) (Limit of Quantification), for n = 3 and the level of significance p = 0.95 was given relative standard deviation expressed as a percentage (% RSD) (Relative Standard Deviations).

Table 6. Ultra-elements (selected)

Element [$\mu g \cdot dm^{-3}$]	Selenium Se	Selenium Se	Selenium Se	Vanadium V	±%	Strontium Sr	±%
Method / Sample	ASA	ICP-OES	ICP-MS	ICP-OES	RSD	ICP-MS	RSD
1	< 3	< 20	< 5	< LOQ	-	600	2.3
2	< 3	< 20	< 5	12	6.4	330	1.6
3	< 3	< 20	< 5	16	5.7	10200	4.2
4	< 3	< 20	< 5	3	7.1	596	1.4
5	< 3	< 20	< 5	14	8.4	179	2.7
6	< 3	< 20	< 5	< LOQ	-	432	1.4

< LOQ – result below the limit of quantification.

Table 7. Minerals (cations)

Minerals [$mg \cdot dm^{-3}$]	Na^{+}	K^{+}	Ca^{2+}	Mg^{2+}	Sr^{2+}	Fe^{2+}	Mn^{2+}	Ba^{2+}	±%	Li^{+}	±%	Cations
Method / Sample	ASA	ASA	ASA	ASA	ICP-MS	ASA	ASA	ICP-OES	RSD	ICP-OES	RSD	Total amount
1	2.3	0.6	154	7	0.60	0.02	0.01	0.058	4.2	0.009	5.8	164.6
2	11.8	0.5	106	24	0.33	11.60	1.12	0.446	2.1	0.004	6.3	155.8
3	1012.1	17.0	195	31	10.20	0.20	0.05	3.238	1.5	1.150	5.1	1270.0
4	65.0	2.2	89	10	0.59	0.07	0.03	0.041	3.8	0.023	5.7	167.0
5	8.7	0.7	73	21	0.18	0.03	0.01	0.096	4.2	0.004	4.2	103.7
6	8.4	1.3	63	4	0.43	0.02	0.01	0.086	3.7	0.005	6.4	77.2

Table 8. Minerals - anions, undissociated substances, mineralization

Minerals [$mg \cdot dm^{-3}$]	Cl^-	SO_4^{2-}	±%	HCO_3^-	±%	Anions	H_2SiO_3 calculated	HBO_2 calculated	Undissociated	Mineralization Kt+An	Type of mineralization
Method / Sample	Argentometry	Turbidimetry	RSD	Acid-base titration	RSD	Total	ICP-OES	ICP-OES	Total	Total amount	-
1	9	147	7.9	451	5.2	607	31.52	0.20	31.72	803	moderately mineralized
2	16	1	10.2	573	4.9	590	35.43	0.07	35.50	781	moderately mineralized
3	2025	13	8.1	342	2.1	2380	29.60	11.83	41.43	3691	highly mineralized
4	34	48	8.4	434	4.3	516	24.52	3.10	27.62	711	moderately mineralized
5	6	19	6.5	329	5.3	354	18.94	0.08	19.02	477	low mineralized
6	5	10	9.3	219	6.8	234	19.63	0.10	19.73	330	low mineralized

5. Discussion

This chapter is a thorough data analysis contained in the Results. Two waters (3, 4) showed slightly alkaline pH > 8 (Table 2). The reason for this is the presence of a large amount of sodium in water (3) (Table 3) (alkali metal), whereas water (4) is sulphide water. Sulfides (hydrosulfides) of alkali metals, e.g. sodium in water (4) (65 mg · dm^{-3} Na, Table 3) dissociate to form HS^- and S^{2-} ions. In turn, the replaced ions are hydrolyzed, resulting in the formation of hydrogen sulphide (the smell of rotten eggs) and hydroxyl ions $HS^- + H_2O = H_2S + OH^-$, which give the water a basic reaction. All sulphide waters are slightly alkaline (Chorostyński et al. 2018). Hydrogen sulfide, on the other hand, is a highly toxic gas and its vapors, which are released in high concentrations, can be a deadly threat to humans (Cykowska et al. 2013, Patniak 2007, Standard Methods 1998). The form in which sulfide compounds occur depends on the pH of the environment. At pH < 6 the form of undissociated H_2S prevails, in the range of 6 < pH < 8 there are mainly HS^- bis hydrosulfite ions, and at pH > 8 (water 4) the dominant form is S^{2-} sulphide ions (Hermanowicz et al. 1999, Cykowska et al. 2013). Natural sulphide spring waters with the right content of divalent sulfur are healing (spa) waters. The same applies to slightly alkaline waters (waters 3, 4) having the properties of alkaline water. Thanks to this, they have pro-health features (Chorostyński and others 2018).

The source (4) "On a Waterfall" is located next to the road from Olchowce to Liszna in the area of the Słonne Mountains Nature Park. The outflowing water is a type HCO_3 - Cl - Ca - Na + H_2S with the mineralisation of 0.7 g · dm^{-3} and H_2S content of 3.8 mg · dm^{-3} (Rajchel 2016b). In the case of sulphidic waters, the water has the characteristics of „specific sulphurous medicinal water” if the content of sulphides (divalent sulfur) exceeds 1 mg · dm^{-3} (pharmacodynamic factors - introduction) (Rozporządzenie 2016, Michalski 2006). Based on the literature (Rajchel 2016b), water (4) with a divalent sulfur content of 3.8 mg · dm^{-3} is „specific sulphide medicinal” water.

Water (2) had ORP potential (-110 mV) and water (4) (-123 mV). The negative redox potential indicates the reducing properties of these waters. Water (2) is rich in iron (II) Fe^{2+} ions (which quickly oxidize to Fe^{3+} ions after water flows to the surface). Fe^{2+} ions have (Łach 2010) reducing properties (because they can be oxidized). Water (4) is sulphide water with the content of S^{2-} ions, which can oxidize, among others, to sulfur S^0, thanks to which S^{2-} ions have reducing properties. The reducing properties cause the negative ORP potential of the tested water. Water with a negative potential is an antioxidant that destroys free radicals and prevents the aging process. Water with a low redox oxidation potential (Horne and Goldman 1994, Suslow 2004) has health benefits.

The high electroconductive index (conductivity), which for water (3) was EC > 5000 µS · cm^{-1}, indicates high salinity of this water (high mineralization). Conversely, in the case of water (6), low conductivity (340 µS · cm^{-1}), this water has low mineralization. Two indicators point out mineralization of spring waters. Firstly, conductivity, secondly, mineralization calculated as the sum of cations, anions and undissociated substances. In experimental data (with correct results), there should be a high correlation between these two indicators. The EC index is often used to quickly assess the salinity of water (table 2).

In Table 3, a high concentration of two macroelements, sodium (> 1000 mg · dm^{-3}) and chlorine (> 2,000 mg · dm^{-3}) is interesting, which informs about „natural mineral water with sodium chloride content" (NaCl > 1000 mg · dm^{-3}). The same water (3) contains a large amount of calcium (> 150 mg · dm^{-3}), so it is „natural mineral water with calcium content" (Rozporządzenie 2011, Michalski 2006).

It is worth paying attention to water (1). In this water, the amount of calcium exceeded 150 mg · dm^{-3}, which makes this water „natural mineral water with calcium content". At the same time, this water has extremely low sodium content (Table 3), with relatively high mineralization. It is medium-mineralized water with a total mineralization exceeding 500 mg · dm^{-3} (Table 8). As far as mineralization is concerned, the current valid classification of natural mineral waters is according to dissolved minerals. Low-mineralized water - below 500 mg · dm^{-3}, medium- mineralized water - from 500 to 1500 mg · dm^{-3}, high-mineralized water - above 1500 mg · dm^{-3}.

The aforementioned water (1) meets the conditions (low sodium content, average mineralization) of "natural low-sodium mineral water" (Rozporządzenie 2011, Michalski 2006, Tchórzewska-Cieślak and Rak 2005, Tchórzewska-Cieślak and Rak 2006). Water (1) contains sodium in the amount of < 20 mg · dm^{-3}.

Iron was classified to microelements 1 (Table 4). Its quantity is high and exceeds 10 mg · dm^{-3}, water (2). Iron in groundwater usually occurs in the form of bicarbonate and iron (II) sulfate (IV) – $Fe(HCO_3)_2$, $FeSO_4$ (Kowal and Świderska-Bróż 2000). Consequently, in underground waters, it occurs exclusively as an Fe^{2+} ion. Only the outflow of water to the surface and contact with atmospheric oxygen causes the oxidation of iron (II) compounds to iron (III) compounds and the precipitation of colloidal iron (III) hydroxide (Kowal and Świderska-Bróż 2000).

$$4\,FeSO_4 + O_2 + 10\,H_2O \rightarrow 4\,Fe(OH)_3 + 4\,H_2SO_4$$
$$4\,Fe(HCO_3)_2 + O_2 + 2\,H_2O \rightarrow 4\,Fe(OH)_3 + 8\,CO_2$$

As shown in Table 4 (iron content) and Table 8 (content of bicarbonates and other anions), spring water (2) contains almost exclusively iron (II) bicarbonate. The analysis was carried out in a short time after taking a sample of water from the source, it can be assumed that Fe^{2+} ion was determined (speciation analysis), not general iron. Generally, in acidic waters with low Eh (ORP) value (in our case -110 mV, water (2), table 2 iron content is higher than in waters with higher pH and Eh (ORP).) Chemistry of iron compounds is exceptionally sensitive to changes in pH and Eh (Kowal and Świderska-Bróż 2000, Łach 2010). The reason for this is that iron has the ability to change the degree of oxidation (electron binding) (Kuras et al., 2015, Ponka 1999). In spring water (2) over 10 mg · dm^{-3}, we can talk about "specific ferruginous water" (pharmacodynamic factors - introduction) (Rozporządzenie 2016, Michalski 2006).

The symptom of insufficient iron supply is anemia, which is manifested by a decrease in hemoglobin (Sułek 2003). The effect of its excess in the body may be: reduced absorption of other minerals (mainly zinc and copper), susceptibility to infection, deposition of iron in tissues, increased production of free radicals leading to an increased risk of cancer and coronary disease (Shander and Sazama 2010, Kuras and others 2015). The excess of iron in the body is demonstrated by, among others significantly elevated serum ferritin and a dramatic increase in free iron in the blood (Cook et al 1992).

Manganese has been included in Microelements 2, concentration of which in the tested water (2) exceeded 1 mg · dm^{-3} (Table 5). Manganese, unlike heavy metals such as lead or cadmium, is an element necessary for the proper functioning of the body. Due to the fact that manganese ions are involved in many processes in the body, over the years it was thought that even excess of them does not result in adverse changes in the body (Gać et al., 2009). For this reason, manganese and its compounds have found a wide application in many industries. Consequently, in recent years, the concentration of manganese ions (II) has risen multiple times in the atmosphere, drinking water and food (Burgoa 2001). Chronic poisoning is the most characteristic for manganese. Symptoms similar to Parkinson's disease increase gradually and appear after a dozen of years (less often after a few years) of contact with manganese (Gać et al. 2009).

The concentration of boron in water (3) reached the value of about 3 mg · dm^{-3} (table 5). This value is easily converted into the amount of HBO_2 metaboric acid (Table 8) (undissociated substance). The calculated HBO_2 acid in water (3) exceeded the concentration of 10 mg · dm^{-3}. Based on pharmacodynamic indices, it can be assumed that water (3) is „specific therapeutic boric" water, because HBO_2 concentration is higher by 5 mg · dm^{-3} (Rozporządzenie 2016, Michalski 2006). At this point, it is worth paying attention to water (3). As previously shown, this water is „natural mineral water with a high content of sodium chloride" (saline), which (NaCl) can be recovered from this water in an economic manner, as discussed in historical papers (Chapter 2. Research area). Other chemical compounds have much greater economic significance for this type of water. And so in this water there is an increased amount of boron (HBO_2 > 10 mg · dm^{-3}) (Table 8), strontium (> 10 mg · dm^{-3}), barium (> 3 mg · dm^{-3}), lithium (> 1 mg · dm^{-3}) (Table 7). This view is also supported by the literature, according to which the brines also often contain significant amounts of elements valuable from an economic point of view, such as iodine, bromine, magnesium, boron, potassium and lithium (Paczyński and Płochniewski 1996).

Boron – a chemical element with an atomic number of 5, halfmetal from p- block of the periodic table. Boron chemically resembles silicon and carbon, because it forms boranes – analogs of hydrocarbons and silicas. The reaction of boron with hot concentrated nitric acid (V) leads to the formation of boric acid H_3BO_3. Boron forms complexes with polyhydric alcohols. The reaction of boric acid with mannitol is one of the methods for determining the boron content in the sample. Boron inorganic chemistry is sometimes described as the most complex of all elements (Greenwood and Earnshaw 1984). It most often takes oxidation state (III) (Pradyot Patnaik 2003). In the vast majority of compounds, it is three-bonded, and has the ability to form compounds with multi-center bonds (Greenwood and Earnshow 1984) (one example is diborane, B_2H_6 containing three-membered electron binding B-H-B). A large number of its compounds are known, especially metal borides (Greenwood and Earnshow 1984). Boron accumulates in the bones and nervous system, interacts with calcium (Enghag 2004). In plants, it is a component of cell walls. It takes part in the metabolism of nucleic acids.

Molybdenum is a very important bioelement (Table 5), but its quantity in spring waters is very small, below 1 μg · dm^{-3}. Although it is worth writing something more about it.

Molybdenum is a silvery-white metal, hard, conducts heat well as well as electricity. It has a very high melting point of 2620 ° C. This metal is often an addition to high-grade special steel. It increases its hardness and durability. The degree of oxidation $^{+6}$ in the case of molybdenum compounds is the most durable oxidation. Molybdenum forms a durable MoO_3 trioxide, white in cold and yellow in hot conditions. It does not dissolve in water and diluted acids, but dissolves in alkali. Phosphoromolybdate ammonium $(NH_4)_3H_4[P(Mo_2O_7)_6]$ precipitates as a characteristic yellow precipitate under the influence of ammonium molybdate from solutions of phosphoric acid (V) with acidified nitric acid (V) (Bielański 2012).

There are between 9 and 16 mg of molybdenum in the human body. The necessity of this element is determined by the fact that it is a component of xanthine oxidase. Molybdenum in higher concentration occurs in the liver, kidneys, adrenal cortex and bone tissue. The role of molybdenum in the body is associated with its participation in enzymes that catalyze the oxidative hydroxylation reaction. Symptoms of molybdenum deficiency include: tachycardia, headache, vomiting, twilight blindness. The recommended daily intake is set at 75-250 μg (Gertig and Przysławski 2006).

Table 6 contains ultraelements. They include silver, gold, radium, mercury, but also some of the microelements such as selenium, vanadium and strontium. Strontium belongs to ultraelements because it is found in very small amounts in living organisms. Therefore, its impact on living organisms has not yet been tested. In this study, we will focus exclusively on strontium chemistry. Strontium, in contrast to organisms in groundwater (spring), including also tested waters (1-6), occurs in relatively large quantities, just after calcium and magnesium. In spas, the amount of strontium in the water is always given.. Strontium is an element that has been determined in water (3) in an amount of more than 10 mg · dm^{-3}.

Stront – a chemical element from the group of beryllium in the periodic table. Strontium is a silvery-gray metal, similar to calcium, but more soft. On its surface, as in the case of aluminum, a protective oxide layer (passivation) is formed. Strontium forms oxides, hydroxides, fluorides and other salts of inorganic and organic acids. Sr^{2+} cations belong to the 4th analytical group and stain the flame with crimson red. Strontium is generally more chemically active than magnesium and calcium, less active than bar (MacMillan et al., 2000).

Selenium is one of the most well-known and popularized bioelements. Selenium is a microelement, but is often classified in the group of ultraelements. Such classification is very accurate, because this element (bioelement) occurs in minimal amounts both in living organisms (ultratrace element) and in minimal amounts in groundwater (source) (trace element). In all tested waters (1-6), selenium was determined by three different methods. No method gave a result higher than 20 μg · dm^{-3}. The range (spread) of the results obtained was relatively small and took values of 3 μg · dm^{-3}, 5 μg · dm^{-3}, 20 μg · dm^{-3}. In this case, it is not possible to calculate statistically whether the differences between the results of the different methods are significant or not, because for these results relative standard deviations were not assigned due to the fact that the obtained results are inequalities (the analysis was carried out on the limit of quantification of this element with given analytical method). Selenium, as already mentioned, occurs in minimal amounts both in living organisms and in spring (underground) waters. However, as with molybdenum, its role and importance on the functioning of the human body are so significant that it is worth paying some attention to this element.

The content of selenium in the Earth's crust is very small, 5 · 10^{-6}%. Selenium is a pollutant of sulfur ores, it is an important product for the production of photocells and rectifiers. It is also used for coloring glass in ruby-red color. Selenium forms several crystalline varieties, similarly to sulfur, it can form eight atomic ring molecules. After heating, it is burned to give SeO_2 (selenium dioxide) (Bielański 2012). The content of selenium in the human body ranges from 13 to

20 mg. Selenium is a component of four isoenzymes of glutathione peroxidase, indirectly also participates in fatty acid metabolism, affects the synthesis of thyroid hormones. It is a component of P, G, W selenoproteins, which play an important role in the antioxidative protection of the body. Yeast contains the most selenium. A good source of this element are also cereal products. The maximum, safe daily dose of selenium is 450 μg a day, while the toxic dose is 700 μg a day (Gertig and Przysławski 2006).

Selenium in geochemical terms is close to sulfur. However, it is found in the earth's crust in smaller quantities, it has extremely high dispersion. In groundwater, the migration of selenium, just like sulfur, depends on the redox conditions, the pH of the water and the activity of microorganisms. At low redox potential, the water is sulphide brine. The basic form in which selenium migrates in groundwater with the Ph similar to neutral, is SeO_4^{2-} anion. In waters with low oxidation potential characteristic for the zone of impeded water exchange, selenium usually migrates in the form of HSe^- ion. Under natural conditions in groundwater of moderate climate selenium occurs in small amounts not usually exceeding 2 μg · dm^{-3} (Macioszczyk and Dobrzyński 2002).

In Table 8, minerals were classified, including the following anions: chlorides, sulphates (VI) and bicarbonates. Table 8 also contains the content of the calculated orthosilicic acid, the amount of which was in the range of 18-35 mg · dm^{-3}. The amount is within the limits of the average H_2SiO_3 content in groundwater (spring). However, anion analysis was performed to calculate (determine) mineralization in mg · dm^{-3} and determine its type. The results are rather interesting - water (3) is highly mineralized with a mineralization of almost 3.7 g · dm^{-3}, whereas water (6) is low mineralized water with a 330 mg · dm^{-3} mineralization. Water (6) is water from the "deep" Bieszczady, one could expect a certain amount of interesting minerals. Interestingly, „Wonderful Spring" water (6) practically does not contain „minerals", but it is, according to the definition (Introduction) (Tchórzewska-Cieślak and Rak 2005, Tchórzewska-Cieślak and Rak 2006), „natural spring water" which „does not differ in properties and mineral composition from water intended for human consumption".

Water (6) may be interesting from another point of view. Using the formula for general hardness (Methods), on the basis of calcium and magnesium content, you can calculate the hardness of this water in German degrees (° dH) and compare with tabular values (Krause 1993). Water (6) is soft water and its general hardness oscillates around 10 ° dH. Such water does not form sedimentation during cooking, it is „crystalline" water. This property may explain the fact that tourists and the locals, taking water from the „Miracle Spring", praise the water for the fact that you can make a very good, tasty tea.

In addition, to maintain objectivity, it should be added that too low general hardness of water may also be undesirable. It was observed that too soft waters (below 5.6 degrees German ° dH) are harmful to humans; they increase the incidence of heart disease.

The reliability of this study is evidenced by the fact that for water (4) (Natural Monument) mineralization was determined (calculated), which according to the authors is 711 mg · dm^{-3} (> 0.7 g · dm^{-3}), whereas the already quoted literary position (Rajchel 2016b) informs that the above-mentioned water contains sulphides in the amount of 3.8 mg · dm^{-3} and has a mineralization above 0.7 g · dm^{-3}.

Critically approaching the publication, it should be added that the study does not include such issues as: bacteriological analysis of the discussed source waters, the efficiency of individual sources and, what may sound absurd, measurement of natural radioactivity, because sources in the Podkarpacie region near Dukla (the Hermitage of St. John) show natural radioactivity. Water from several sources was examined in terms of the concentration for selected radioactive elements: radium – 226, radon and cesium – 137. Radium concentration – 226 in water from the Hermit Stream is almost six times higher than the norm for drinking water (Pociask-Karteczka and Rzeszutek 2007).

6. Conclusions

1) Two waters (3, 4) showed slightly alkaline reaction (pH > 8), which suggests their health-promoting properties.
2) Water (4) is „specific sulphuretic water" with a divalent sulfur content of 3.8 mg · dm^{-3}.
3) Water (2, 4) is characterized by low ORP potential (< -100 mV), which makes them antioxidants „destroying free radicals„ (they prevent the aging process).
4) Water (3) is „natural mineral water with a content of sodium chloride" (NaCl > 1000 mg · dm^{-3}) containing admixtures of economic importance: boron, strontium, bar, lit. In addition, the same water is „natural mineral water with calcium content" (> 150 mg · dm^{-3}).
5) „Natural mineral water with calcium content" is also water (1). In addition, the water has a low sodium content (< 20 mg · dm^{-3}), at the same time it is medium-mineralized water (a necessary condition), which makes it „natural low-sodium mineral water".
6) „Healing specific iron water" (2) contains iron (II) in an amount above 10 mg · dm^{-3} (pharmacodynamic factors), suitable for people with anemia.

7) Water (3) is „specific therapeutic boron water", because the concentration of HBO_2 metaboric acid here is higher than 5 mg · dm^{-3}. The appropriate level of boron is important for the bones and nervous system.
8) Two very important bioelements (selenium and molybdenum) for the body occur in spring waters in small quantities, smaller than 20 µg dm^{-3} in the case of selenium and smaller than 1 µg · dm^{-3} for molybdenum. These elements should be supplied with food or as a dietary supplement.
9) Strontium, which in water (3) has been determined in an amount exceeding 10 mg · dm^{-3}, shows little demand in living organisms, and its supply from mineral waters is probably sufficient.
10) The analyzed spring waters (1-6) are low, medium and high-mineralized waters. Highly mineralized water (3) exceeded the amount of solids above 3.7 g · dm^{-3}, while low mineralized water (6) (< 330 mg · dm^{-3}) is recommended for tea.

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Abstract

The analysis of underground (spring) waters concerned 6 springs located in the eastern part of the Sanok District on the border of the Eastern and Western Carpathians (analysis of bioelements). There have been detected „natural mineral waters with sodium chloride content" with chemical admixtures such as: boron (HBO_2 > 10 mg·dm^{-3}) strontium (Sr > 10 mg·dm^{-3}), barium (Ba > 3 mg·dm^{-3}), Lithium (Li > 1 mg·dm^{-3}), in a potential perspective of economic importance. The above-mentioned water from Tyrawa Solna, has a historical aspect, connected with salt-works, as signified by the name of the village. The publicly availablespring of Chopin from the Sanok park is characterized by „natural mineral water with calcium content" at the same time it is „low-sodium water" with a sodium content (< 3 mg·dm^{-3}). The spring from Bykowce near Sanok, has "specific healing iron water" with iron (II) content above 10 mg·dm^{-3}, while the spring on the Olchowce-Liszna route called „Nad Wodospadem" („At the Waterfall") (Nature Monument) is rich in "specific healing sulphide water" with a divalent sulphur content of 3.8 mg·dm^{-3} (characteristic odour). The criterion of „specific boric therapeutic water" with HBO_2 metaboric acid concentration higher than 5 mg·dm^{-3} (pharmacodynamic factors) (Regulation of the Minister of Health) meets the already mentioned water from Tyrawa Solna. This water also contains large amounts of sodium potassium, calcium and magnesium, and its mineralization exceeded 3500 mg·dm^{-3} (highly mineralized brine). On the border of the Eastern and Western Carpathians, moving south towards Slovakia, two sources were found in the Bieszczady Mountains (Mików, Radoszyce). Water from „Cudowne Źródełko" („The Miraculous Spring") in Radoszyce (surroundings) belongs to soft waters (hardness = 10 German degrees) and to low mineralized ones (mineralization < 500 mg·dm^{-3}). Bioelements that are found in trace amounts in spring waters i.e. iodine < 0.3 and fluorine < 0.1 [mg·dm^{-3}] and selenium and vanadium < 20, zinc and copper < 10, chromium and nickel < 5, molybdenum < 1 [μg·dm^{-3}] were also determined. Chemical analyses were performed using the following methods: AAS, ICP-OES, ICP-MS, IC, potentiometry (pH), conductometry (EC), ORP potential, turbidimetry, argentometry and acid-base titration. The influence on the functioning of the human body and some bioelements is described.

Keywords:
springs, bioelements, mineral waters, medical waters, trace analysis, AAS, ICP-OES, ICP-MS, IC

Analiza biopierwiastków w wodach źródlanych Powiatu Sanok na granicy Karpat Wschodnich i Zachodnich oraz ich wpływ na funkcjonowanie organizmu człowieka

Streszczenie

Analiza wód podziemnych (źródlanych) dotyczyła 6 źródeł zlokalizowanych we wschodniej części Powiatu Sanok na granicy Karpat Wschodnich i Zachodnich (analiza biopierwiastków).Wykryto „naturalne wody mineralne z zawartością chlorku sodu" z chemicznymi domieszkami: boru (HBO_2 > 10 mg · dm^{-3}) strontu (Sr > 10 mg · dm^{-3}), baru (Ba > 3 mg · dm^{-3}), litu (Li > 1 mg · dm^{-3}), w ewentualnej perspektywie o znaczeniu gospodarczym. Wymieniona woda z Tyrawy Solnej, posiada aspekt historyczny, związany z warzelnictwem soli, o czym świadczy również nazwa miejscowości. Ogólnodostępne źródło Chopina z parku sanockiego cechuje „naturalna woda mineralna z zawartością wapnia" jednocześnie jest to „woda niskosodowa" o zawartości sodu (< 3 mg · dm^{-3}). Źródło z Bykowiec niedaleko Sanoka, posiada „wodę swoistą leczniczą żelazistą" o zawartości żelaza (II) powyżej 10 mg·dm^{-3}, natomiast źródło na drodze Olchowce-Liszna „Nad Wodospadem" (Pomnik Przyrody) jest bogate w „wodę swoistą leczniczą siarczkową” o zawartości siarki dwuwartościowej 3,8 mg · dm^{-3} (charakterystyczny zapach). Kryterium „wody swoistej leczniczej borowej” o stężeniu kwasu metaborowego HBO_2 wyższym od 5 mg · dm^{-3} (współczynniki farmakodynamiczne) (Rozporządzenie Ministra Zdrowia) spełnia już wspomniana woda z Tyrawy Solnej. Woda ta zawiera również duże ilości sodu potasu, wapnia i magnezu, a jej mineralizacja przekroczyła 3500 mg · dm^{-3} (wysokozmineralizowana solanka). Na granicy Karpat Wschodnich i Zachodnich przemieszczając się na południe w kierunku Słowacji znaleziono w Bieszczadach dwa źródła (Mików, Radoszyce). Woda z „Cudownego Źródełka” w Radoszycach (okolice) należy do wód miękkich (twardość = 10 stopni niemieckich) oraz niskozmineralizowanych (mineralizacja < 500 mg · dm^{-3}). Oznaczono również biopierwiastki, które występują w wodach źródlanych w ilościach śladowych tj. jod < 0,3 i fluor < 0,1 [mg · dm^{-3}] oraz selen i wanad < 20, cynk i miedź < 10, chrom i nikiel < 5, molibden < 1 [µg · dm^{-3}]. Analizy chemiczne wykonano następującymi metodami: ASA, ICP-OES, ICP-MS, IC, potencjometria (pH), konduktometria (EC), potencjał ORP, turbidymetria, argentometria, alkacymetria. Opisano wpływ na funkcjonowanie organizmu człowieka, niektórych biopierwiastków.

Słowa kluczowe:
źródła, biopierwiastki, wody mineralne, wody lecznicze, analiza śladowa, ASA, ICP-OES, ICP-MS, IC

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Analysis of Mercury Content in Feed Coal and Rejects for Selected Hard Coal Cleaning Processes

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1. Introduction

Mercury is commonly found in hard coal (Ketris & Yudovich 2009) and its combustion is one of the main sources of the anthropogenic mercury emission into the atmosphere (Pacyna et. al 2016). Due to the toxicity of mercury (Li & Tse 2015) a reduction of its emission is the objective of many legislative actions, among others the BAT conclusion for large combustion plants adopted by the European Commission (BAT-LCP 2017). In the case of the large combustion plants, there are well-known and widely used methods allowing for the removal of mercury from flue gases (the post-combustion stage), among others a sorbent injection into the flue gases stream (Wierońska et al. 2018). In the case of households and small-scale combustion installations these methods are not used. This is caused by both lack of technical possibilities as well as high investment costs. The most effective solution for this group of customers is the removal of mercury from coal (the pre-combustion stage), which can be obtained with the use of various methods (Dziok 2018).

The removal of mercury from hard coal can be achieved, among others, through the cleaning process (Baic & Blaschke 2018, Dziok & Strugała 2017, Dziok 2018). This process yields: (i) clean coal with a reduced ash content and an increased calorific value, (ii) middling products that are used in the power industry, and (iii) rejects. The rejects are directed to a landfill or are used as a substitute for the natural aggregates (Baic & Blaschke 2013). Thus, they are not directed to the thermal processes and, therefore, mercury contained in the rejects is not released into the atmosphere during coal combustion.

The washing processes are commonly used in hard coal preparation plants. Recently, the dry separation methods allowing for the efficient deshaling of raw coal have become more popular (Baic et al. 2014, 2014a, 2015, 2015a, Blaschke et al. 2016). The Authors' scientific works confirmed the possibility of mercury removal from coal in these processes, although the effectiveness of mercury removal together with rejects varied from 8 to 96% (Dziok & Strugała 2017, Dziok 2018). This should be explained by the difference in the mode of mercury occurrence in individual coals. In Polish hard coals mercury is mainly found in pyrite (Dziok et al. 2019), and the effectiveness of mercury removal from coal in the washing processes increases along with the growth in the amount of removed pyrite (Dziok et al. 2015). Effective pyrite removal from hard coal, and, consequently, also mercury removal, may be achieved with the use of the pneumatic vibrating separators (Baic & Blaschke 2017, 2017a, 2018, Dziok & Strugała 2017). The aim of the study was to assess the effectiveness of mercury removal from hard coal with the rejects in the washing and dry deshaling processes.

2. Methodology

The coal cleaning processes which are commonly used in Polish coal preparation plants were analyzed, i.e. dense media separation, grain and fine coal jigging, flotation, as well as dry deshaling using the pneumatic vibrating FGX type separator. The first four are the washing processes and the last one is the dry separation process. In the case of the washing processes, samples for analysis were derived from industrial installations located in the Polish hard coal preparation plants. In the case of the dry deshaling process, samples were obtained from a pilot test plant equipped with the pneumatic vibrating FGX type separator with a capacity of 10 Mg/h. The feed coals were supplied by different mines and therefore were characterized by different parameters.

For each of the analyzed processes, the samples of feed coals and rejects were investigated. In all samples the mercury content was determined with the use of the MA-2 analyzer (Nippon Instruments Corporation), based on cold vapor atomic absorption spectroscopy (CVAAS). The measurements were carried out in compliance with the EPA 7473 Method. The obtained results are given in Table 1.

In order to determine the effectiveness of the analyzed processes, the *RF* factor was used. *RF* was calculated as the ratio of the mercury content in the rejects ($Hg_{rejects}$) to the mercury content in the feed coal (Hg_{feed}) – Eq. (1). *RF* values higher than 1 indicate the accumulation of mercury in the rejects and those lower than 1 indicate a lower mercury content in the rejects in comparison to the mercury content in the feed coal.

Table 1. Mercury content in analyzed samples

Case no.	Coal-cleaning process	Particle size [mm]	Mercury content Hg^d [µg/kg]	
			feed coal	rejects
1	dense media separation	>20	57	62
2			54	62
3			114	249
4			67	116
5	grain coal jigging	0.5-70	148	79
6			83	71
7	fine coal jigging	0.5-20	99	88
8			75	55
9			131	190
10			134	114
11	flotation	<0.5	66	148
12			218	136
13			56	69
14			137	115
15			127	127
16			93	93
17	dry deshaling (pneumatic vibrating FGX type separator)	0-25	113	319
18			146	121
19			88	162
20			131	132
21			65	78
22			124	160

$$RF = \frac{Hg_{rejects}}{Hg_{feed}}\ ,[-] \quad (1)$$

where:

RF – factor of mercury accumulation in the rejects separated from coal in the washing/deshaling processes [-],
$Hg_{rejects}$ – mercury content in the rejects [µg/kg],
Hg_{feed} – mercury content in the feed coal for the coal washing/deshaling processes [µg/kg].

3. Results and discussion

The mercury content in the feed coals for the coal cleaning process varied from 54 to 218 μg/kg (the average of 106 μg/kg) and was smaller than the mercury content in the rejects separated from coal – from 55 to 319 μg/kg (the average of 125 μg/kg). For the entire population of analyzed samples a significant correlation between the mercury content in the feed coal and in the rejects was not found (Fig. 1a). Such a relationship was obtained only for the beneficiation in dense media separators (Fig. 1b). The significance of the correlation was verified with the use of the F-Snedecor test at the confidence level of 0.95. The lack of correlation for the entire population may be caused by, both, differences in the mode of mercury occurrence in individual coals (Dziok et al. 2015) as well as by differences in mercury content in the grains of pyrite and other sulfides which occur even within a single grain (Dziok et al. 2019). The results of the preliminary statistical analysis obtained for the dense media separation may indicate that for coarse size fractions of hard coal the dominant mode of mercury occurrence is the adventitious inorganic constituents which undergoes separation very well. However, due to the small number of samples (4 cases), the results obtained should be verified in further investigations.

A comparison of mercury content in the rejects derived from the analyzed processes is shown in Fig. 2. The highest mercury content and the highest dispersion of results were recorded for the rejects derived from the dense media separation as well as from the dry deshaling process. The lowest values were obtained for the grain coal jigging. In the case of the coal jigging, low mercury content may be related to its accumulation in the middling products, which was pointed out in our previous work (Dziok et al. 2019). The mercury content in the analyzed middling products was 313 and 246 μg/kg (dry basis), respectively. Their examination using an electron probe microanalyzer (EPMA) showed the occurrence of mercury mainly in the grains of pyrite, marcasite as well as chalcopyrite and the mercury content in them reached 0,1%.

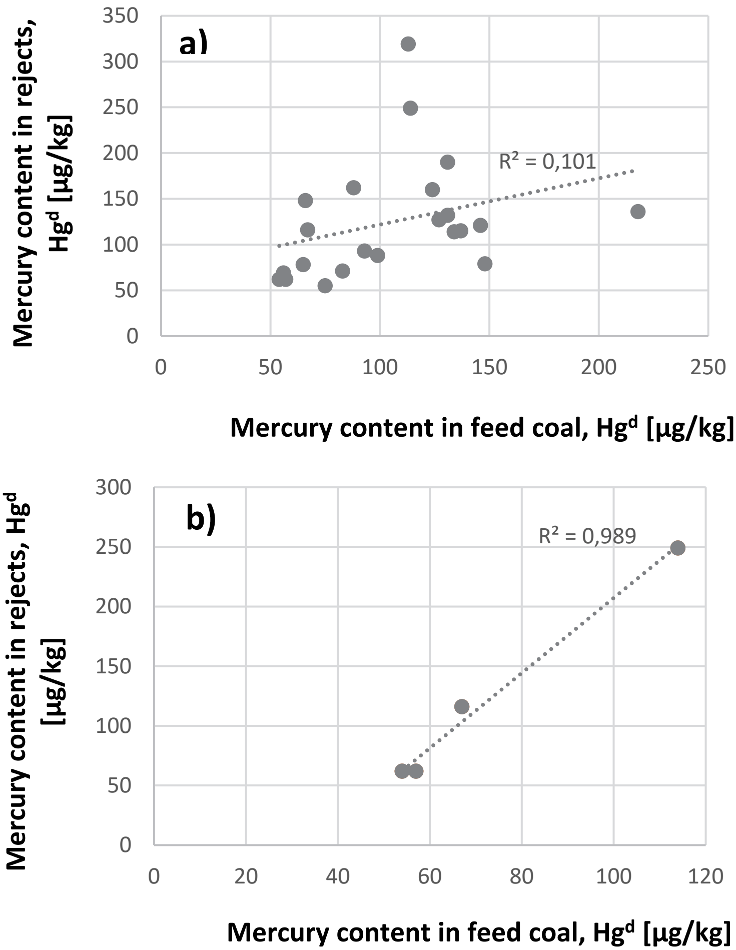

Fig. 1. Relationship between mercury content in feed coal and rejects derived from the coal washing/deshaling processes: a) all analyzed cases, b) dense media separation

In Fig. 3 a comparison of the *RF* values determined for the analyzed hard coal washing process was presented. The influence of grain size on the mercury content in the rejects is noticeable. Only in the case of beneficiation in dense media separators for each of the analyzed cases the *RF* was higher than 1 (from 1.09 to 2.18 with the average at the level of 1.54). This shows, as previously mentioned, a very good separation of mercury from the raw coal of large grain size in the coal washing process in the dense media separators (coal grain size >20 mm). In the case of the grain coal jigging (coal grain size 0.5-70 mm) for each of the analyzed cases the mercury content in the rejects was lower than in the feed coal. The *RF* value varied from 0.53 to 0.89 with the average of 0.69. A relatively low value of *RF* was obtained for the fine coal jigging as well (coal grain size 0.5-20 mm): from 0.85 to 1.45 with the average of 1.10. This may suggest difficulties in the separation of grains rich in mercury during these processes or the lack of such grains in feed coals.

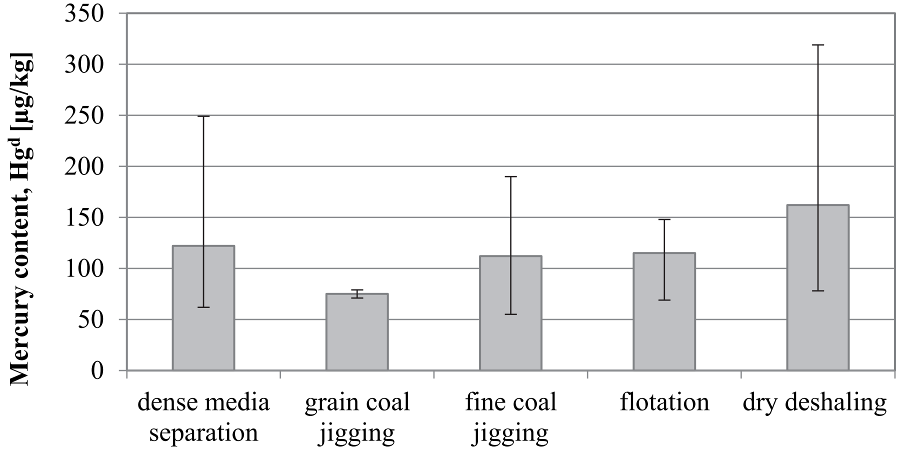

Fig. 2. Comparison of mercury content in the rejects derived from individual cleaning processes (the whiskers represent the dispersion of the obtained results)

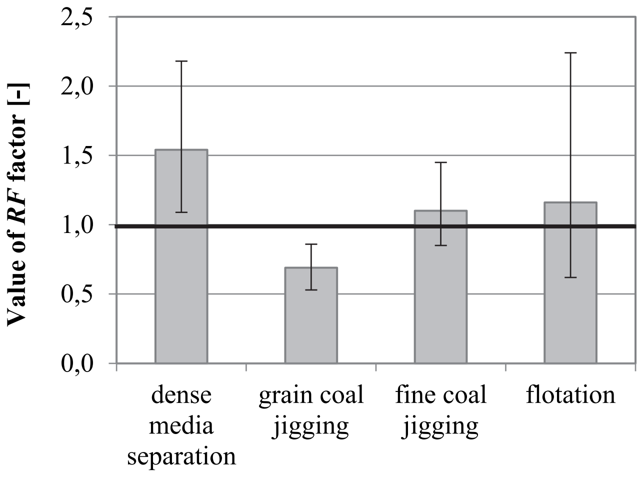

Fig. 3. Comparison of the *RF* values determined for the analyzed hard coal washing process (the whiskers represent the dispersion of the obtained results)

For the flotation (coal grain size <0.5) the obtained results were not obvious. For individual cases very low or very high values of *RF* were observed. This can be explained by the different mode of mercury occurrence in the analyzed coals.

In Fig 4 a comparison of the *RF* values determined for the analyzed cleaning processes was presented. In the light of the obtained results, it can be concluded, that mercury shows a tendency to occur in higher amounts in the rejects when compared to the feed coal both in the washing process (*RF* from 0.53 to 2.24 with the average of 1.15) and in the deshaling process (*RF* from 0.83 to 2.82 with the average of 1.50).

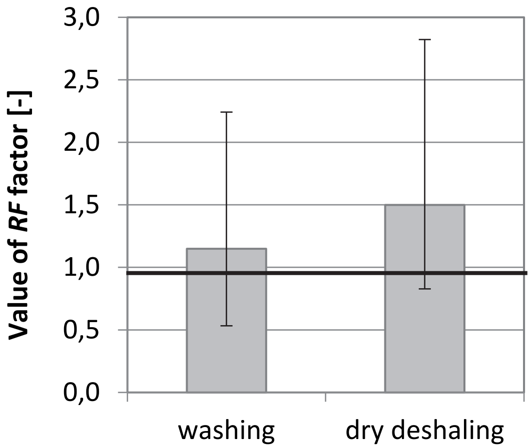

Fig. 4. Comparison of the *RF* values determined for analyzed hard coal washing and deshaling processes (the whiskers represent the dispersion of the obtained results)

This shows the possibility of the effective removal of mercury occurring in the adventitious inorganic constituents of the analyzed Polish hard coals. However, it should be noted, that the obtained results varied within a relatively high range, which should be explained by the difference in the mode of mercury occurrence in individual coals (Dziok et al. 2015, Zheng et al. 2008). This variability may cause low effectiveness of mercury removal for some coals. For such coals, the solution may be the thermal pretreatment of clean coals derived from the washing and deshaling processes at the temperatures of 200-300°C. This process allows for the removal of mercury occurring both in the organic matter as well as in the inorganic constituents characterized by a relatively low temperature of decomposition (Dziok & Strugała 2017). However it should be noted that the choice of an appropriate solution will depend on: (i) the investment and operating costs, (ii) on the quality requirements for hard coal including ash content and calorific value, as well as (iii) the technological properties of coal, including the forms of mercury occurrence. When compared to the washing methods, the pneumatic vibrating FGX type separators are characterized by lower investment and operating costs (Baic et al. 2015).

4. Conclusions

The mercury content in the feed coals for coal cleaning varied from 54 to 218 μg/kg (the average of 106 μg/kg) and was smaller than the mercury content in the rejects separated from coal – from 55 to 319 μg/kg (the average of 125 μg/kg). The highest mercury content and the highest dispersion of results were recorded for the rejects derived from the dense media separation as well as from dry deshaling using the pneumatic vibrating separators. The lowest values were obtained for the grain coal jigging.

In the light of the obtained results, it can be concluded that mercury shows a tendency to occur in higher amounts in the rejects when compared to the feed coal both in the washing process (*RF* from 0.53 to 2.24 with the average of 1.15) and in the deshaling process (*RF* from 0.83 to 2.82 with the average of 1.50), while the higher *RF* values were obtained for the dry deshaling process. This shows the possibility of effective mercury removal from the Polish hard coals. However, the choice of an appropriate solution will depend on: (i) the investment and operating costs, (ii) the quality requirements for hard coal, including ash content and calorific value as well as (iii) the technological properties of coal, including the forms of mercury occurrence.

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Abstract

Due to the toxicity of mercury a reduction of its emission is the objective of many legislative actions. In the case of power plants, there are well-known methods allowing for the removal of mercury from flue gases (post-combustion). In the case of households and small-scale combustion installations these methods are not used, which is caused by high investment costs. The most effective solution for this group of customers is the removal of mercury from coal (pre-combustion). This can be obtained in the washing and deshaling processes.

The coal-cleaning processes which is commonly used in Polish coal preparation plants were analyzed, i.e. dense media separation, grain and fine coal jigging, flotation, as well as dry deshaling using the pneumatic vibrating FGX type separator. The first four are the washing processes and the last one is the dry separation process. The effectiveness of the coal cleaning process was assessed with the use of the *RF* factor (the ratio of the mercury content in the rejects to the mercury content in the feed coal). The obtained values of the *RF* factors show that mercury has a tendency to remain in the rejects, while higher values of the *RF* factors were obtained for the dry deshaling process (from 0.83 to 2.82 with the average of 1.15) than for the washing process (from 0.53 to 2.24 with the average of 1.50). This shows the possibility of the effective removal of mercury occurring in the adventitious inorganic constituents of the analyzed Polish hard coals. However, it should be noted, that the obtained results varied within a relatively high range, which should be explained by the difference in the mode of mercury occurrence in individual coals.

Keywords:
hard coal, washing, deshaling, mercury, removal

Analiza zawartości rtęci w nadawie i odpadach dla wybranych procesów wzbogacania węgla kamiennego

Streszczenie

Emisja rtęci, z uwagi na jej toksyczne właściwości jest przedmiotem wielu działań legislacyjnych których przykładem jest m.in. przyjęcie w UE konkluzji BAT dla dużych obiektów energetycznego spalania. W przypadku dużych energetycznych instalacji znane i stosowane są różne metody usuwania rtęci ze spalin (etap post-combustion), natomiast w przypadku użytkowników domowych i instalacji energetycznych o małej mocy te metody nie są stosowane. Jest to spowodowane w głównej mierze wysokimi kosztami inwestycyjnymi. Najskuteczniejszym rozwiązaniem dla tej grupy użytkowników węgla jest usuwanie rtęci z węgla (etap pre-combustion), co umożliwia uzyskanie węgla o niskiej zawartości rtęci. Taki węgiel może być przygotowany w wyniku jego wzbogacania lub odkamieniania.

Analizie poddano procesy wzbogacania węgla kamiennego stosowane w polskim sektorze przeróbczym: wzbogacanie w płuczkach zawiesinowych cieczy ciężkich, wzbogacanie w osadzarkach miałowych i ziarnowych, flotację a także proces odkamienianie przy wykorzystaniu separatora powietrzno-wibracyjnego. Cztery pierwsze procesy są stosowane do wzbogacania węgla kamiennego na mokro, a ostatni do suchej separacji. Dla analizowanych procesów przebadano próbki nadaw kierowanych do wzbogacania oraz odpady. Dla oceny efektywności procesu wzbogacania wykorzystano wskaźnik RF, wyznaczony jako stosunek zawartości rtęci w odpadzie do nadawy kierowanej do wzbogacania. Uzyskane wartości RF wskazują na tendencję do pozostawania rtęci w odpadach zarówno w procesie wzbogacania na mokro (od 0,53 do 2,24 przy średniej 1,15) jak i suchego odkamieniania (od 0,83 do 2,82 przy średniej 1,50), przy czym wyższe wartości wskaźnika uzyskano dla suchego odkamieniania. Świadczy to o możliwości efektywnego usuwania rtęci z badanych polskich węgli kamiennych. Należy zaznaczyć, że uzyskane wyniki wahały się w dość szerokim zakresie, co należy tłumaczyć różnicami w formach występowania rtęci w poszczególnych węglach.

Słowa kluczowe:
węgiel kamienny, wzbogacanie, odkamienianie, rtęć, usuwanie

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Influence of Mesophilic Digestion of Dairy Sewage Sludge on Content of Chosen Heavy Metals and their Fractions

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1. Introduction

The problem of sewage sludge management, which is the inseparable product of sewage treatment, concerns almost each municipal or industrial wastewater treatment plant (WWTP) (Kogut 2014). The requirements, which have to be fulfilled with the use of sludge in agriculture, are mentioned in regulation concerning municipal sewage sludge. The basic criteria is the content of chosen heavy metals both in sludge and in soil, on which sewage sludge can be used. The largest dairy processing plants are located in podlaskie voivodeship. Some of them have WWTPs. That is why the sludge, which is produced during the treatment process, is used in 100% to fertilize soil (Dąbrowski 2010). Except of high content of such elements like nitrogen or phosphorus, sludge includes also a lot of alkaline elements for example sodium, potassium, calcium and manganese, which is very essential in case of the dominance of light and acid soils in podlaskie voivodeship (Dąbrowski 2009). On account of the production specification in dairy industry, the sewage and sludge are deprived of sanitary contamination. That is why, the basic criteria conditioning safe use of sludge from dairy WWTPs, is the total content of heavy metals. It is also important in which fraction metals will be introduced to the environment and to what expend they will be available for the plants. The most mobile are metals occurring in ion-exchange carbon fractions.

To the end of 2012, podlaskie dairy WWTPs used only aerobic digestion of excessive sludge with the use of separate chambers or simultaneously with the process of sewage treatment. On account of the lack of experience connected with co-digestion of excessive and floatation sludge from pretreatment of dairy sewage, the researches of digestion process in laboratory scale were conducted. There were determined many parameters among others reject water and sludge composition. In the paper, there are shown the researches of labile and stable combination of chosen metals in sludge before and after digestion process.

2. Materials and methods

Sewage sludge, which was exposed to anaerobic digestion process in a laboratory installation, came from the sewage treatment plant of Mlekovita dairy cooperative. The average sewage effluent flow was approximately 5893 m^3 per day, while the amount of sludge produced per year reached about 2500 Mg of dry matter. According to the modernization project, the throughput of wastewater treatment plant will increase up to 7500 m^3 per day, while the amount of sludge – up to 3500 Mg of dry matter per year. Sharp rise of sludge amount is the result of high load of BOD_5 in dairy sewage (Dąbrowski 2009). According to the modernization project, the sludge samples were prepared to the research as the mixture of excessive sludge after thickening (70% of input per dry matter) and floatation sludge from pretreatment of dairy sewage (30% of input). The load of chamber for anaerobic digestion assumed to be approximately 0.7 kg d.m./m^3 per day, which is characteristic value for the classical sludge digestion. The research installation in laboratory tests (Fig. 1) was composed of three closed chambers. Each of them with capacity of 10 dm^3 was equipped with stirring and heating system with and control units. The produced biogas was removed by the system of valves. The process was carried out as a *mesophilic* digestion for 20 days. The automatic control system provided to maintain constant temperature of the process and periodic mixing of the chambers contents.

Within the researches connected with the determination of total content and chosen heavy metals fractions, there were conducted five experiment series covering testing of sludge samples during and after digestion process in mesophilic conditions. Stable sludge was dehydrated using a special hydrophobic cloth used in the bag filter press. Metals were determined by means of inductively coupled plasma atomic emission spectrometry (ICP-OES; Varian apparatus VISTA MPX) after sample digestion with concentrated HNO_3. Samples were digested using microwave digestion. The content of Hg was marked with the AMA-254 spectrum analyzer directly through the sample's catalytic incineration in oxygen. In order to check the process of mineralization, the labeling of each sample was confirmed with a certified material for sewage sludge reference BCR-146 R and material for confirming curie and the whole analytical process SPS-SW2. Moreover, blind samples were used to control the limit of quantification. The metals were tested on interference lines: Cd – 214,439 nm, Cr-267,716 nm, Cu- 327,395 nm, Ni-231,604 nm, Pb-220,353 nm, Zn-213,857 nm (PNEN ISO 11885:2009).

Fig. 1. Laboratory scale research installation for anaerobic sewage sludge digestion (source: W. Dąbrowski)

Modified BCR method with a use of ultrasonic probe Sonics VCX 130 was used to evaluate fractional composition of metals in sludge samples (Tessier 1979, Łukowski 2014, Rao et al. 2008, Shrivastava and Banerjee 2004). Extraction included four stages:

1. Acid soluble and exchangeable fraction (F1) – 1 g of sludge in 100 cm^3 centrifuge tube with 40 cm^3 of 0.11 mol/dm^3 acetic acid was sonicated for 7 min (power – 20 W) at temperature 22 ± 5°C. Then, the mixture was centrifuged for 20 min at 3000×g. The extract was separated for analysis. Residue with 20 cm^3 of deionized water was sonicated for 5 min (power – 20 W) and centrifuged for 20 min at 3000×g. Water was discarded.
2. Reducible fraction, bound to Fe/Mn oxides (F2) – to the residue from the first step was added 40 cm^3 of 0.5 mol/dm^3 hydroxylamine hydrochloride fresh solution, pH 1.5, and sonicated for 7 min (power – 20 W) at temperature 22 ± 5°C. Then, the mixture was centrifuged for 20 min at 3000×g. The extract was separated for analysis. The residue was rinsed with deionized water, alike in the first step.

3. Oxidizable fraction, bound to organic matter (F3) – to the residue from the second step was added 20 cm^3 of 30% hydrogen peroxide and sonicated for 2 min (power – 20 W) at temperature 22 ± 5°C. Then, the volume of H_2O_2 reduced to approx. 1 cm^3 using water bath. 50 cm^3 of 1 mol/dm^3 ammonium acetate and sonicated for 6 min (power – 20 W) at temperature 22 ± 5°C was added to the moist residue. Then, the mixture was centrifuged for 20 min at 3000×g. The extract was separated for analysis. The residue was rinsed with deionized water, alike in the previous steps.
4. Residual fraction (F4) – residual fraction (option) F4 was calculated from the difference between 100% and summarized percentage of other fractions.

Results are represented as arithmetic mean of three replicates. The differences between the obtained values were determined by one-way ANOVA with Tukey's post-hoc test at confidence level $p < 0,05$.

3. Results and discussion

In table 1 there were shown the research results of exploiter of WWTP connected with the content of metals in dairy sludge exposed to aerobic digestion. This way of sewage sludge stabilization will be used to the moment of startup of digestion chambers and the whole modernized installation in order to treat sludge. Sewage sludge produced during the process of dairy sewage treatment is characterized by differentiated content of heavy metals. Its amount is low comparing to the requirements described in regulation concerning municipal sewage sludge and also the characteristic values for municipal WWTP using aerobic and anaerobic sludge digestion. It is proved by the researches of Rosik Dulewska et al. (2005) concerning the composition of sludge from wastewater treatment plant located within the area of Silesia. Admissible values of metals content in sludge, which was used to fertilize soil, were also presented in Table 1.

Table 1. Heavy metals contents [mg/kg d.m.] in aerobically stabilized sludge in Wysokie Mazowieckie

Metal	Pb	Hg	Cu	Cd	Ni	Zn	Cr
Minimum	-	0.06	17.0	-	1.9	99.8	6.6
Maximum	-	0.21	23.3	-	6.01	145.0	18.8
Mean	<12.5	0.17	20.0	<0.375	3.72	119.0	10.04
Maximum for agriculture reuse*	750	16	100	20	300	2500	500

*Regulation Concerning Municipal Sewage Sludge

In Tables 2 and 3 but also on Figures 2 and 3 were shown the authors' research results with the use of laboratory installation (Fig. 1) connecting the process of anaerobic digestion in *mesophilic* conditions as the determination of total forms and metals fractions. Comparing the total content of metals in aerobically digested sludge (Tab. 1) with those aerobically digested (Tab. 2), the similar amount of lead was stated, while in case of the rest of meals, their content was higher after anaerobic digestion. The content of metals in sludge in case of aerobic digestion used in WWTP of Mlekovita was similar to the one after anaerobic digestion conducted in laboratory conditions and it was far lower than the admissible value while the use of sludge as fertilizer. During conducted digestion process, there was observed the decrease of organic matter content from 79,8 to 58% on average. On the basis of the analysis of heavy metals content before and after anaerobic digestion process, there was stated the increase of metals content per dry matter after anaerobic digestion. The following results were reached: substantial increase of total content of copper and nickel, slight rise of zinc, while the content of lead, cadmium, chromium and mercury changed a little (Tab. 3).

Table 2. Total heavy metals contents [mg / kg d.m.] in row dairy sewage sludge and after *mesophilic* digestion.

Parameter	Pb	Hg	Cu	Cd	Ni	Zn	Cr
Before *mesophilic* digestion							
Minimum	1.2	0.005	16.0	1.2	8.0	185.0	4.5
Maximum	5.0	0.12	28.0	1.4	10.4	216.0	5.7
Mean	3.7	0.078	20.0	1.3	10.0	195.0	4.8
After mesophilic digestion							
Minimum	2.1	0.09	70.0	1.4	56.0	238.0	4.4
Maximum	6.2	0.16	89.0	1.7	69.0	268.0	5.2
Mean	4.8	0.14	85.0	1.6	64.0	255.0	4.6
Maximum for agriculture reuse*	750	16	100	20	300	2500	500

*Regulation Concerning Municipal Sewage Sludge 6.02.2015

Table 3. Fractions of heavy metals contents (mean values) [mg /kg d.m.] before and after *mesophilic* digestion

Metal	Fraction	Before digestion	After digestion
Pb	F I	1.6	1.4
	F II	1.5	2.4
	F III	0.6	0.6
	F IV	0.0	0.4
	Total	3.7	4.8
Cu	F I	0.5	0.7
	F II	1.2	1.5
	F III	15.2	44.2
	F IV	3.1	0.2
	Total	20.0	46.6
Cd	F I	0.04	0.07
	F II	0.75	1.24
	F III	0.5	0.26
	F IV	0.01	0.03
	Total	1.3	1.6
Ni	F I	4.4	4.7
	F II	1.6	12.1
	F III	3.4	6.6
	F IV	0.5	0.6
	Total	10.0	24.0
Zn	F I	31.4	20.9
	F II	62.8	86.7
	F III	97.1	144.3
	F IV	3.7	3.1
	Total	195.0	255.0
Cr	F I	1.8	2.6
	F II	1.0	0.6
	F III	1.5	0.9
	F IV	0.5	0.5
	Total	4.8	4.6

F I – Exchangeable, F II – Reducible, F III – Oxidizable, F IV – Residual

The decay of organic matter during the digestion process was the reason of increase of metals content in dry matter of digested sludge. It is proved by the research of municipal sludge digestion conducted by Dąbrowska (2011) and Obarska-Pempkowiak (2003) together with the team researched metals fractions in sludge from wastewater treatment plant of Gdańsk-Wschód, while Chipasa, except of the total content of metals in sludge, also examined their content in sewage on different stage of its treatment. The results of their researches prove the tendency of increase of metals content after anaerobic digestion process (Kangala 2001).

Sewage sludge is valuable organic waste, which should come back into soil, especially to the light and acid soils. However, in case of high doses of sludge used on such types of soils, it is extremely important to determine in them not only total forms of heavy metals but also their fractions. In case of acid soils, the release of metals is faster and they are more available for plants, which is noticed by Wiater and Łukowski (2014). The process of anaerobic digestion caused the limitations of lead, nickel and zinc mobility (Tab. 3, Fig. 2 and 3). In case of these metals, there was observed the decrease of their content in most available fraction F I. Lead, before and after digestion, occurred mainly in F I and F II fraction, but it clearly moved to second fraction combined with oxides and Fe/Mn hydroxides in result of digestion process. Lead content in fraction combined with organic matter decreased. After digestion process, about 9,7% of lead occurred in residual fraction F IV, which is unavailable for plants. The increase of lead in fraction IV is proved by the researches of Dąbrowska and Solis et al., who determined the speciation of metals in sludge from chosen wastewater treatment plant in Spain (Dąbrowska 2011, Solis 2002). Wilk and Gworek (2009) noticed that lead in sludge is more mobile than in soils, which is proved by conducted researches. Lead is the element, which is stored on the surface of fertilized soils, causing the limitations of organic matter decay.

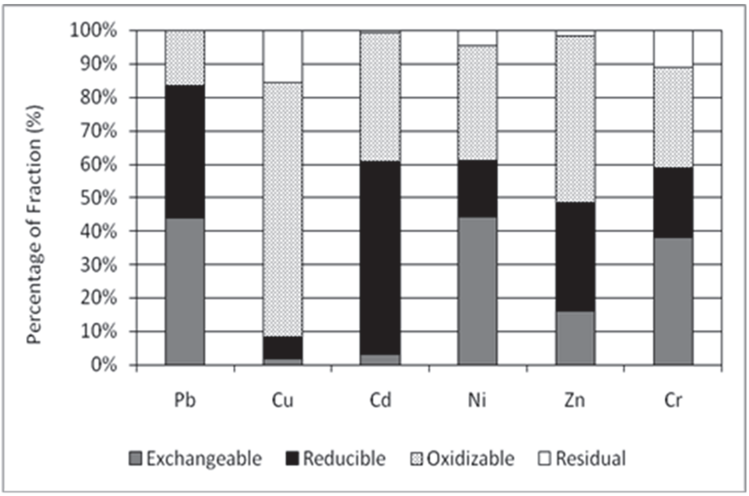

Fig. 2. Fractions of heavy metals in sewage sludge before anaerobic digestion

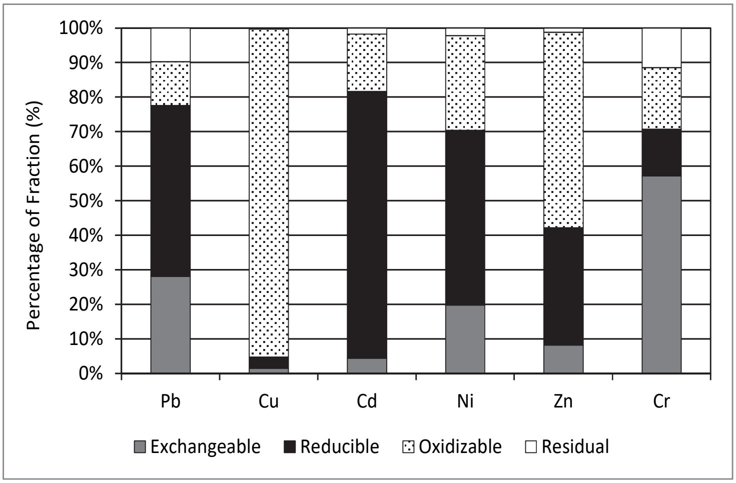

Fig. 3. Fractions of heavy metals in sewage sludge after anaerobic digestion

The process of anaerobic digestion of sludge from dairy WWTP, did not influence copper content in changeable fraction F I, but it decreased its share in fraction F II almost twice from 6,2 to 3,2%. (Fig. 2 and 3). Copper makes stable combination with organic matter, which is proved by the data from References. Ignatowicz (2017) states that copper in municipal sludge occurs mainly in fraction combined with organic matter. Similar conclusions can be found in researches made by Latosińska and Gawdzik (2003), who examined metals fractions in sludge, which was aerobically and anaerobically digested. The digestion process causes sludge thickening and decrease of organic matter, which is proved by copper content in this fraction with the decrease of residual fraction from 15,6% to at least 0,3%. Immobilization of copper is not always favorable, especially when sludge, which is indispensable element for plants, is used to fertilize poor soils.

Cadmium is the most mobile element in soil environment and each external introduction of it can cause the danger of its bioaccumulation. In dairy sludge exposed to digestion, it occurred mainly in reducible fraction F II and fraction with organic matter F III. After digestion process, cadmium was moved from fraction combined with organic matter to residual fraction. In result of anaerobic digestion, the potential mobility of cadmium increased of about 20% (Tab. 3, Fig. 2 and 3). Latosińska and Gawdzik (2003) claim that anaerobically digested sludge includes cadmium mainly in immobile fractions, similarly to the researches of Dąbrowska (2011). In case of nickel, the conducted digestion process decreased its content in the most mobile fraction F I over twice. More nickel was found in reducible fraction F II on charge of changeable fraction F I and fraction combined with organic matter. When the sludge was used on acid soils, less of reducible fraction could move to the changeable one and when soil reaction was higher, this movement was postponed in time. Authors who examined nickel in municipal sludge and composts obtained different results. In analyzed sludge, nickel occurred mainly in fractions combined with organic matter (Ignatowicz 2011, 2017, Wilk 2009).

Digestion process, to the little extent, influenced the zinc content in fraction F II and F III, and it decreased its content in changeable fraction F I almost twice. It proves that zinc mobility is limited by digestion process. Residual fraction F IV slightly decreased from 1,9 to 1,2%.

On the other hand, anaerobic digestion process influenced differently chromium content in particular fractions. This metal mobility increased of about: 20% comparing with the sludge before digestion, 7% – on charge of fraction F II and 13% – comparing with fraction III. Residual fraction did not change. However, different results are given not only by Dąbrowska, who shows the increase of immobile fraction after municipal sludge digestion, but also Gawdzik and Gawdzik (2012) who claim that sludge contains mainly chromium in immobile fraction.

4. Conclusions

1. The total content of heavy metals in dairy sludge both before and after digestion process in *mesophilic* conditions, is low comparing with the requirements of regulation concerning municipal sewage sludge in soil fertilization.
2. In result of aerobic digestion, metals content increased in dry matter, which is mainly caused by the decrease of organic matter content during properly conducted digestion process.
3. The researches of anaerobic digestion of dairy sludge showed slight increase of immobile fraction in case of lead, copper and zinc. The decrease of this fraction was observed in case of cadmium, nickel and the most - chromium.
4. The total content of metals in digested sludge do not show the possibility of their release and availability by plants cultivated on soils fertilized by sludge from dairy comparing wastewater treatment plant. The determination of metals speciation is necessary in case of sludge used to soil fertilization and reclamation. Dairy sewage sludge can be the valuable source of organic matter on light soils occurring in the area of Podlasie region.

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Abstract

In this work, there were shown the research results concerning anaerobic digestion in the *mesophilic* condition. There was done the assessment of content of chosen heavy metals and their fractions in dairy sewage sludge before and after digestion process. The research was conducted with the use of laboratory installation on the base of mixture of excessive and floatation sludge. The process parameters were adopted from the modernization project of dairy sewage treatment plant of Mlekovita cooperative in Wysokie Mazowieckie. The results showed that in case of agricultural use of sludge, the total amount of heavy metals in sludge after anaerobic digestion was sharply lower that the values demanded in regulation concerning municipal sewage sludge. The process of sludge digestion caused the increase of metals content in dry matter of sludge. Metals speciation was determined with the use of scheme in accordance with methodology worked by BRC, which meant indicating four fractions. In case of lead, copper and zinc, the researches of anaerobic digestion process of dairy sludge showed the little increase of immobile fraction. The decrease of metals fraction was observed in case of cadmium, nickel and the clearest – chromium.

Keywords:
heavy metals, fraction, sewage sludge treatment

Wpływ procesu fermentacji mezofilowej na zawartość wybranych metali i ich frakcji w osadzie z oczyszczalni ścieków mleczarskich

Streszczenie

W pracy zaprezentowano wyniki badań dotyczących procesu stabilizacji beztlenowej w warunkach mezofilowych. Dokonano oceny zawartości wybranych metali ciężkich i ich frakcji w osadzie mleczarskim przed i po procesie stabilizacji. Badania prowadzono z zastosowaniem układu laboratoryjnego w oparciu o mieszaninę osadu nadmiernego i flotacyjnego. Parametry procesu zostały adoptowane z projektu modernizacji oczyszczalni ścieków mleczarskich firmy Mlekovita w Wysokiem Mazowieckiem. Stwierdzono, iż ogólna ilość metali ciężkich w osadzie po procesie stabilizacji beztlenowej jest znacznie niższa niż wartości wymagane w rozporządzeniu w sprawie komunalnych osadów ściekowych w przypadku rolniczego wykorzystania osadu. Proces stabilizacji osadu spowodował wzrost zawartości metali w suchej masie osadu. Specjację metali określono za pomocą schematu zaproponowanego przez zgodnie z metodyką opracowaną przez BCR wyodrębniając cztery frakcje. Przeprowadzone badania procesu stabilizacji beztlenowej osadów mleczarskich wykazały niewielki wzrost frakcji niemobilnej w przypadku ołowiu, miedzi i cynku. Zmniejszenie tej frakcji metali zaobserwowano w przypadku kadmu i niklu, i najwyraźniej w przypadku chromu.

Słowa kluczowe:
metale ciężkie, frakcje metali, przeróbka osadów

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Assessment of the Content of Cr, Cu, Fe, Mn and Ni in Water and Algae from the Region of Makarska Riviera in Croatia

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1. Introduction

Trace metals play a key role in the functioning of oceanic and sea ecosystems. Many of them, like manganese and iron are elements indispensable for the growth of living organisms, however, other physiological roles have not been found yet. Trace elements are particularly significant for ecosystems of saline reservoirs thanks to a low concentration found in oceanic and sea water (Aparicio-Gonzalez et al. 2012, Kováčik et al. 2018). The content of trace elements in sea water is several or several hundred times lower compared to their concentration in fresh water. Additionally, bio-assimilability of these elements in sea environment is lower than in fresh water. These conditions cause that sea organisms as a result of evolution have developed an ability to intensify collection of trace elements to satisfy a physiological demand for them (Titilawoa et al. 2018). These abilities of sea organisms induce a threat, both for them as well as for organisms from higher levels of a trophic chain mainly in the regions of the increased anthropopressure. The shallow coastal zones or estuaries with a greater amount of nutrients and favourable thermal conditions are especially exposed to the increased content of trace elements (Li et al. 2018). In such zones there are particularly good conditions for development of sea organisms living in water and outside it. In coastal regions and estuarine areas, a high variability of their reaction and oxygen content in water is observed (Jureczko et al. 2018). Bio-accumulation is an ability to collect elements or chemical compounds by living organisms (Goher et al. 2016). Assessment of the quality of the environment very often is made based on the bio-indication method, because it helps to determine not only the level of pollution in biotic elements of the ecosystem but also their impact on living organisms from subsequent levels of the trophic chain (Niemiec & Wiśniowska-Kielian 2015, Niemiec et al. 2018). Methods with the use of algae are the most often used for assessment of marine environmental pollution (Brito et al. 2012, Szeląg-Sikora et al. 2016). The main issue related to these organisms is selection of a suitable species, development of which will not be inhibited by such factors as water temperature, flow speed or salinity. There are some algae which have great abilities for accumulation of elements (Sikora et al. 2018), but they are sensitive to salinity which limits their use in monitoring tests (Sinaei et al. 2018). It is of particular meaning in the zones of strong mixing of river water with sea water on the areas of great seasonal fluctuation of river water flow. The use of algae as a material for research is an incredibly significant practical aspect since ca. 6 million tons of these organisms annually is used in the food industry. Moreover, even their greater use for production of medicines, cosmetics and fodder is observed (Naser 2013, Wang et al. 2017). A high content of protein with a favourable composition of amino acids decide about exceptional value of algae. Moreover, algae have anti-septic properties. Macro-algae have a great ability to accumulate potassium thus, their use as a fertiliser or fodder constitutes an unconventional source of this element. *Cystoseira* and *Ulva* algae are the most popular organisms that live in the sea and estuary bottoms since they are resistant to the above-mentioned factors. Therefore, they meet all criteria for bio-indicators. Due to a strong root system they may collect elements related to bottom deposits (Horta-Puga et al. 2013). Moreover, algae form a living and reproductive environment for water organisms and constitute their food and buffer the waving intensity.

The objective of the paper was assessment of Cr, Cu, Fe, Mn and Ni in water and algae collected in the region of Makarska Riviera.

2. Material and methods

The paper assesses the content of five elements in water and algae collected from the Adriatic Sea in the region of Makarska Riviera. Water and algae samples were collected in August 2016 from nine sampling points located in: Makarska, Podgora, Baska Voda, Split ul. Jana Pawła II, Storbeč, Podstrana, Omiš, Mimice, Dvernik (Figure 1). Water samples were collected from the surface layer (depth of 0-120 cm).

Samples of algae *Cystoseira barbata* and *Ulva rigida* were collected in the same points. The collected species of algae are popular on the investigated area. Water after collection was preserved by adding nitric acid (V) in the amount of 2 cm^3 per each 100 cm^3 of water sample, then samples were transported to a laboratory while algae were cleaned in distilled water, dried and homogenised. Five laboratory samples of water and algae were collected from the sampling point. Laboratory samples of algae were mineralised in the closed microwave system by Anton Paar Multivawe 3000. An analytical portion was 0.5 g per dry mass. Material was solubilised in the mixture of HNO_3 and H_2O_2 in the proportion of 5:1, *v*/*v*. The content of chromium, cooper, iron, manganese and nickel in water and solubilised algae samples were determined using the optical emission spectrometry technique by Perkin Elmer Optima 7600 DV. Certified reference material EA-V-10 was used for the control of correctness of analysis of the investigated elements. Results of analysis of the referential material and a value of recovery estimated based on analyses made in 4 iterations were presented in Table 1.

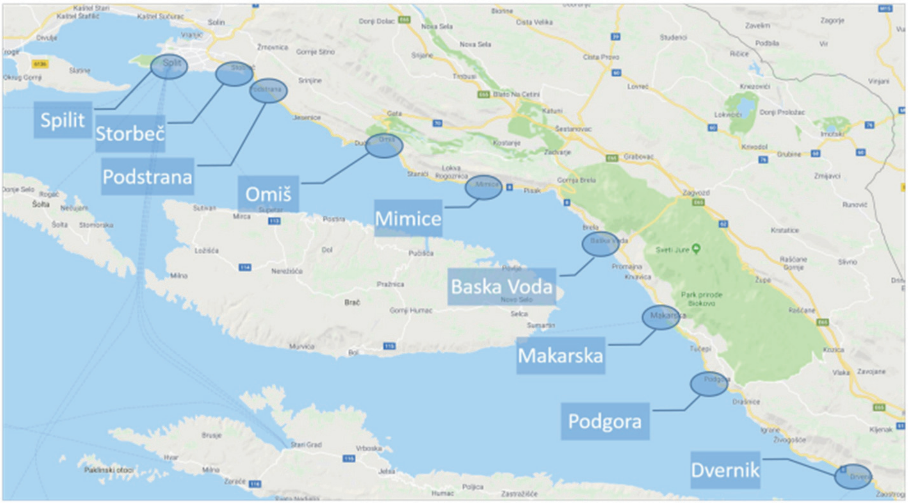

Fig. 1. Location of sampling points

Table 1. Parameters of the applied analytical method

Element	Length of waves	Limit of determination	Content in the referential material	Measured content	Coefficient of recovery
	(nm)	($mg \cdot dm^{-3}$)	($mg \cdot kg^{-1}$)	($mg \cdot kg^{-1}$)	(%)
Cr	267.707	0.0071	6.5	6.412	98.6
Cu	327.393	0.0097	9.4	9.125	97.1
Fe	238.204	0.0046	185	201.2	108.8
Mn	257.608	0.0014	47	48.56	103.3
Ni	231.604	0.015	4	3.856	96.4

3. Results of research and discussion

The highest content of chromium in *Cystoseira barbata* algae biomass was found in plants collected in Mimice point at the level of 3.417 mg·kg^{-1} and the lowest in Podstrana (1.367 mg·kg^{-1}) (Table 2). In case of *Ulva rigida* algae - the chromium content ranged from 7.570 to 13.26 mg·kg^{-1} with the highest amount in Baska Voda and the lowest in samples collected in Podgora (Table 3). A lower concentration of this element in *Ulva* in comparison to its amount in *Cystoseira* by 50% was reported. The content of chromium in both species of algae does not pose any risk to environment. The content of chromium in various species of algae collected from Aegean Sea in coastal regions of Turkey was slightly higher than the ones obtained in own research (Akcali & Kucuksezgin 2011). Those authors concluded higher concentration of this element in *Cystoseira barbata* compared to its amount in *Ulva rigida*. Brito et al. (2012) provide approximately two times higher values of chromium in biomass of various species of algae from the area in Brazil under high anthropopressure, while accumulation of this element in algae collected in the Turkish coastal zone of the Black Sea was comparable to the ones obtained in own research. Caliceti et al. (2002) provide an average chromium content in *Cystoseira barbata* at the level of ca. mg·kg^{-1} in algae from Venice Lagune collected from the regions with varied intensity of anthropopressure. Strezov and Nonova (2009) provide chromium content in both algae collected from the Bulgarian coastal zone of the Black Sea at a similar level as the ones reported in this study in the points of the lowest accumulation of this element.

The concentration of copper in the investigated algae *Ulva rigida* range of 4.236 to 8.367 mg·kg^{-1} with the average content 5.622 mg·kg^{-1} (Table 3). The highest copper content in *Cystoseira* algae was observed in the sampling point located in Baska Voda and the lowest in Podstrana (Table 2). In case of *Ulva rigida* the highest amount of copper was observed in the sample collected in Storbec, while the lowest in algae from Podgora. Akcali and Kucuksezgin (2011) observed in the studies in the Aegean Sea that the copper content in *Cystoseira* algae was 0.269 mg·kg^{-1}. On the other hand, Strezov and Nonowa (2009) reported the copper content in *Ulva rigida* at the level from 2.2 to 10.9 mg·kg^{-1}.

The iron content in *Cystoseira barbata* algae in own research was within 48.28 mg·kg^{-1} and 225.1 mg·kg^{-1} and in *Ulva rigida* algae from 201.9 to 412.9 mg·kg^{-1} (Table 3). A relatively low content of iron was reported in algae collected in Omiš. The content of this element in *Ulva rigida* algae was almost threefold higher compared to *Cystoseira barbata*. Strezov and Nonova (2009) state that the average iron content in both species collected in the Bulgarin coastal zone ca. 450 mg·kg^{-1}, but these authors did not find any differences of this element in both algae species. Wallenstein et al. (2009) provide much lower,

(< 50 mg·kg^{-1}) iron content in *Cystoseira humilis* from regions of a varied intensity of anthropopressure. The manganese content in *Cystoseira barbata* ranger from 20.62 mg·kg^{-1} to 66.53 mg·kg^{-1} (Table. 2), while in *Ulva rigida* from 44.15 mg·kg^{-1} to 197.5 mg·kg^{-1} (Table 3). Results of own research show a higher manganese content in *Ulva* algae biomass than in *Cystoseira* biomass. The highest amount of this element was determined in algae collected in Mimice, Dwernik and Omiš. In the remaining samples, the content of this element was similar and within 44.15 to 63.38 mg·kg^{-1}. Brito et al. (2012) in various algae species from the region in Brazil under an elevated level of anthropopressure, provide the content of this element from 10 to almost 500 mg·kg^{-1}. Wallenstein et al. (2009) reported much lower content of manganese from 4 to 5 mg·kg^{-1} in *Cystoseira humilis* from Azores.

Table 2. Content of elements in biomass of *Cystoseira barbata* algae

Sample collection point	Cr	Cu	Fe	Mn	Ni
Unit	(mg·kg^{-1})				
Makarska	1.433a*	5.683b	141.5c	59.28bc	3.662c
Podgora	1.660a	3.967a	84.26b	20.62a	2.253b
Baska voda	2.236ab	6.236c	225.1d	33.35a	2.967bc
Split ul. Jana Pawła II	3.333c	5.333b	104.2b	51.78b	3.617c
Storbeč	3.033c	5.167b	64.25ab	43.25ab	2.417b
Podstrana	1.367a	3.560a	50.98a	33.58a	1.633a
Omiš	3.258c	3.836a	48.28a	63.23bc	3.948c
Mimice	3.417c	4.817ab	123.9c	61.78bc	3.567c
Dvernik	3.257c	5.456b	156.2	66.53c	3.586c
Average	2.555	4.895	111.0	48.16	3.072
Standard deviation	0.876	0.920	57.72a	16.21	0.799

*Letters at values in particular locations stand
for statistically significant differences at $p = 0.05$

The nickel content in *Cystoseira barbata* algae was within 1.633 to 13.26 mg·kg^{-1} (Table 2). The highest amount of this element was reported in samples collected in Mimice, Dwernik and Omiš, and the lowest in Podstrana and Podgora. The content of nickel in *Ulva rigida* was within 2,493 to 5,617 mg·kg^{-1}, with the average of 4,021 mg·kg^{-1} (Table 3). The results obtained in own research concerning the nickel content in algae in majority of case are not high and similar to the content of this element in algae from the areas with a low coefficient of anthropopressure. Brito et al. (2012) provide the nickel content that is several times higher in algae of various species from the region in Brazil with a prominent level of anthropopressure. Caliceti et al. (2002) reported the average content of this element from Venice Lagune at the level of 1.8 $mg \cdot kg^{-1}$, at slight differences of concentration in algae collected in the region with a varied intensity of anthropopressure. Wallenstein et al. (2009) provide much lower, ca.1 $mg \cdot kg^{-1}$, nickel content in *Cystoseira humilis* from the region of Azores from stations under a varied intensity of anthropopressure. In Chlorophyta (green algae) collected in the contaminated region of the coastal zone of Saudi Arabia, the concentration of this element was within 25 to 44 $mg \cdot kg^{-1}$ (Naser 2013). On the other hand, Rodriguez-Figueroa et al. (2009) provide the maximum content of nickel in algae from the Gulf of Mexico in the region with the impact of the copper mine at the level of 28 $mg \cdot kg^{-1}$. The nickel content in *Ulva rigida* collected from San Jorge in Argentina was within 0.9 - ca. 4 $mg \cdot kg^{-1}$ (Perez et al. 2007).

Water samples collected from particular sampling points were variable with regard to the concentration of the investigated elements. The biggest number of the tested elements was in water collected in Split and Dwernik, and the lowest in Podgora and Podstrana (Table 4). In case of majority of samples, water was enriched in chromium, copper, iron, and nickel (Bonnand et al. 2013, Akcali & Kucuksezgin 2011).

Sea alga are much related to trace elements (Niemiec et al. 2015). Due to the specificity of physiological processes, they can collect massive amounts even in the conditions of their small concentrations in a biotype (Chakraborty et al. 2014).

The results of the research show that the highest value of the bio-accumulation ratio was in case of manganese both in case of *Cystoseira barbata* and *Ulva rigida* (Figure 2 and 3).

The chromium bio-accumulation coefficient in organisms used in the research was at a level of 1102 to 2527 respectively for the sampling points Makarska and Mimice (Figure 2). The chromium bio-accumulation factor in *Ulva rigida* algae was within 6626-11984 (Figure 3). Literature data show similar values of chromium bio-accumulation coefficient in macro-algae from various regions of the world. Akcali and Kucuksezgin (2011) claim that the value of the chromium bio-accumulation coefficient in algae from the Aegean Sea were from several to several thousand.

Table 3. Content of elements in the biomass of *Ulva rigida* algae

Samples collection points	Cr	Cu	Fe	Mn	Ni
Unit	$(mg \cdot kg^{-1})$				
Makarska	8.957a*	4.967ab	348.6c	62.28ab	4.657b
Podgora	7.570a	4.236a	266.6b	51.24a	2.235a
Baska Voda	13.26b	6.159bc	299.6bc	56.56ab	3.867b
Split ul. Jana Pawła II	11.27b	5.657b	353.2c	63.38ab	4.425b
Storbeč	10.10ab	8.367d	412.9d	155.8cd	3.667ab
Podstrana	8.550a	6.685c	261.2b	44.15a	2.493a
Omiš	11.20b	4.438a	403.7d	75.33b	4.375b
Mimice	13.18b	4.667a	201.9a	197.5d	5.617c
Dvernik	12.26b	5.423b	245.7ab	132.5c	4.856b
Average	10.70	5.622	310.4	93.19	4.021
Standard deviation	2.047	1.307	73.24	54.78	1.096

*Letters at values in particular locations stand
for statistically significant differences at p = 0.05

Table 4. Content of elements in water

Samples collection points	Cr	Cu	Fe	Mn	Ni
Unit	$(\mu g \cdot dm^{-3})$				
Makarska	1.300b*	12.00b	132.0ab	13.00cd	2.400b
Podgora	0.900a	8.000a	120.0a	5.000a	1.800ab
Baska Voda	1.400b	15.00bc	144.0b	9.000b	2.500b
Split ul. Jana Pawła II	1.700c	21.00d	162.0c	8.000b	3.100c
Storbec	1.200ab	17.00c	139.0b	11.00c	1.800ab
Podstrana	1.000a	12.00b	112.0a	9.000b	1.200a
Omis	1.500b	11.00b	144.0b	12.00c	1.300a
Mimice	1.100a	13.00b	115.0a	9.000b	1.400ab
Dvernik	1.300b	18.00c	135.0ab	14.00d	2.600b
Average	1.267	14.11	133.3	10.00	2.011
Standard deviation	0.250	4.014	16.48	2.784	0.666

*Letters at values locations stand for statistically significant differences at p = 0.05

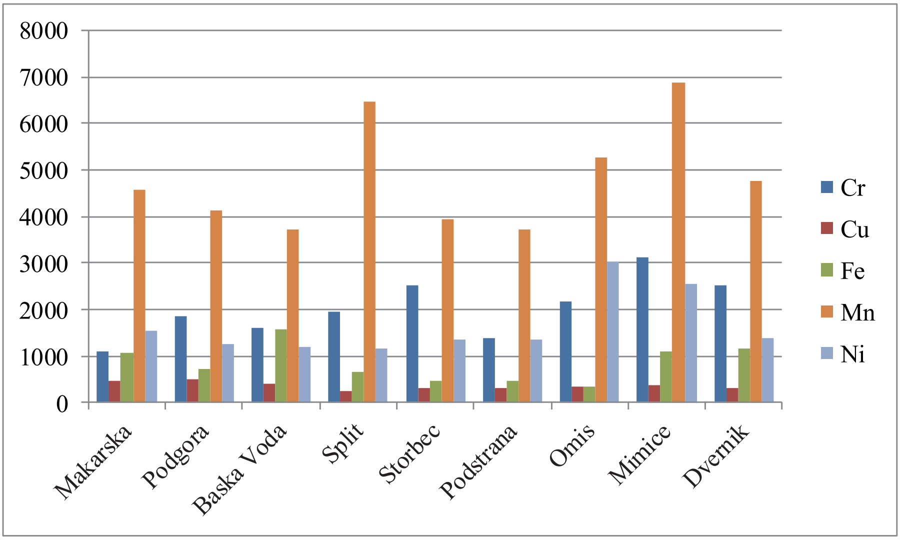

Fig. 2. Bio-accumulation coefficient in *Cystoseira barbata* algae

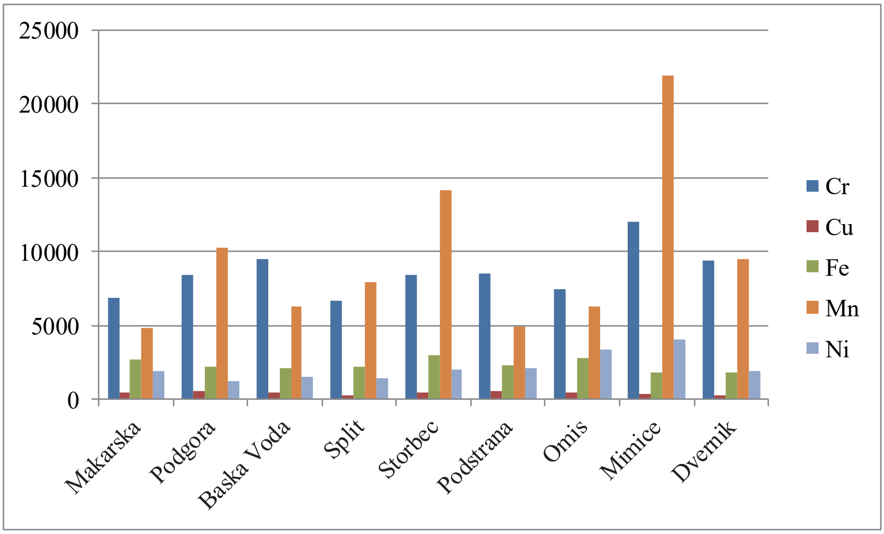

Fig. 3. Bio-accumulation factor in *Ulva rigida* algae

The copper bio-accumulation coefficient in *Cystoceira barbata* ranged from 253 to 495 respectively in Split and Podgora, while *Ulva rigida* algae these values were respectively 269 and 528 (Figure 2 and 3). The average value of the iron bio-accumulation coefficient was 1574. In *Cystoseira barbata* algae, the bio-accumulation coefficient of this element was threefold lower than in *Ulva rigida* algae tissues. The lowest value of iron coefficient in case of both algae was in Mimice and its highest values were in the samples of *Cystoseira barbata* collected in Baska Voda and *Ulva rigida* collected in Storbec. Results of the research show big differences of the investigated parameters in studied area. Melville and Pulkownik (2007) concluded a noticeably big variability of the iron content in algae at a low diversity of concentration of this element in water for various estuaries. It resulted from differences in bio-availability of the analysed element in test stations which mainly result from water properties. The bio-accumulation coefficient of iron in various regions of the Aegean Sea were from 4000 to 9000 (Akcali & Kucuksezgin 2011). The bio-accumulation coefficient of manganese was at the level of 3705 to 21941 respectively for Baska Voda and Mimice. The stated values of the manganese bio-accumulation coefficient were high which is related mainly to a low content of this element in water. Sanders et al. (2012) say that the analysed coefficient for manganese in algae present in few estuaries in the Western Australia was ca. 50. The last analysed element is nickel for which the bio-accumulation coefficient was within 329.3-857.1 for Mimice and Split. Melville and Pulkownik (2007) provide values of the nickel bio-accumulation coefficient in various species of algae collected in the estuaries of the western Australia at a similar level for the one stated in own research.

In case of nickel, a slightly higher value of the bio-accumulation coefficient was found in *Ulva rigida* compared to *Cystoseira barbata*. The average values for those algae were respectively 2168 and 1644. According to the data presented by Strezow and Nonova (2009), values of these coefficients in algae from the Bulgarian coastal zone of the Black Sea are like the ones presented in this paper.

4. Conclusions

1. The content of the investigated elements in water collected from particular sampling points show anthropogenic enrichment.
2. Higher concentrations of the investigated elements in water collected in Split compared to samples from other places were determined.
3. The content of all investigated elements in *Cystoseira barbata* and *Ulva rigida* algae from the region of Makarska Rivera are characteristic for non-contaminated regions.

4. Algae collected in Split region which is under increased anthropopressure, generally did not show up higher amounts of the investigated elements compared to the samples from the regions located far from urban centres.
5. The content of the investigated elements in water decreased in the order Fe>Cu>Mn>Ni>Cr. In the biomass of *Cystoseira barbata* algae in the order Fe>Mn>Cu>Ni>Cr and in *Ulva rigida* Fe>Mn>Cr>Cu>Ni.
6. Bigger differences of the content of the investigated elements in the biomass of algae were determined when compared to their concentration in water from particular sampling points.

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Abstract

The aim of this paper was to assess the content of Cr, Cu, Fe, Mn and Ni in water and in algae collected in the region of the Makarska Riviera. The samples of water and algae were collected in August 2016 from nine sampling points: Makarska, Podgora, Baska Voda, Split ul. Jana Pawła II, Storbeč, Podstrana, Omiš, Mimice, Dvernik. The concentrations of the elements in the water and in the digested algae samples were determined using the ICP-OES method. The study results indicate anthropogenic enrichment of all studied elements in water, with the exception of manganese. Higher contents of studied elements in water collected in Split were found. The concentrations of elements in algae do not indicate pollution of the natural environment and are characteristic of non-contaminated areas. The content of the studied elements in the water decreased in the order Fe>Cu>Mn>Ni>Cr in *Cystoseira barbata* algae decreased in the order Fe>Cu>Mn>Ni>Cr and in *Ulva rigida* in the order Fe>Mn>Cr>Cu>Ni.

Keywords:
macroalgae, bio-accumulation, trace elements, Adriatic Sea

Ocena zawartości Cr, Cu, Fe, Mn i Ni w wodzie i algach z region Riwiery Makarskiej w Chorwacji

Streszczenie

Celem pracy była ocena zawartości Cr, Cu, Fe, Mn i Ni w wodzie i glonach pobranych w rejonie Riwiery Makarskiej. Próbki wody oraz glonów pobrano w sierpniu 2016 roku z dziewięciu punktów badawczych: Makarska, Podgora, Baska Voda, Split ul. Jana Pawła II, Storbeč, Podstrana, Omiš, Mimice, Dvernik. Zawartość pierwiastków w wodzie oraz roztworzonych próbkach glonów oznaczono metodą spektrometrii emisyjnej, w aparacie Optima 7600 DV firmy Perkin Elmer. Wyniki przeprowadzonych badań wskazują na antropogeniczne wzbogacenie wody we wszystkie badane pierwiastki z wyjątkiem manganu. Stwierdzono większe zawartości badanych pierwiastków w wodzie pobranej w Splicie w porównaniu do próbek z innych miejsc. Zawartości pierwiastków w glonach nie wskazują na zagrożenie na środowiska naturalnego i są charakterystyczne dla obszarów niezanieczyszczonych. Zawartość badanych pierwiastków w wodzie malała w kolejności Fe>Cu>Mn>Ni>Cr. W biomasie glonów z rodzaju *Cystoseira barbata* w kolejności Fe>Mn>Cu>Ni>Cr, zaś w glonach *Ulva rigida* Fe>Mn>Cr>Cu>Ni.

Słowa kluczowe:
makroglony, bioakumulacja, pierwiastki śladowe, Morze Adriatyckie

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Emissions of Air Pollutants in European Union Countries – Multidimensional Data Analysis

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1. Introduction

Pollution of air with various kinds of compounds is the cause of many diseases. Numerous studies have shown the relationship of the harmful composition of air with the increase in mortality and hospitalization due to respiratory and cardiovascular diseases. These effects were found in both short-term and long-term studies (Dockery et al. 1993, Brunekreef & Holgate 2002, Pope III et al. 2002, Frumkin et al. 2004, Smith & Ezzati 2005, Whitmee et al. 2015). Pollution with nitrogen dioxide and dust is particularly harmful for human health. In turn, the European ecosystem is exposed to the deposition in the soil and the penetration of sulfuric acids and nitrogen compounds into the waters (SO_x, NO_x, NH_3). Forests are used to remove contaminants. This method is especially important in cities where urban vegetation is used for spatial diversification of the urban area (Smith 1974, Gorham 1976, Ulrich & Pankrath 1983, Ulrich 1984, Escobedo & Nowak 2009; Whitmee et al. 2015).

The cause of air pollution is human activity, mainly related to the combustion of fuels. Therefore, industrial plants, households and transport are the biggest emitters of pollution. In each of these activities, the aim is to reduce pollutant emissions. An example is the metallurgical industry, in which stricter standards were introduced, which in turn meant the use of modern technological equipment (Hartman et al. 1997, Mani & Wheeler 1998, Rokicki 2016, 2017, 2018, Cepeda et al. 2017, Cheremisinoff 2018).

The presented dependencies show that the problem of air pollution is crucial for the health of the human population and the quality of natural environment. This article presents the relationship between environmental pollution and the economy in EU countries. The main objective of the paper was to show the level of air pollution and its relation to economic development in the European Union countries. The specific objectives are: to present the differentiation of pollutant emissions in the EU countries and the dynamics of these changes, to determine the relationships and regularities between the level of economic development and the emission of air pollutants in EU countries.

A hypothesis was put forward in the paper, according to which in the EU countries in the years 2005-2016, the regularities between the level of economic development and emission of pollution in line with the environmental Kuznets curve. In the paper authors propose the method which allow to calculate the decrease of emission to the air harmful compounds in years 2005-2016 with the use of created synthetic index. This index was built on the basis of the measures connected to GDA. Index was used to build the ranking of countries with the greatest decrease of those pollutants and also to divide them into groups of countries with the largest/the smallest decrease in air pollution emission.

2. Literature review

According to the World Health Organization (WHO), air pollution caused the deaths of about 3 million people a year, mainly due to non-communicable diseases. In addition, only one in ten people lived in the city in accordance with WHO air quality guidelines. In high-income areas in the Americas, Europe and the Western Pacific, there has been a reduction in air pollution, while in other regions there has been an increase. As a result, global air pollution increased (Stern 2006, Ambient… 2016).

In the world, the problem of air pollution has existed for centuries. In London, the first complaints about smog were recorded in the 13th century. Historically, it is the easiest to reproduce air pollution caused by sulfur dioxide (SO2). Such estimates date back, in most countries, even up to 1850. The development of industry was associated with the consumption of a large amount of sulfur-containing fuels. In Europe, a rapid increase in sulfur pollution was recorded as first, followed closely in North America in the mid-19th century (Brimblecombe 1977). In North America, SO_2 emissions peaked in 1970, in Europe in 1980, and in South America in 1990. Since then, emissions in these regions have shown a downward trend. Industrialization in Latin America, Asia (besides Japan) and Africa began much later. As a result, emissions of air pollutants in Asia and Africa increased (Kuznets 1955, Cohen et al. 2017, Ritchie & Roser 2019).

In the second half of the twentieth century, there was rapid economic development, especially in countries conducting relatively open economic policy. In the 1960s, regulations on pollution in industrial economies were tightened up. Dirty industries have moved to unregulated economies. At the same time, economic growth in these countries resulted in increased regulations, technical knowledge and investment in cleaner production. The scale of pollutant emissions was therefore limited (Mani & Wheeler 1998).

The environmental Kuznets curve assumes a connection between environmental pollution and economic development. According to it, economic development causes an increase in environmental pollution, but only to a certain point, as this impact decreases along with economic development. In other words, environmental pressure is growing faster than income at the early stages of the country's development and slows down in relation to GDP growth with higher income levels (Stern et al. 1996, Ansuategi et al. 1998, Andreoni & Levinson 2001). There are empirical studies confirming this dependence on the example of developed economies (e.g. Apergis & Ozturk 2015, Jebli et al. 2016, Lau et al. 2018), but also studies which not fully confirm that dependencies in developing countries (Al-Mulali et al. 2015, Dasgupta et al. 2002, Harbaugh et al. 2002, Cole 2003, Dinda 2004). Generally, the authors have not determined the level of income from which environmental degradation begins to diminish. In the case of developing countries, economic liberalization, dissemination of low-emission technologies and a new approach to pollution regulation in these countries are of particular importance for environmental protection. It was also found that developing countries deal with environmental issues sometimes by adopting developed country standards with a short delay and sometimes achieving better results than some rich countries (Stern 2004).

3. Materials and methods

All European Union member states were selected for research purposefully as at December 31, 2016 (28 countries). The research period concerned the years 2005-2016. The sources of materials were EUROSTAT data and literature on the subject. For the sake of clarity, the results from the three-year time periods were taken into account. Only these chemical compounds are included (in Mg = 1,000,000 g = ton), which are covered in the EU emission limits, that is sulfur dioxide (SO_2), nitrogen oxides (NO_x), emissions of non-methane volatile organic compounds (NMVOC), ammonia emissions (NH_3) and PM2.5 fraction dust (particulate matter).

For analysis and presentation of materials, one of the methods of multidimensional data analysis - Grade data analysis (GDA) was used. In this method, the so-called overrepresentation maps that illustrate both underrepresentation and overrepresentation of structures describing a given object by comparing them with average values of these structures are of special importance (Kowalczyk et al. 2004). The basis for creating rankings may be the so-called scores, which on the map are the means of ordered rows for individual countries (the height of these rows shows, in the case of drawing for NMVOC, shows the share of individual EU countries in its emissions over the 12 years studied). Determination of these scores for each substance will allow to elaborate an appropriate synthetic index that will allow the creation of a proper ranking for all substances together. In this case, such an indicator may be the average of scores for individual substances. The scores for each substance were calculated and the values of the synthetic index were marked as Q for each country.

The division into groups was based on the division made using the parameter k, where for:

$$R(Q_i) = \max Q_i - \min Q_i = 0{,}6979 \quad \text{and} \quad k = \frac{R(Q_i)}{3} = 0{,}2326$$

particular groups were created in accordance with the following pattern:

Group 1: $Q_i \in [\max Q_i - 3k, \max Q_i - 2k]$ so in our case:
$Q_i \in [0.1331, 0.3657]$

Group 2: $Q_i \in [\max Q_i - 2k, \max Q_i - k]$ so in our case: $Q_i \in [0.3657, 0.5983]$

Group 3: $Q_i \in [\max Q_i - k, \max Q_i]$ so in our case: $Q_i \in [0.5983, 0.8310]$

4. Research results

In the years 2005-2016, the level of pollutants emission to air was generally reduced. To illustrate the scale of emission of pollutants, data for 2016 for all European Union countries were used (Figure 1). In terms of volume measured in tons, nitrogen oxides were emitted the most, and not much less non-methane volatile organic compounds. The smallest emission was in the case of PM2,5 particulate matter. The harmfulness of individual compounds differs. There is no doubt, however, that one should strive to reduce emissions of all types of air pollutants.

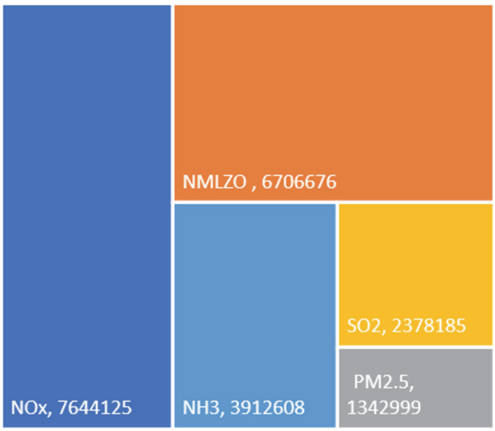

Fig. 1. Emissions of limited air pollutants in EU countries 2016 in tons

As the aim of the paper is to investigate how EU countries dealt with reducing harmful emissions in the air in 2005-2016, Figure 2 presents this problem globally for the entire EU. For this purpose, the overrepresentation map was used, which is a square with sides equal to 1. The column widths represent in this case the structures of emission of harmful substances in total in particular 3-year periods in relation to the entire 12-year period. It can be noticed that these columns are becoming narrower with time, which indicates a gradual decrease in the amount of these substances in the air. The row widths, in turn, show the structure of emissions of individual compounds over the entire 12-year period. It can also be seen that NO_x and NMVOC were emitted the most. Shades of gray on the map depict overrepresentation (darker color) and underrepresentation of structures (brighter color) of emission of particular harmful compounds in relation to the average value. The example of extreme rows shows a clear decrease in the share of SO_2 and an increase in the share of NH_3 in relation to the global emission of harmful dust in subsequent periods. The order in which the individual relationships are shown on the map is not accidental. It strives for such a ranking (in this case) of rows, so as to obtain the highest contrast between the colors and the columns. This goal is accomplished by the GCA (Grade Correspondence Analysis) algorithm, which is the basic tool used to create a clear and structured map. It seeks to such arrangement of rows or columns on the map that maximizes some τ and ρ independence index (Ciok et al. 1995, Kowalczyk et al. 2004)

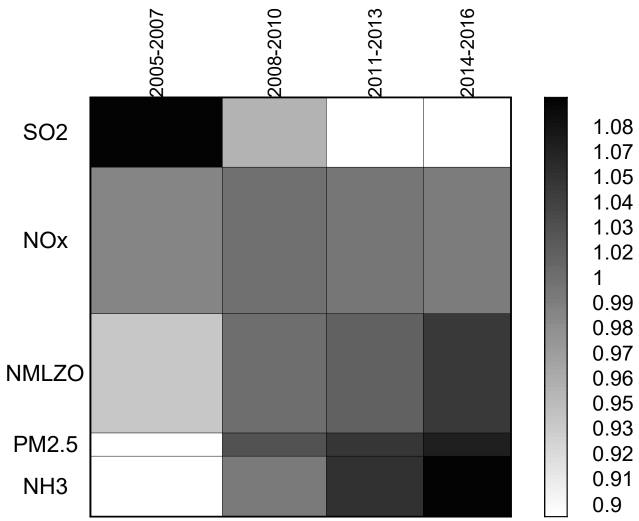

Fig. 2. Overrepresentation map of air pollutants emission in EU in 2005-2016

Since the aim of the paper is to examine the emission of air pollutants in EU countries, similar maps can be made for individual substances in 3-year time periods, ordering countries depending on the degree of decline in dust emissions over time. Such map (for example for NMVOC) is shown in Figure 3. The map is formally a square, but the drawing has been scaled to a rectangle for better transparency.

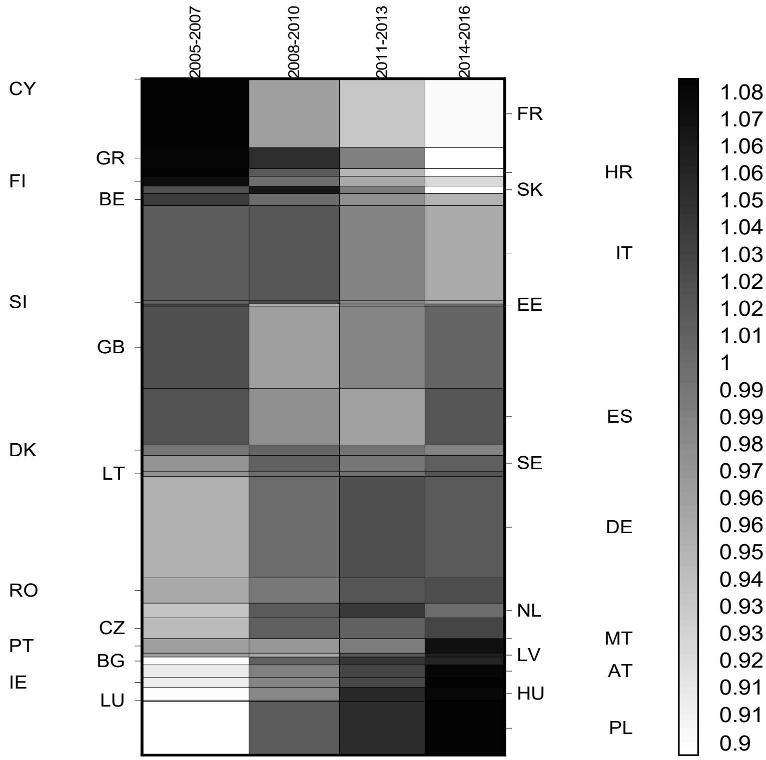

Fig. 3. Overrepresentation map of NMVOC emissions in EU countries in 2005-2016

In general, in the years 2005-2016, the emission of NMVOC dust decreased by 29% across the EU. The reduction of this substance emission (in the sense of structures) in relation to the average for the entire European Union took place in Cyprus, Greece and Croatia (Figure 3). At the bottom of the map are the countries in which the emission of this dust was gradually over-represented in relation to structures for the entire EU. In the case of the NMVOC, Poland occupies a disastrous position. When writing about the position of countries in the non-trivial order, as regards changes in dust emission structures, it is impossible not to refer to the idea of creating appropriate rankings for the dynamics of changes in emissions of individual substances over time. The scores used to calculate synthetic index for each substance and the values of the synthetic index marked as Q for each country are presented in Table 1. In addition, the table sorted the countries in an insufficient manner in relation to Q, thus creating a fairly natural ranking of countries. The top of the ranking is represented by countries in which the emission of harmful substances decreased in terms of structures over time in comparison with emission structures for the entire EU (Greece, Croatia, Belgium). The ranking is closed by countries in which globally the emission of these substances has been over-represented with the passage of time.

Table 1. Scores for harmful substances and synthetic indicator (Q) values for EU countries in 2005-2016 (Source: own research on the basis on GradeStat, country codes: ISO3166-1)

Countries	**Scores for air pollutants emission**						**Group**
	NMVOC	**NH3**	**PM2.5**	**SO_2**	**NO_x**	**Q**	
GR	0.1176	0.3583	0.0344	0.1339	0.0210	0.1331	Group 1
HR	0.1388	0.0394	0.0108	0.2881	0.3400	0.1634	
BE	0.1788	0.3753	0.0830	0.2998	0.4582	0.2790	
CY	0.0008	0.0913	0.0009	0.6170	0.7561	0.2932	
DK	0.5493	0.1754	0.2711	0.4407	0.0464	0.2966	
ES	0.4997	0.4707	0.4628	0.0528	0.1068	0.3186	
MT	0.8279	0.0001	0.0002	0.4380	0.3439	0.3220	
FI	0.1517	0.1899	0.2407	0.6391	0.6054	0.3653	
FR	0.0519	0.7296	0.1667	0.4731	0.5401	0.3923	Group 2
IT	0.2580	0.2445	0.6740	0.4124	0.3949	0.3968	
PT	0.8388	0.3021	0.3990	0.1718	0.3030	0.4029	
NL	0.7863	0.0174	0.0543	0.6089	0.6314	0.4197	
IE	0.8925	0.6152	0.0673	0.2808	0.4774	0.4666	
LU	0.9197	0.8268	0.0604	0.6324	0.0018	0.4882	
GB	0.3971	0.5660	0.7900	0.5540	0.2259	0.5066	
SI	0.3307	0.3292	0.9409	0.3860	0.7061	0.5386	
SK	0.1644	0.3136	0.7414	0.8550	0.6531	0.5455	
RO	0.7568	0.0674	0.8968	0.3461	0.6905	0.5515	
SE	0.5687	0.3913	0.2559	0.8450	0.7471	0.5616	
EE	0.3347	0.9985	0.0965	0.6258	0.7592	0.5629	
BG	0.8610	0.4045	0.9556	0.2293	0.7312	0.6363	Group 3
CZ	0.8124	0.3409	0.8428	0.8850	0.3250	0.6412	
LT	0.5841	0.3222	0.5115	0.8644	0.9971	0.6559	
PL	0.9603	0.1287	0.5651	0.7458	0.9474	0.6695	
AT	0.8760	0.8175	0.3750	0.6475	0.6675	0.6767	
DE	0.6630	0.9103	0.3301	0.9552	0.8330	0.7383	
LV	0.8523	0.9950	0.2853	0.6140	0.9921	0.7478	
HU	0.9093	0.6397	0.9831	0.9069	0.7160	0.8310	

Table 1 also presents the division of countries into 3 groups. In group 1 there were countries in which the decrease in dust emissions compared to the EU average was the highest, in group 2 – moderate and in group 3 the smallest.

It seemed interesting to verify how the change in GDP values at the same time affects the emission of harmful substances in EU countries. In order to maintain the comparability of the results obtained in the case of GDP, it was done in an analogous manner. A map of overrepresentation of changes in GDP structures in time was created (arranging rows – countries in a similar way as previously) and proper scores were determined. Next, Pearson's linear correlation coefficients were determined between scores determined for GDP and scores for individual dusts and the Q synthetic index. A test was also carried out on the irrelevance of the linear correlation coefficient. The values of individual correlation coefficients together with the t and p-value statistics (at the level of significance of $\alpha = 0.05$) were presented in Table 2.

Table 2. Pearson's correlation coefficients for GDP scores and pollutants emission's scores

	r	t	p-value
NH_3	0.2176	1.1368	0.2660
NMLZO	0.4646	2.6750	0.0128
PM2.5	0.0941	0.4818	0.6340
SO_2	0.4578	2.6257	0.0143
NO_x	0.4180	2.3463	0.0269
Q	0.5400	3.2719	0.0030

Together with the decreasing in time structures for GDP in comparison with the average values for the EU, the structure for NMVOC, SO_2 and NO_x decreased significantly in time. The relatively high value of the correlation coefficient between GDP scores and Q synthetic factor was mainly influenced by scores for these substances. The value of this coefficient would be significantly higher if it was not for the results obtained for Hungary, where with a low score for GDP, a very high value of the Q coefficient occurred, as shown in Figure 4.

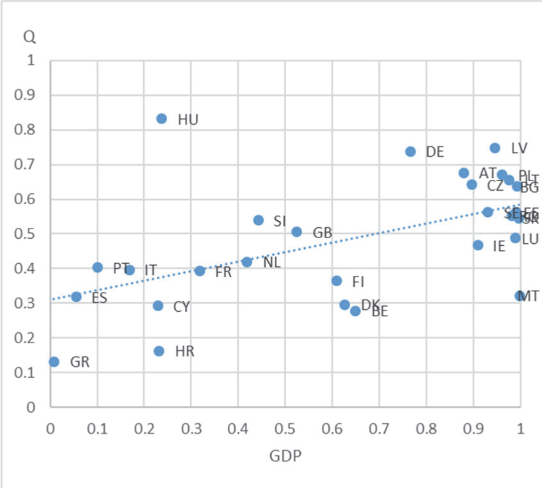

Fig. 4. Wykres rorzutu wskaźnika Q a scory dla GDP

5. Conclusions

1 Air pollution contributes to the development of many diseases and increased mortality in society. The emission of harmful substances increased with the economic development of the world. In individual countries and continents, the stages of economic development were different, therefore the experiences in this area are different. Europe, apart from North America, began to pay attention to the reduction of air pollution as the first one. The environmental Kuznets curve assumes a connection between environmental pollution and economic development. According to it, economic development causes an increase in environmental pollution, but only to a certain point, because this influence then decreases with economic development.

2 The article focuses on harmful compounds that are subject to emission limits (in total there were five such substances). Nitrogen oxides and non-methane volatile organic compounds were the most emitted in the EU. The smallest emission was for PM2,5. In the years 2005-2016, sulfur oxide emissions fell the fastest, while emissions of ammonia and PM2.5 dust increased.

3 In individual EU countries, changes in the emission of harmful substances into the air were different. For example, the decrease in NMVOC dust emission in relation to the EU average was the fastest in Cyprus, Greece and Croatia. There were also countries that were declining from the EU average, such as Poland, Luxembourg and Hungary. At a pace similar to the EU average, emissions of this substance were reduced in Denmark, Sweden and Lithuania.

Taking into account all five pollutants, the ranking of countries meeting the emission obligations against the EU background is presented. Greece, Croatia and Belgium were the best in this area, while Hungary, Latvia and Germany were the worst.

4 A positive relationship was found between the strength of changes in the level of GDP and the emission of air pollutants. In countries where GDP grew slower than the EU average, emissions were lower. In countries with high GDP growth, pollution reduction was very limited. However, there was a reduction of pollutant emissions in all countries. Therefore, the research hypothesis was confirmed, because in the EU countries in the years 2005-2016, the regularities between the level of economic development and emissions were in line with the environmental Kuznets curve. In the economically developed EU countries, despite the pressure of economic development, there was a reduction in air pollution.

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Abstract

The main purpose of the paper was to show the level of air pollution and its relation to economic development in the European Union countries. All European Union member states were selected for research purposefully. The research period concerned the years 2005-2016. Data was obtained from EUROSTAT and from the literature on the subject. For the analysis and presentation of materials, descriptive, tabular, graphical and gradual data analysis methods were used, including overrepresentation maps and Pearson's linear correlation coefficients. The issue of emissions of air pollutants is crucial because harmful substances contribute to the emergence of many diseases and increased mortality of society. The article focuses on harmful compounds that are subject to emission limits, i.e. sulfur dioxide (SO_2), nitrous oxide (NOx), emissions of non-methane volatile organic compounds (NMVOC), ammonia (NH_3) emissions and PM2.5 fraction dust. Nitrogen oxides and non-methane volatile organic compounds were the most emitted in the EU. The smallest emission was for PM2.5. In the years 2005-2016, sulfur oxide emissions decreased the fastest, while emissions of ammonia and PM2.5 dust increased. Taking into account all five pollutants, the ranking of countries meeting the emission obligations against the EU background is presented. Greece, Croatia and Belgium were the best in this area, while Hungary, Latvia and Germany were the worst. A positive relationship was found between the strength of changes in the level of GDP and the emission of air pollutants. In the EU countries, in the years 2005-2016, regularities between the level of economic development and pollution emissions in line with the environmental Kuznets curve were confirmed. In the economically developed EU countries, despite the pressure of economic development, there was a reduction in air pollution.

Keywords:
environmental protection in EU, emissions of air pollutants,
environmental Kuznets curve, grade data analysis, synthetic indicator

Emisja zanieczyszczeń powietrza w krajach Unii Europejskiej – wielowymiarowa analiza danych

Streszczenie

Celem głównym pracy było ukazanie poziomu zanieczyszczenia powietrza i jego związku z rozwojem gospodarczym w krajach Unii Europejskiej. W sposób celowy wybrano do badań wszystkie kraje członkowskie Unii Europejskiej. Okres badań dotyczył lat 2005-2016. Dane pozyskano z EUROSTAT oraz z literatury przedmiotu. Do analizy i prezentacji materiałów zastosowano metody opisową, tabelaryczną, graficzną, gradacyjną analizę danych, w tym mapy nadreprezentacji, współczynniki korelacji liniowej Pearsona. Problematyka emisji zanieczyszczeń powietrza jest kluczowa, gdyż szkodliwe substancje przyczyniają się do powstawania wielu chorób oraz zwiększonej śmiertelności społeczeństwa. W artykule skupiono się na szkodliwych związkach, które podlegają limitom emisji, a więc dwutlenku siarki (SO_2), tlenku azotu (NO_x), emisji niemetanowych lotnych związków organicznych (NMLZO), emisji amoniaku (NH_3) i pyłów frakcji

PM2.5 (PM2.5). W UE najwięcej emitowano tlenków azotu i niemetanowych lotnych związków organicznych. Najmniejsza zaś była emisja pyłów frakcji PM2,5. W latach 2005-2016 najszybciej spadała emisja tlenków siarki, zaś rosła amoniaku i pyłów frakcji PM2,5. Przy uwzględnieniu wszystkich pięciu związków zanieczyszczających powietrze przedstawiono ranking krajów wywiązujących się z obowiązków emisji na tle UE. Najlepiej w tym zakresie radziły sobie Grecja, Chorwacji i Belgia, zaś najgorzej Węgry, Łotwa i Niemcy. Stwierdzono dodatnią zależność między siłą zmian poziomu PKB a emisją zanieczyszczeń powietrza. W krajach UE w latach 2005-2016 potwierdzone zostały prawidłowości między poziomem rozwoju gospodarki i emisją zanieczyszczeń zgodne ze środowiskową krzywą Kuznetsa. W rozwiniętych gospodarczo krajach UE mimo presji rozwoju gospodarczego następowała redukcja zanieczyszczeń powietrza.

Słowa kluczowe:
ochrona środowiska w UE, emisja zanieczyszczeń powietrza,
środowiskowa krzywa Kuznetsa, gradacyjna analiza danych, wskaźnik syntetyczny

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Biofiltration of Contaminated Air – Current Status, Development Trends

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1. Introduction

Most of the production processes are accompanied by the emission of various waste, in particular waste gases. Among the methods of their purification, biofiltration plays an increasingly important role. Its essence is the distribution of air pollutants by microorganisms, deposited on a solid carrier. Consortia of microorganisms composed of both, fungi and bacteria cover the surface of the carrier with a biofilm. Biofilms form microorganisms that adhere to each other as well as to the surface of the bed through secreted mucus. Organized this way, they work efficiently and are able to survive adverse periods of hunger, dryness, extreme temperatures or intoxication with toxins (Sauer 2017).

In biological methods of gas cleaning, we can distinguish typical solutions such as biofilter and biotrickling filter. The biofilter bed are only moistened, while in biotrickling filter aqueous solution of the medium is assured all the time on bed, what provides ensuring adequate hydration and supply of elements necessary for microorganisms, absent occur in the stream of purified gases. The success of gases cleaning depends on many factors, such as the material, structure, moisture content of the bed and the gas to be purified, as well as temperature, pH, nutrients and the concentration of impurities at the inlet. Due to the fact that biofiltration is a biological method, on the assumption is intended to be pollution must be biodegradable.

2. Area of application

Primary and natural applications of biofiltration are air deodorisation and waste gas treatment from other biological processes, such as composting, and wastewater treatment. This is a consequence of the fact that, this method works best for humid gases with a low concentration of easily biodegradable pollutants, released in the mentioned processes. Later, it was used to remove impurities in higher concentrations, xenobiotic and inorganic substances and in case of hot and dry gases.

In the literature, we can find many descriptions of both research work and the practical use of biofiltration (Cheng Z. et al. 2016a, Hernández et al. 2010, Liao et al. 2015, Rodriguez et al. 2014). The range of removals of pollution is also very wide. Among them are saturated and unsaturated, aliphatic and aromatic hydrocarbons, occurring both individually and in mixtures, such as toluene, xylenes, trimethylbenzenes, and styrene (Hu et al. 2015, Liao et al. 2015, Paca et al. 2012, Rene et al. 2010, Rodriguez et al. 2014, Wang et al. 2015, Xi et al. 2014). Also presented are organic compounds with oxygen in the molecule, synthetic and natural in origin such as formaldehyde, ethyl acetate, acetone, methyl ketone, alpha-pinene (Cabeza et al. 2013, García-Pérez et al. 2013, Li et al. 2012, Zare et al. 2012), with nitrogen in the molecule like triethylamine (Gandu et al. 2013), with sulfur in a molecule like thiols (mercaptans) and organic sulphides (Hernández et al. 2010, Lebrero et al. 2012), or hardly degradable chlorosubstituted substances such as trichloroethene, chloroform, and chlorobenzene (Balasubramanian et al. 2011, Balasubramanian et al. 2012, Liao et al. 2015, Shukla et al. 2010). Inorganic compounds such as hydrogen sulphide and ammonia are also removed by biofiltration (Hernández et al. 2010, Maestre et al. 2010). The biofiltration was also subjected to air contaminated with multi-component mixtures containing organic and less inorganic compounds found in various combinations. For example: benzene, toluene, chlorobenzene, ethylbenzene, m- / o- / p-xylene, styrene, benzoic aldehyde, 1,2,3- / 1,2,4- / 1,3,5-trimethylbenzene, n-acetate butyl, DMS (dimethyl sulfide), DMDS (dimethyl disulfide), MEK (methyl ethyl ketone), MIBK (methyl isobutyl ketone), ammonia, methanethiol, α-pinene, hexane, styrene, acetone, ammonia, nitrogen oxides, and hydrogen sulphide (Hernández et al. 2010, Hu et al. 2015, Lebrero et al. 2012, Lebrero et al. 2010, Li et al. 2012, Liao et al. 2015, Sempere et al. 2010, Wieczorek 2005).

3. Biofilter – division, construction, operation

Taking into account the principle of operation, biofilters are divided into typical biofilter (classic) and biotrickling filter (Rybarczyk et al. 2019, Mudliar et al. 2010). The construction of a biofilter, and actually a bioreactor, is very similar to an adsorber. The main difference is that the adsorber only traps contaminants and the biofilter traps and decomposes them, as a result of microorganisms (Nanda et al. 2012, Ralebitso-senior et al. 2012). Due to the specificity of the process, packing material of non-biological filters are kept dry, and biofilters wet, which is a prerequisite for colonization by microorganisms (Showqi et al. 2016). By colonizing a bed, microorganisms produce a moist film on its surface called biofilm, which provides them with favourable conditions for the development and survival of stressful situations, e. g. dryness, poisoning (Sauer 2017). The efficiency and effectiveness of biofiltration depends on the parameters of gas flow, its composition and conditions in the packing material in which these microorganisms are present (Kumar et al. 2011). These include gas flow rate, pollutant concentration, type of pollutant and its properties, temperature and humidity of gases and deposits, bed texture, availability of oxygen, salinity, and pH of the deposit, as well as availability of nutrients not found in the treated gases (Varjani 2017). Biotrickling filters are equipped trickle bed with a nutrients for microorganisms, which is a solution of suitable minerals and in some cases, different organic substances such as vitamins and minerals. Their packing material are generally composed on the basis of inert mineral or polymeric materials. Biofilter bed are usually based on biodegradable organic material. Such materials are also susceptible to easily occurring abiotic degradation (Lebrero et al. 2010). Polluted air or other ventilation gases directed to the biofilter bed should be free of excessive amounts of dust, their humidity should not be less than 90%, and the temperature should not be higher than 40°C. If these requirements are not met, the gases require pre-conditioning, in particular dust extraction and through humidification. A typical industrial biofilter has the shape of a short, rectangular or cylindrical column with a grate at the bottom. There is packaging material on the grate, above which the system of spraying nozzles is mounted. The biodegradation process of pollutants on the bed in a biofilter usually takes place under aerobic conditions, and local oxygen deficiency is treated as one of the reasons for the low efficiency of the process. In some situations, however, lack of oxygen is a positive phenomenon. For example, biofiltration of biogas to remove hydrogen sulphide from biogas under aerobic conditions is dangerous because of the possibility of explosion (Fernández et al. 2013). Designing industrial biofilters, contrary to appearances, is not a simple activity. It is relatively easy to design a biofilter designed for the purification of gases from other biological processes, such as sewage treatment or composting. The waste gases originating from them are moist, their impurities are biodegradable and these concentrations are lower than toxic. In such cases, it is sufficient to base the design process on well-established principles recorded in the available engineering and scientific literature. In the case of waste gases contaminated by gases and vapours of xenobiotic substances or containing dust particles with unknown, often toxic properties, this is a difficult process and should be preceded by tests to limit the possibility of large errors.

4. Packing materials for biofiltration

The most important features of packing material, which is a key element of the biofilter, are the high specific surface area necessary for the development of microorganisms (Anet et al. 2013), porosity ensuring homogeneous distribution of gases, low flow resistance, and good water retention, as well as appropriate mechanical properties (Gutiérrez-Acosta et al. 2012, Lebrero et al. 2012) and also low price (Li et al. 2012).

The beds of Biofilter are composed on the basis of natural products, both organic and inorganic, synthetic materials and mixtures of natural and synthetic products. Typical organic materials of natural origin include compost, peat, wood chips, and bark, coconut fibres (Dorado et al. 2010). Less typical are dried corn cobs (Rahul et al. 2013), and walnut shells (Zare et al. 2012). Among natural and synthetic mineral materials we can find lava rock (Rene et al. 2011), vermiculite (Brandt et al. 2016), perlite (Xi et al. 2014, Schmidt & Anderson 2017), obtained from natural silicates maifanit (Chen X. et al. 2016), poraver (García-Pérez et al. 2013), and wood charcoal (Singh K. et al. 2010). The hybrid materials include mixtures and composites from activated carbon, wheat bran and sawdust in the ratio 1:2:1 (Cheng Z. et al. 2016b), scorii and compost (Rodriguez et al. 2014), coral rock, bark, keramzite, coal and compost in proportions 160:120:100:60:15 (Sun et al. 2012), keramzite and compost (Hernández et al. 2010), high-density polyethylene and fibers of Agave in the ratio 70:30 (Robledo-Ortíz et al. 2011). The latter also includes deposits of synthetic polymers of the polyvinyl chloride type (Balasubramanian et al. 2012), polypropylene Pall rings (Fernández et al. 2013), also polyurethane foam (Singh R. et al. 2010). The bed, adapted to the needs, increases the efficiency of biofiltration and facilitates its management.

5. Microorganisms

Initial, to move into on biofilter beds microorganisms capable of decomposition of air pollution is achieved in two ways. The first, largely natural, consists in filling the chamber of the apparatus with the packing material, preferably already richly inhabited by microorganisms, for instance compost and to start in motion air flow the polluted. As a result of the natural selection of microorganisms presented, in the material of the bed and applied to them along with the flowing air, a consortium of microorganisms degrading the pollutants is formed. The second way depends on the inoculation of fresh packing material from an admixture of an overworked the bed or other material containing microorganisms for instance sewage sludge or a specially prepared vaccine. It can be expected that the effect of vaccination will be better if the biofiltration conditions as well as the composition and concentration of contaminants will be closer to those used during the preparation of the vaccine. Almost twenty years of experience of one of the authors in biofiltration and biofilter exploitation indicates, however, that there are no obvious, benefits achieved by inoculating the deposit. Biofilters by nature operate under non-sterile conditions, so that microorganisms colonizing the packaging material at a given time are subjected to constant pressure from external microorganisms flowing mainly from the air flowing through them. In many cases, frequent and unexpected changes in the morphology of the microorganisms inhabiting the bed are easily noticeable even with a naked eye (Fig. 1). Changes in stuff the microbial of the packing material, and in particular in the proportional of quantitative microorganisms, may also cause environmental factors. For example, (Borin et al. 2006) describe changes in the microbial density ratio along the column height and also with the change in relation to the benzene load. In this situation, the grafting of the bed can only be significant if the pollutants to be eliminated by biofiltration are broken down by microorganisms rarely found in a given geographical location. The lack of suitable microorganisms in the environment results with an unacceptable waiting time for the biofilter to start working effectively.

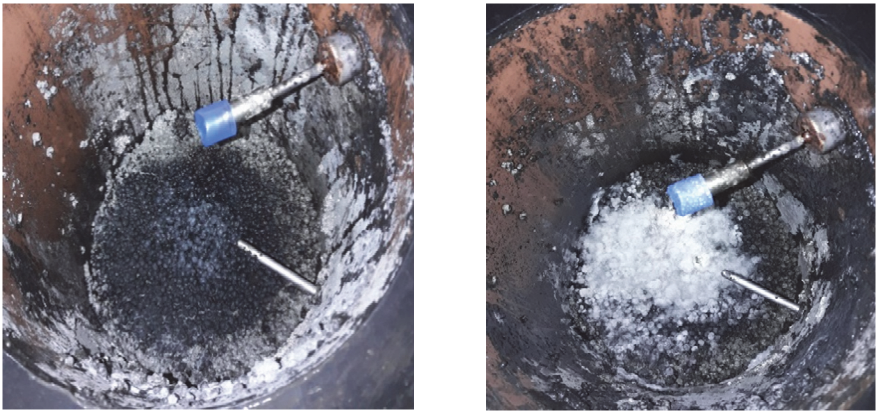

Fig. 1. A bed of biofiltration column inhabited by a consortium of microorganisms;
Left drawing 4 days after the introduction of the substance.
Right drawing 10 days after the introduction of the substance (own photograph)

Such contaminants include commonly used anti-knock additives for unleaded petrol, for example some aliphatic ethers (Fortin & Deshusses 1999, Wieczorek et al. 2013). It seems, however, that for undisturbed operation of biofilters it is more important to ensure proper biofiltration conditions, especially temperature and humidity of both purified gases and biofilter beds, than vaccination.

In the case of vaccine preparation, active microorganisms specialized in the degradation of specific contaminants (chemical compounds) are obtained mainly by screening from the natural environment, preferably contaminated with substances to be filtered out. In addition, microorganisms are extracted from composting biomass, sediments from sewage treatment plants or from the bed of exploited biofilters. Another source of such microorganisms may be soils polluted with oil, and soils located in the vicinity of pollution emission sources (Liao et al. 2015, García-Pérez et al. 2013). Activeies sewage sludge from industrial wastewater treatment plants, e.g. from the pharmaceutical industry (Wang et al. 2015, Xi et al. 2014) or refineries (Rene et al. 2012), can also be used for the same purpose.

In order to achieve the assumed degradation activity of biofilter bed, various strategies of management are applied. Typically, after loading of the fresh bed, and especially at the first start-up of a biofilter, low loads are applied, by feeding gases at low speed or by lowering the concentration of contaminants, either by lowering the concentration and flow rate at the same time. However, we can find, descriptions of procedures when the opposite was done, where a high concentrations of pollutants was used initially applied and then lowered (Zamir et al. 2012). The initial period of operation of a biofilter is called its adaptation. During this time, there are changes in the numbers, composition and properties of the microorganisms consortium also occurs changes in the properties of the bed material, e. g. release of biogenic elements as a result of chemical and biochemical transformations. For microorganisms that break down hydrocarbons directly, adaptation consists of: induction or depression (inhibition) of specific enzymes, genetic changes resulting in modification of metabolic pathways and selective enrichment in microorganisms capable of metabolising hydrocarbons (Chikere et al. 2011). One of the main factor condition of genetic transformations in bacteria is horizontal gene transfer (Obayori & Salam 2010). Another way to obtain microorganisms that are effective in the biodegradation of specific substances is to acclimatize them in a bioreactor beforehand. For example, Amin or Lebrero and their associates, used a bioreactor fed with a nutrient solution with periodical addition of the compound of interest (Amin et al. 2014, Lebrero et al. 2012). All these activities are aimed have the breed a consortium of microorganisms that effectively break down selected pollutants.

The period of acclimatization of microorganisms to the conditions prevailing in the deposit may last from a few weeks to several months (Rahul et al. 2013, Hernández et al. 2010). Microorganisms that to populate biofilter beds can form consortia that are typically fungal or bacterial as well as mixed (Revah et al. 2011, Estrada et al. 2013, Cheng Z. et al. 2016b, Vergara-Fernández et al. 2018) capable of biological gas purification. A number of interesting information was obtained during the research, carried out by various methods and techniques, including molecular biology, aimed at the identification of microorganisms and their consortia biodegrading individual impurities or their mixtures. An exemplary statement of microorganisms and break down a pollutants by them is presented in Table 1. A different summary of microorganisms and degraded substances by them, with divided into aliphatic, monoaromatic, polyaromatic and resin hydrocarbons, we can find in the work of (Varjani 2017).

Table 1. Microorganisms degrading environmental pollutions

Microorganisms	Pollution	Author
Candidia tropicalis, Phialophora Trichoderma viride	Toluen	(Song et al. 2012) (Zhai et al. 2017) (Cheng Z. at al. 2016b)
Pseudomonas sp.	Styren	(Kasperczyk et al. 2012)
Sporothrix variecibaus	Styren	(Rene et al. 2011)
Pandoraea sp. JB1, *Xanthomonadales bacterium*	Styren, toluen, aceton, MEK	(Li et al. 2012)
Exophiala sp.	BTEX	(Rene et al. 2012)
Pseudoxanthomonas spandix BD-a59	BTEX	(Choi et al. 2013)
Janibacter sp.	BTEX	(Jin et al. 2013)
Strain FMB08 9, *P. putida* F1*, Echerichia coli* DH5a	BTEX	(Morlett-Chávez et al. 2010)
Pseudomonas Putida F1	B,T,o-X	(Robledo-Ortíz et al. 2011)
Mycovacterium cosmeticum byf-4	B,T,E,o-X	(Zhang L. et al. 2013)
Ralstonia picketii L2	Chlorobenzen	(Zhang L. L. et al. 2011)

As it was shown, many groups of microorganisms participate in the catabolytic degradation of hydrocarbons and their derivatives. Initially it was assumed that this process takes place only in the presence of oxygen, netheless some microorganisms are capable of such action also in anaerobic conditions (Abbasian et al. 2015, Meckenstock et al. 2016). Reactions typical for both metabolic pathways are oxidation and reduction, hydroxylation and dehydrogenation (Abbasian et al. 2015, Wilkes et al. 2016). As a result of progressive degradation in the reaction environment, the proportion of polar fractions grow, and the proportion of saturated and aromatic hydrocarbons to decline (Varjani 2017). Biodegradation by bacteria a aliphatic hydrocarbons that can be considered as representatives of the whole family of organic compounds is usually initiated by oxidation involving a system of monooxygenase or dioxygenase - electron conveyor (various forms of NADH nicotine-amidoadenine dinucleotide) according to two paths.

On the first of them, during the reaction (Fig. 2), the oxygen atom is attached to the hydrocarbon, which leads to the formation of an appropriate I-order alcohol (Abbasian et al. 2015, Chikere et al. 2011) oxidized at subsequent stages to aldehyde and fatty acid. According to the second, dioxygenase attacks the extreme (terminal) methyl group, allowing it to attach two oxygen atoms with the formation of peroxide, which is then converted through alcohol and aldehyde to fatty acid.

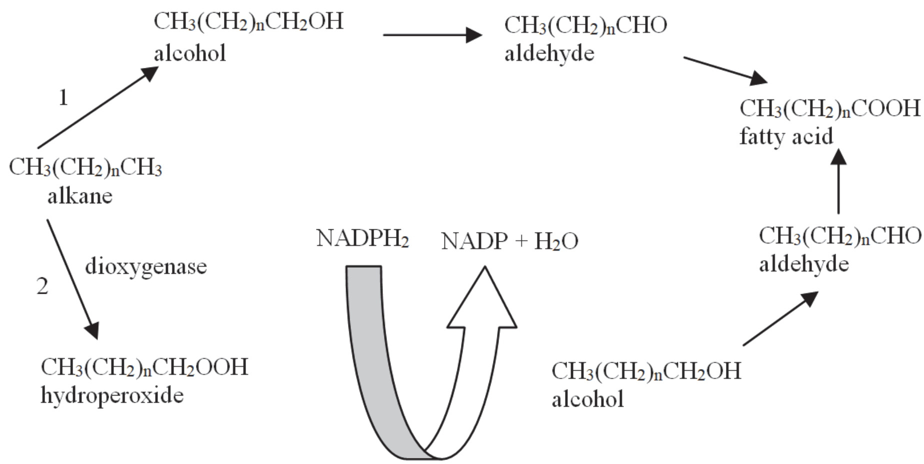

Fig. 2. Diagram of biodegradation of alkanes (Chikere et al. 2011). 1 – pathway 1, 2 – pathway 2, NADP - nicotinamide adenine dinucleotide phosphate, $NADPH_2$ – nicotinamide-adenine dinucleotide phosphate (reduced)

The resulting fatty acid, regardless of pathway, is further metabolised according to the β-oxidation mechanism specific to live cells to acetyl or propionyl coenzyme A (CoA). These compounds are further metabolized in the tricarboxylic acids cycle (TCA or Krebs cycle) to CO_2 and H_2O. In this way, the methyl group can be oxidized at the end of the chaine of alkanes, the methylene group adjacent to the extreme methyl group and the two extreme methyl groups, respectively terminal oxidation, sub-terminal oxidation and ω-oxidation (di-terminal oxidation) (Fig. 3).

More information on the biodegradation of alkanes and alkenes as well as descriptions for branched alkanes and cycloalkanes can be found in the works of other authors such as Abbasian and his contributors (Abbasian et al. 2015) or (Kwapisz 2006).

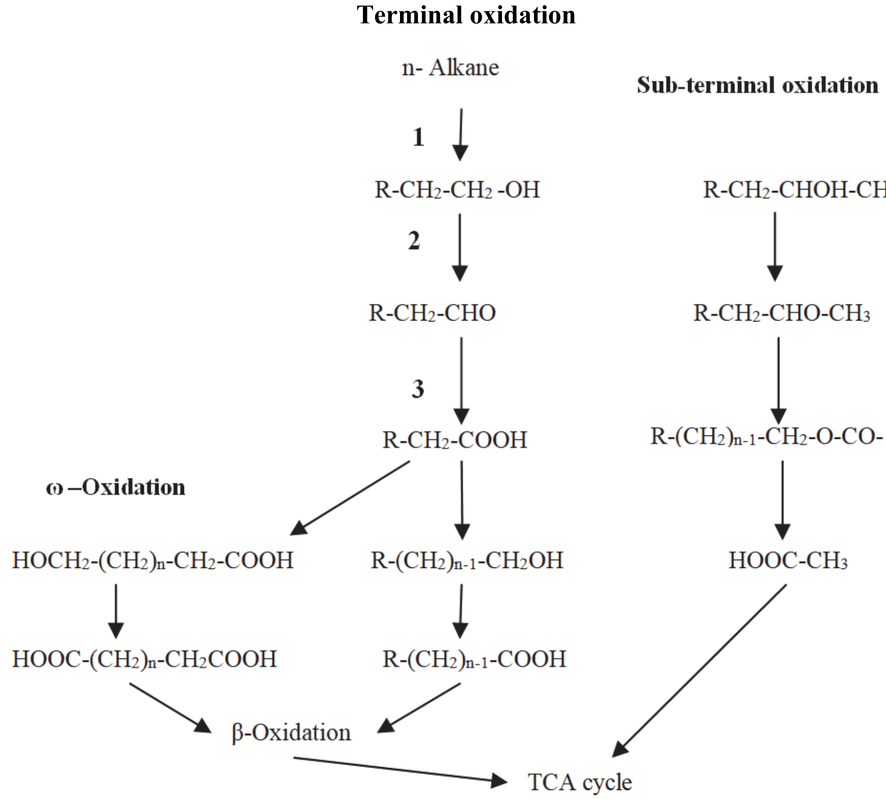

Fig. 3. Possible paths of aerobic biodegradation of n-alkanes (Abbasian et al. 2015, Varjani 2017). 1 – n-alkane monooxygenase, 2 – alcohol dehydrogenase, 3 – aldehyde dehydrogeanse

Biodegradation of aromatic hydrocarbons, especially polycyclic hydrocarbons (PAHs), is significantly hampered by their greater chemical stability, very poor water solubility, the formation of metabolites toxic to microorganisms and the co-occurrence of more easily decomposable substances or the lack of suitable cometabolites (Chikere et al. 2011). So far, no microorganisms have been found to degrade polycyclic aromatic hydrocarbons by themselves. They are broken down in cometabolic processes (Van Elsas et al. 2007). In order for aromas to biodegradation, molecular oxygen is necessary for enzyme assisted attack on the PAH ring. Catalyzed by dioxygenase, oxidation with aerobic bacteria enables the transformation of arenas into cis-dihydrodioles with neighbouring hydroxyl groups. (Sun et al. 2012). In the next step, as a result of the action of appropriate dihydrogenases, the dihydrodiols ring is cleaved between carbon atoms substituted hydroxyl groups or between carbon atoms bound to hydroxyl groups and adjacent carbon without this group. These reactions are called respectively ortho- and meta- split (Chikere et al. 2011, Padhi & Gokhale 2016, Van Elsas et al. 2007). Some derivatives of aromatic hydrocarbons, e. g. styrene, are broken down in the same way (Przybulewska & Wieczorek 2006).

Considering the enormous number of organic compounds, it is impossible to present in one work even only the most typical examples of biodegradation paths occurring in biofilters during their operation. In most cases, when it is necessary to answer how this process takes place, it will be necessary to search for appropriate literature indications and possible research works.

6. Additives improving the bioavailability

Most of the pollutants removed by biofiltration are organic compounds, which of many are difficult to dissolve in water, and thus also in fluids and cellular secretions. This makes it much more difficult to transfer contaminants from the gas stream to the biofilm and further into the cells, in other words, reduces their bioavailability. One way, to increase the performance of biofiltration is to use special additives to improve bioavailability, and as a result efficiency of the biodegradation. The addition of organic substances such as surfactants, in particular Tween 20 (Cheng Y. et al. 2016, Avalos Ramirez et al. 2012), Triton X-100 (Sówka et al. 2016a), β-cyclodextrin (Sówka et al. 2016b), silicone oil (Shukla et al. 2010) or methanol (Zehraoui et al. 2012) can be distinguished.

These additives sometimes also improve the stability of the biofiltration process.

7. Construction novelties - an exemplary solutions

Biofilters, in comparison with conventional gases stream cleaning devices, have large cross-sectional areas, which makes uniform flow of the purified gases stream difficult and humidification of the bed. These problems could be alleviated by the use of biofilters with a rotating drum (Chen J. et al. 2016, Padhi & Gokhale 2016). Figure 4 shows such a device developed by Chen with co-workers (Chen J. et al. 2016). Biofilters with a rotating drum are more costly, both at the investment stage and on move.

This can be avoided by using a tubular biological filters with a fixed cylindrical bed (Fig. 5) proposed by Chen with co-workers (Chen et al. 2012). That solution works well during the treatment of waste gases with low concentrations of pollutants even at high flow rates and long-term operation.

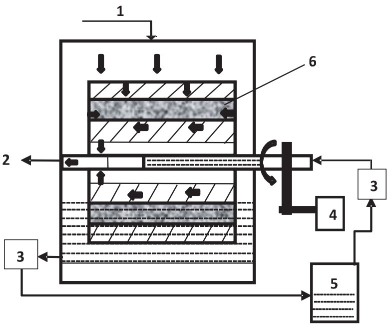

Fig. 4. Biofilter diagram with a rotating drum (Chen J. et al. 2016). 1 – polluted air, 2 – purified air, 3 – metering pump, 4 – motor , 5 – nutrients reservoir, 6 – biofilter bed

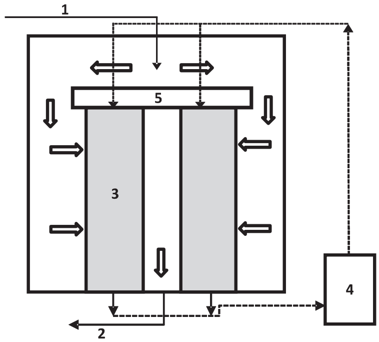

Fig. 5. Diagram of a tubular biological filter (Chen et al. 2012). 1 – polluted air, 2 – purified air, 3 – thick walled tube of polyurethane foam, 4 – nutrient solution tank, 5 – nutrient solution distributor

8. Hybrid systems

One of the more known solutions of hybrid systems type are biofilters equipped with a buffer in the form of a pre-filter with active carbon (Chang et al. 2015, Sempere et al. 2010). A novelty is the biofiltration system supported by photocatalytic oxidation (Hinojosa-Reyes et al. 2012, Wei et al. 2010). Photodegradation and biofiltration have been integrated to improve the efficiency of the removal of resistant contaminants. The intermediates of photodegra-dation of pollutants flow to the biofilter where they are biologically subject to decomposed.

UV pre-treatment not only improves the removal of contaminants, but also has a positive impact on the microbiological community (Jianming et al. 2014). Such solutions have been checked on a pilot scale. Multi-component mixtures of volatile organic compounds were eliminated efficiently and ecologically (He et al. 2012).

The idea for the future is to use biofiltration for simultaneous generation of electric current. The integrated BF-MFC (biotricklin filter–microbial fuel cells) system (Fig. 6) combines the biodegradation of off-gas pollution with the generation of electricity.

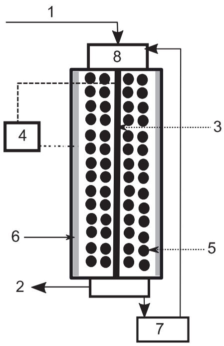

Fig. 6. Diagram of a biofilter with generation of electric current (Wu et al. 2016). 1 – polluted air, 2 – purified air, 3 – anode (graphite), 4 – multimeter, 5 – bed (coke), 6 – polymer cathode, 7 – water tank, 8 – sprinkler

According to the classical scheme, electrons are released in the process of anaerobic decomposition of contaminants by microorganisms, which are then transferred to the anode directly or with the aid of a mediator. On the cathode there is a reaction of oxygen with protons and electrons returning, throughout the external circuit (Evelyn et al. 2014). According to Wu et al. (Wu et al. 2016), the mechanism proposed by Evelyn et al. (Evelyn et al. 2014) by which metabolites with electron transfer function are produced during biofiltration is unsatisfactory. Therefore, another solution, taking into consideration the presence of a gas diffusion layer, in which waste gas diffuses into an anode converting it into electric current has been proposed (Wu et al. 2016). The packing material in such a biofilter should exhibit the characteristics of a good carrier for microorganisms and demonstrate electrical conductivity, which is necessary to serve as a cathode of a microbial fuel cell forming an oxygen electrode with the oxygen reducing on it. Coke (Wu & Lin 2016), high-performance activated carbon (Janicek et al. 2015) and graphite (Wu et al. 2016) are used for this purpose, among others.

9. Summary

Biofiltration despite the passage of time, still enjoys great interest among researchers and engineers of industrial development. Due to the complexity of the biological processes underlying the basis of operation, many aspects of the action are not sufficiently well understood and therefore continue to be the subject of research combining different fields of science. Moreover, due to the possibility of aggregating biofilters with other devices such as UV and ozone radiation generators and using them as generators of electric current, new possibilities open up for it. The presented review of literature data is an attempt to draw attention to this research topic, which still poses new challenges.

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Abstract

The study presents a description of both the main problems of biofiltration as well as the new research directions. Discussion of the first subject covered the area of biofiltration applied in purification of exhaust gases. The method traditionally used for the purification of waste gases from biological processes is also suitable for the treatment of hot and dry air, contaminated with substances of high toxic concentrations. According to the literature reports, hydrocarbons belonging to all groups: compounds containing oxygen in the molecule such as aldehydes, ketones and esters, compounds containing nitrogen and sulphur in the molecule like amines, thiols or organic sulphides can all be filtered out. Chlorinated hydrocarbons and some inorganic compounds like ammonia and hydrogen sulphide can also be removed. All these substances can be present individually or in multicomponent mixtures.

The biofilters have been divided into conventional ones provided with a wet bed and the ones fitted with a biotrickling bed. A set of information on the materials used to compose a bed with a division into natural and synthetic has been given. The division of natural beds has been described as biodegradable, like peat, compost, wood chips and non-biodegradable as volcanic rocks. Among the synthetic beds mention are the ones made of mineral types of expanded clay aggregates and other minerals, as well as synthetic organic plastics, for example polyurethane foams.

Factors influencing the biofiltration process, such as gas flow rate, concentration of pollutants, their type and properties, temperature, humidity of gases and sediments, structure a bed, oxygen availability, salinity and pH of the bed, as well as the availability of nutrients not found in treated gases, were presented in the paper.

An extensive chapter was devoted to the microorganisms colonizing the bed of biofilter, which are responsible for the decomposition of filtered out pollutants. They can be introduced to the biofilter as microorganisms that naturally inhabit given building material or placed on a bed in the form of a vaccine. A consortium of microorganisms, formed during the start-up of a biofilter (adaptation), composed of bacteria and fungi, undergoes constant changes caused by the influx of new microorganisms along with purified air and the influence of environmental factors. These changes can be both quantitative and qualitative, manifested by the occurrence of genetic mutations. The microorganisms that colonize the bed belong to many species, such as *Pseudomonas, Pseudoxanthomonas, Xanthomonadales, Ralstonia, Mycobacterium, Exophiala i Candidia*. They metabolize environmental pollutants. This most often takes place during the catabolic process initiated by enzyme-assisted oxygen attack per molecule. As a result, appropriate alcohols are first formed, which than undergo successive transformations to aldehydes, fatty acids and further down to water and CO_2.

The chapter devoted to additives improving the bioavailability of pollutants such as methanol, silicone oils and surfactants, was included in the paper. New products in the field of construction solutions and hybrid systems were explained. Solutions such as rotary biofilters and cylindrical beds aim to reduce problems with even gas flow and excessive flow resistance. Among the hybrid systems, pre-filter solutions with active carbon and a UV pre-treatment module were presented. The idea of a biofilter combining the removal of pollutants with the generation of electric current in microbial fuel cells is also presented.

Keywords:
biofiltration, air biofiltration, biofiltration of air pollutants,
biofiltration – development trends

Biofiltracja zanieczyszczonego powietrza – stan aktualny, trendy rozwojowe

Streszczenie

W opracowaniu przedstawiono opis zarówno podstawowych zagadnień biofiltracji jak i nowych kierunków badawczych. Omawiając pierwsze z zagadnień zakreślono obszar zastosowań biofiltracji w oczyszczaniu gazów odlotowych. Metoda tradycyjnie przydatna do oczyszczania gazów odlotowych z procesów biologicznych nadaje się również do obróbki powietrza gorącego i suchego oraz zanieczyszczonego substancjami o wysokich toksycznych stężeniach. Zgodnie z doniesieniami literaturowymi odfiltrowywane mogą być

węglowodory przynależne do wszystkich grup, związki zawierające tlen w cząsteczce jak aldehydy, ketony i estry, związki zawierające azot i siarkę w cząsteczce jak aminy, tiole czy siarczki organiczne. Usuwane są także chlorowcopochodne węglowodorów oraz niektóre związki nieorganiczne jak amoniak i siarkowodór. Wszystkie wymienione substancje mogą występować pojedynczo oraz w wieloskładnikowych mieszaninach.

Podzielono biofiltry na klasyczne zaopatrzone w złoże utrzymywane w stanie wilgotnym oraz te ze złożem przepłukiwanym. Podano zbiór informacji o materiałach wykorzystywanych do komponowania złóż z podziałem na naturalne i syntetyczne. Podział naturalnych uściślono na biodegradowalne jak torf, komposty, zrębki drewna i naturalne nie biodegradowalne jak skały wulkaniczne. Wśród syntetycznych wymieniono mineralne typu poryzowane glinki i inne minerały oraz syntetyczne organiczne jak tworzywa sztuczne, przykładowo pianki poliuretanowe.

Zaprezentowano czynniki wpływające na bieg biofiltracji takie jak natężenie przepływu gazów, stężenie zanieczyszczeń, ich rodzaj i właściwości, temperatura, wilgotność gazów i złoża, tekstura złoża, dostępność tlenu, zasolenie i pH złoża, a także dostępność składników pokarmowych nie występujących w oczyszczanych gazach.

Obszerny rozdział poświęcono mikroorganizmom zasiedlającym złoża biofiltrów odpowiedzialnym za rozkład odfiltrowywanych zanieczyszczeń. Mogą być one wprowadzane do biofiltra jako mikroorganizmy naturalnie zasiedlające dany materiał budulcowy złoża lub wprowadzane na złoże w formie szczepionki. Uformowane w okresie rozruchu biofiltra (adaptacji) konsorcjum mikroorganizmów złożone z bakterii i grzybów ulega nieustannym zmianom wywoływanym napływem nowych mikroorganizmów wraz z oczyszczanym powietrzem oraz wpływem czynników środowiskowych. Zmiany te mogą mieć charakter zarówno ilościowy jak i jakościowy przejawiający się występowaniem mutacji genetycznych. Mikroorganizmy zasiedlające złoża należą do wielu gatunków takich jak np. *Pseudomonas, Pseudoxanthomonas, Xanthomonadales, Ralstonia, Mycobacterium, Exophiala i Candidia.* Metabolizują one zanieczyszczenia środowiska. Najczęściej ma to miejsce w procesie katabolicznym zapoczątkowanym wspomaganym enzymami atakiem tlenu na cząsteczkę. W efekcie najpierw powstają odpowiednie alkohole ulegające kolejno zachodzącym przemianom do aldehydów, kwasów tłuszczowych i dalej aż do wody i CO_2.

Zawarto dział poświęcony dodatkom poprawiającym biodostępność zanieczyszczeń takim jak metanol, oleje silikonowe czy surfaktanty. Omówiono nowości w zakresie rozwiązań konstrukcyjnych oraz układy hybrydowe. Rozwiązania takie jak biofiltry obrotowe i ze złożem cylindrycznym mają ograniczać problemy z równomiernym przepływem gazów i nadmiernymi oporami przepływu. Wśród układów hybrydowych zaprezentowano rozwiązania z przedfiltrem z węglem aktywnym oraz modułem wstępnej obróbki promieniami UV. Przedstawiono też ideę biofiltra łączącego usuwanie zanieczyszczeń z generacją prądu elektrycznego w mikrobiologicznych ogniwach paliwowych.

Słowa kluczowe:
biofiltracja, biofiltracja powietrza, biofiltracja zanieczyszczeń powietrza,
biofiltracja – trendy rozwojowe

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Analysis and Evaluation of Water Losses in the Collective Water Supply System

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1. Introduction

One of the main problems of water supply companies is water losses. Among many factors, the greatest impact on water losses is caused by the poor technical condition of the piping system, the level of pressure in the network and its fluctuations within the daily cycle. Rapid pressure changes and the associated hydraulic shocks affect both the failure rate and the outflow rate of water from the network. The amount of losses, regardless of their types, affects the cost of water supplied to consumers and has a negative effect on the financial standing of water supply companies (Nasirian et al., 2013, Venkatesh 2012). By reducing leakages, the production of water treatment agents and energy production are reduced globally, which is highly desirable for environmental reasons. Reduction in losses does not only lead to cost reduction but it also protects the limited water resources available for consumption, which accounts for ca. 2.5% of the world's total (Kuczyński & Żuchowicki 2010). Water losses generate not only resource and environmental costs of lost water, but also other costs resulting from leakages, such as subsidence of buildings or road collapses, and even costs incurred as a result of traffic jams resulting from the elimination of water supply failures (Ashton & Hope 2001). Therefore, companies that manage water distribution systems, in order to reduce operating costs, improve the reliability of the operation of water supply systems and to protect water resources, must perform multifaceted activities aimed at reducing water losses (Rak, et al., 2019). These measures include active leakage control, efficient pressure management, and speed and quality of repairs and regular pipe materials management. The basis for such actions should be a reliable analysis and evaluation of water losses. (Lee & Lam 2012, Clarke et al., 2012, Nasirian et al., 2013, Fujimura 2007, European Environment Agency 2012).

The research indicates that accurate evaluation of water losses and their objective assessment are difficult for many water supply companies. In order to obtain full knowledge of the amount of water lost from the system, many European countries such as Great Britain, Germany, Switzerland, Austria, Denmark, Spain and Denmark have developed and implemented special programs to analyse technical, economic and reliability indices of the operation of water distribution systems. (European Environment Agency 2012, Mutikanga et al., 2013, Jin & Piratla 2016).

The International Water Association (IWA) plays an important role in the implementation of best practices of sustainable water management. The organization has also made a significant contribution to the development and implementation of methods and programs to reduce water losses. An assessment of water losses based on the water balance method and numerous indices provides reliable information on the amount of water lost. The adoption of the standardised methodology for the determination of water losses proposed by the IWA allows for the comparison of losses in different water supply systems and the assessment of their levels (Lambert & Hirner 2000, Michalik &Rak 2017, Hug et al., 2002, Pietrucha-Urbanik & Studziński 2019).

The aim of the paper is to analyse and evaluate water losses in a collective water supply system, compare water loss indices in these systems to Polish and international standards, and to indicated and evaluate the company's activities leading to the reduction of water losses. The paper uses standard testing methodologies (water balance according to the International Water Association and index method). Water losses in the entire distribution system in 2012-2018 were analysed. The evaluation of water loss indices was conducted in accordance with the guidelines of AWWA (American Water Works Association), IWA (International Water Association), and WBI (Water Band Index). The opportunities for reducing the level of water losses and, consequently, increasing the reliability of water supply were indicated.

2. Water loss characterization

Water losses are divided into real and apparent losses. Real losses are caused by leakages of water from the networks and systems, fittings, overflow from compensation tanks and theft of water. Real water losses also occur in internal installations due to leaks smaller than the starting flow rate of the water meters. The causes for apparent losses include inaccuracy and inconsistency of measurement of water supply and consumption (Hotloś 2003). Contrary to real losses, apparent losses do not constitute actual losses, but only affect the numerical result of the balance of the volume of water supplied to the network and that sold to consumers. Since they do not represent real water losses, they are difficult to identify and determine accurately. In practice, a specific amount of water is supplied to consumers, but is not measured due to the metrological properties of the water meters (flows below the starting flow rate). The 1023heoreticcal measurement error should be not higher than 10%, but in practice it is difficult to determine the measurement error of the flow meter. According to Siwoń et al. (Siwoń et al., 2004), apparent losses may amount to ca. 5% depending on the installation and measurement conditions. It is also important to ensure the simultaneous measurement of water supply and intake. Simultaneous measurement affects the accuracy of water balance and thus the reliable determination of apparent losses. The amount of water from the pipeline used for internal purposes is generally difficult to quantify and is therefore often roughly estimated. It means water used mainly for the technological needs of the water supply system, and often for the sewage system (flushing of tanks, water pipes or channels). The values of water consumed for internal purposes are frequently overestimated in order to underestimate the actual water losses.

The difficulty of balancing the volume of water consumption in the distribution system is caused by various factors that can be divided into: dependent and partly independent on the plant operating a given water supply system (Piechurski 2014).

The dependent factors include:

- water leakages from pipes and leaking water supply pipes,
- flushing of the water supply system,
- leakages on water pipe connections.

Factors that are partly independent include:

- water theft,
- water supply failures,
- the accuracy class of the measurement instruments.

3. Characterization of the water distribution system operated by Water and Sewage Company in Końskie

Water and Sewage Company in Końskie operates water supply systems in the city and gmina of Końskie, Poland, in the area of 57 towns and villages. The total length of the water supply network is 287.8 km (data from 2018), including 0.6 km of mains and 287.2 km of distribution pipes. The water supply system is supplied from three underground water intakes located in the villages: Modliszewice, Paruchy and Wąsosz. The company operates 6,894 connections with a length of 187.1 km.

Fig. 1 shows the material structure of the water supply network. The material structure is closely related to the age of the water supply systems used (Fig. 2). The variety of materials used for the construction of water supply networks in Poland resulted primarily from their availability in the market, which was related to the period of construction of water supply systems.

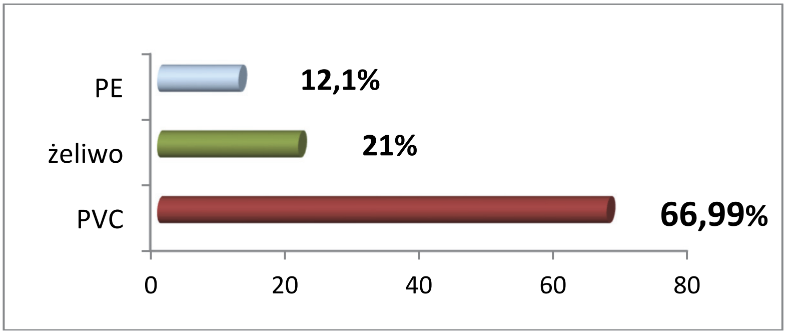

Fig. 1. Material structure of the network

The total percentage of PVC and PE is ca. 88%, which indicates that the networks are relatively recently installed, with their period of use not exceeding 20 years (Fig. 2). The company uses only few percent of old networks built before 1980.

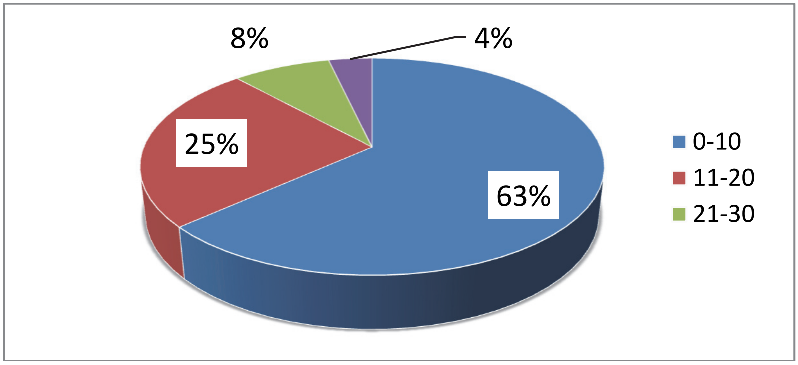

Fig. 2. Age structure of the network

Table 1 presents the length of the water supply network and the number of water supply connections operated by the company in 2012-2018. These data and pressure values are necessary for calculation of water loss indices recommended by IWA and presented in the further part of this study.

Table 1. Characteristics of the water supply network

year	water supply network [km]			number of house connections, L_{wc}	average pressure in the tested network, p – m H_2O
	length of the water supply network, M+R	length of house connections, W_c	total length, M+R+W_c		
2012	266.5	165.7	432.2	6183	40
2013	266.5	168.5	435.0	6290	40
2014	266.5	170.9	437.4	6382	38
2015	268.4	174.7	443.1	6522	38
2016	268.8	178.9	447.7	6670	38
2017	286.5	183.9	470.4	6803	35
2018	287.8	187.1	474.9	6894	35

4. Material and Methods

The analysis of water losses was carried out using the two research methods: balance method according to the International Water Association (IWA) and the index method. The analysis covered the data from the period of 2012-2018, obtained from the Water and Sewage Company which include: water supplied to the network, water used for social welfare purposes, non-production and production purposes, network length, quantity and length of water supply connections, the number of recipients, average pressure in the tested network, and number of failures in individual years.

These data were used to calculate failure intensity index (λ), percentage ratio of water loss (WS) and index of hydraulic load of the network (q_o), and indices recommended by the International Water Association (IWA) (Lambert & Hirner 2000):

- Real Leakage Balance (RLB)
- Non-Revenue Water Basic (NRWB)
- Unavoidable Annual Real Losses (UARL)
- Infrastructure Leakage Index (ILI)

Unit indices of water losses per capita and unit indices of water losses per kilometre of the network were also determined. Water loss indices, widely described in the literature (Hotloś 2007, Lambert & Hirner 2000, Bergel 2012) and characterized in detail in the further part of the study, were calculated from formulae (2) to (13) presented in Table 2 and 3.

Table 2. Compilation of water loss indices

Water loss index	Index formula
Water loss in the distribution system – V_{los}, m^3/year	$V_{los} = V_{sup} - V_{wł} - V_{sol}$ (2) V_{sup} – water supplied to the network, m^3/year $V_{wł}$ – water for the internal needs of the company, m^3/year V_{sol} – water sold, m^3/year
percentage water loss index – WS, %	$WS = (V_{los}/V_{sup}) \cdot 100\%$ (3)
unique real leakage balance index – RLB_2, dm^3/connection/day	$RLB_2 = (V_{los} \cdot 1000)/(L_{wc} \cdot 365)$ (4) L_{wc} – number of house connections
non-revenue water basic index – NRWB, %	$NRWB = [(V_{sup} - V_{sol})/V_{sup}] \cdot 100$ (5)
unavoidable annual real losses – UARL, m^3/year	$UARL = [18 + (M + R) + 25 \cdot Wc + 0.8 \cdot L_{wc}] \cdot 0.365 \cdot p$ (6) M – main network's length, km R – distribution pipes, km W_c – length of house connections, m p – average pressure in the tested network, m H_2O 0.365 – conversion factor per year and m^3
infrastructure leakage index – ILI, -	$ILI = V_{los}/UARL$ (7)

The failure intensity indices λ in total for distribution pipes and water mains in the companies studied were calculated from the formula (1).

$$\lambda = \frac{N}{L \cdot t} \tag{1}$$

where:
λ – failure intensity index (failure/(km·year),
N – number of failures per year,
L – total length of distribution pipes and water mains (km),
t – time in which a given number of failures occurring was equal to 1 year.

When analysing water losses, one should pay attention to unit indices per capita and unit index of water losses per kilometre of the network that characterize the operation of water supply systems. These indices are determined according to the formulae presented in Table 3.

Table 3. Unit water loss indices

Unit water loss index	Index formula
Amount of water supplied q_{sup}, dm^3/ (inhabitant·day)	$q_{sup} = (V_{sup}\ 1000)/(IN \cdot 365)$ (8) IN – number of inhabitants using the water supply system
Amount of water sold in total q_{sol}, dm^3/ (inhabitant·day)	$q_{sol} = (V_{sol} \cdot 1000)/(IN \cdot 365)$ (9)
Amount of water losses q_{los}, dm^3/ (inhabitant · day)	$q_{los} = (V_{los} \cdot 1000)/(IN \cdot 365)$ (10)
Amount of water consumed for internal purposes $q_{wł}$, dm^3/ (inhabitant · day)	$q_{wł} = (V_{wł} \cdot 1000)/(IN \cdot 365)$ (11)
Amount of non-revenue water q_{nd}, dm^3/ (inhabitan · day)	$q_{nd} = (V_{sup} - V_{sol}) \cdot 1000)/(IN \cdot 365)$ (12)
water loss rate per kilometre of network q_s, m^3/(km h)	$q_s = V_{los}/(M+R)$ (13) V_{los} – water loss in the distribution system, m^3/h

The hydraulic load index was also calculated using the formula 14 due to the effect of the load of the network on water losses. The strong effect of the network load on water losses has been observed in the studies by e.g. Kwietniewski (Kwietniewski 2013).

$$q_o = V_{sup}/(M+R) \cdot 365 \tag{14}$$

where:
q_o – hydraulic loads of water supply, $m^3/(km\ d)$,
V_{sup} – water supplied to the network, m^3/year,
M – main network's length, km,
R – distribution pipes, km.

5. Results and discussion

5.1. Pipe failure rate

One of the most important indices for the assessment of the technical condition of a water supply system is failure intensity index for the pipelines (λ). The frequency of failures is mainly related to the age of the pipes, material, pressure, and operating conditions. The number of failures and the time of their elimination may have a substantial effect on the amount of water losses. It should be stressed, however, that failure rate of the network does not always have a significant effect on the amount of water losses. This is indicated, among others, by the studies by Rak for the municipal network of Jasło and Jarosław (Rak & Sypień2013, Rak & Misztal, 2017). Table 4 presents the number of failures in the analysed years and the value of the damage intensity index (λ).

Table 4. Mean values of unit intensity of water pipeline failures λ, failure/(km·year)

Years	2012	2013	2014	2015	2016	2017	2018
Number of failures	25	23	31	28	29	33	40
Distribution network length	265.9	265.9	265.9	267.8	268.2	285.9	287.2
Failure intensity index (λ)	0.094	0.086	0.117	0.105	0.108	0.115	0.139

Research indicates that in the analysed period of time, the number of failures was insignificant and little varied in individual years. Failure intensity indices for the water supply system in the analysed years was low. According to the recommendations of the PN-EN 60300-3-4 2008 standard, the failure intensity for mains should not exceed 0.3 failure/(km·year) and, for distribution pipes, 0.5

failure/(km·year). Kwietniewski proposed the following criteria for failure intensity λ (Kwietniewski 2013):

- Low failure rate = high reliability $\lambda \leq 0{,}1$
- Medium failure rate = medium reliability $0.1 < \lambda \leq 0.5$
- High failure rate = low reliability $\lambda \geq 0.5$

According to the above criteria, it can be concluded that the network is characterised by high reliability. Failure intensity for to the analysed water supply system is within the European criteria and should not have a significant effect on water losses. The evaluation of the network failure rate was made based on the failures to the water supply network, but undetected failures are also possible.

5.2. Water balance

To prepare water balance, data on the amount of water supplied to the network, the amount of water used for the internal needs of the water supply company, and the amount of water sold to all customers are required. These data were obtained from the company and presented in Table 5. The amount of water losses in the water supply system (V_{los}) was calculated from the formula (2).

Table 5. Summary of water balance for 2013-2017

Year	Water supplied to the network, V_{sup} thousand m^3/year	Water for the internal needs of the company, $V_{wł}$ thousand m^3/year	Water sold, V_{sol} thousand m^3/year	Water loss in the distribution system, V_{los} thousand m^3/year
2012	2 050.7	13.7	1,440.7	596.3
2013	1 822.5	14.3	1,429.9	378.3
2014	1 718.2	15.7	1,402.4	300.1
2015	1 794.1	64.8	1,402.3	327.0
2016	1 685.0	28.6	1,374.9	281.5
2017	1 673.9	21.7	1,355.7	296.5
2018	1,736.9	14.4	1,408.0	314.5

5.3. Water loss indices

Table 6 presents water loss indices in 2012-2018 calculated from the formulae 3-7. Analysis of water loss indices (Table 6) reveals relatively low values of the indices in this collective water supply system. In recent years, all the indices were lower than the average values obtained by Bergel (Bergel 2012) for 67 water supply systems serving 10,000 to 20,000 inhabitants. The value of PWS in 2012 amounted to as much as 29.1% of the amount of water injected into the network. This index reached the level of 17-19% in the last few years and was below the Berger's average of 21.4%. An analysis of the percentage water loss indices shows the lowest levels of leakages in the Netherlands (3-7%), while in most countries, these figures are higher: 15% in the USA, 13.8% in Canada, 42% in Italy, and 34.9% in Greece (Mutikanga 2012). However, it should be stressed that comparison and evaluation of water losses for different distribution systems using only the percentage water loss index is insufficient or even misleading. Distribution systems vary in terms of network length, number and length of connections, material, age of the network, hydraulic pressure and load to water supply networks. These factors have an effect on the amount of water loss. Furthermore, the value of the percentage water loss index is affected by the volume of water used for internal needs of the water supply company, which is provided by the companies as an estimate. For these reasons, it is recommended to use it only to assess the variability of water losses over many years in a given distribution system (Kwietniewski 2013).

Table 6. Water loss indices in 2012-2018

Year	WS, %	RLB_2, dm^3/connection/day	UARL, thousand m^3/year	NRWB, %	ILI, -
2012	29.1	268.9	197.7	29.7	3.01
2013	20.7	164.5	199.9	21.5	1.90
2014	17.5	128.6	201.8	18.3	1.50
2015	18.2	137.0	205.2	21.8	1.59
2016	16.7	115.3	208.5	18.4	1.35
2017	17.7	119.4	194.1	19.0	1.52
2018	18.1	124.9	196.4	18.9	1.60

In order to ensure a comprehensive and more reliable evaluation of water losses, it is recommended to establish loss indices developed by IWA. These include, among others, the NRWB water volume index. This index does not take into account the volume of water used for internal purposes of the water supply system, thus avoiding errors resulting from deliberate overestimation of the volume of this type of water by certain enterprises. In 2016 and 2018, it ranged from 18 to 19%, which shows that it remains at the country's average level and is below the 24% indicated by Berger. It should be emphasised that it was reduced by 10% in the last years of the study compared to 2012.

Another index recommended by IWA to assess the condition of water distribution systems is the RLB_2 index, which measures water losses per day per water supply connection. It is recommended if connection density is greater than 20 per km of the network. This index decreased significantly in the last years of the study, reaching the level of 115-125 dm^3/(connection-day) in 2016-2018, which demonstrates that it is at a lower level than in other collective water supply systems in Poland. The RLB_2 index in Poland was approximately ca. 150 dm^3/(connection·day) in 2015 (Bergel 2012). It should be noted that also this index decreased significantly for the analysed company in the period studied. In 2012, its value was more than twice as high as at present. This index is often very diverse, whereas extensive research presented in the Water Use and Loss Report shows its value in New Zealand ranging from 100 to 290 dm^3/(connection-day) (Water Use and Loss Report 2014). In western European countries, however, the maximum allowable value for RLB_2 is 100 dm^3/(connection-day).

Comparison of different water distribution systems can be made based on the infrastructure leakage index (ILI). This index represents the multiplication factor for actual water losses compared to the minimum level (URAL) to be achieved in a properly operated water supply system. It is recommended to be used when the number of connections in a given water supply system is greater than 5,000 and their density exceeds 20 per km of water supply network and the network pressure is at least 0.25 MPa (Dohnalik & Jędrzejewski 2004, McKenzie & Lambert 2003). The distribution system analysed shall meet the above criteria.

The ILI in 2014-2018 has decreased sharply compared to 2012. In the last five years, it ranged from 1.35 to 1.60 (Tab. 6). According to the IWA standards, the WBI Banding System for developed countries, and the criteria adopted by the American Water Works Association (AWWA), the value of ILI of ≤ 1.5 indicates a very good technical condition of the water distribution network. It should be noted that the value of this index in 2012 was 3.01, which indicated a poor condition of the network (according to IWA criteria).

The results of the Berger's study among of 67 Polish systems supplying water to 10,000-20,000 inhabitants showed that the average ILI for these systems is 1.9. (Bergel 2012). The ILI for the analysed system is lower than the average presented by other Polish authors. The ILI value given by these authors for many Polish cities in recent years ranged from 1.6 to 4.7 (Ociepa et al., 2018, Ociepa et al., 2019, Ociepa-Kubicka &Wilczak 2017, Rak & Sypień 2013, Rak & Misztal 2017). In contrast, the data provided by Lambert and McKenzie for 44 water distribution systems, including 5 systems from New Zealand, 17 from Australia and 22 from Europe, show a very wide range of ILI, from less than 1.0 for two systems to more than 5.0 for eleven of the systems analysed. Research for 16 water supply systems from different countries in Europe such as Austria, Belgium, Bulgaria, Denmark, England, France, Germany, Italy, Malta, Portugal, Scotland, Serbia and Croatia also point to a very wide IMI range, from 0.7 to 5.8 (Water Use and Loss Report 2014, Dohnalik & Jędrzejewski 2004, McKenzie & Lambert 2003).

Table 7 presents unit water loss indices per capita per day and per kilometre of network per hour.

Table 7. Unit water loss indices in 2012-2018

Years	Number of inhabitants served by the water supply system	Unit water loss indices per capita, $dm^3/(inhabitant \cdot day)$					Unit water loss index per km of the network, $m^3/(km\ h)$
		q_{sup}	q_{sol}	q_{los}	$q_{wł}$	q_{nd}	q_s
2012	30,915	181.70	127.67	52.80	1.22	54.02	0.26
2013	31,450	158.70	124.56	32.91	1.25	34.16	0.16
2014	31,910	147.50	120.40	25.73	1.35	27.08	0.13
2015	32,610	150.70	117.82	27.40	5.45	32.85	0.14
2016	33,350	138.40	112.95	23.07	2.35	25.42	0.12
2017	35.000	131.00	106.12	23.20	1.70	24.90	0.12
2018	35.000	135.90	110.20	24.62	1.13	25.75	0.12

Calculation of unit water loss indices per capita per day provided a detailed picture of the use of the water supply system. Analysis of the unit water loss indices in 2012-2018 presented in Table 7 shows that the index of water supplied was the highest in 2012 and amounted to 181.73, whereas it was the lowest in 2017 and amounted to 131.00 dm^3/(inhabitant·day). The unit volume of water sold was the highest in 2012 and the lowest in 2017, with 127.67 and 106.12 dm^3/(inhabitant·day), respectively. The unit water loss index ranged from 52.80 in 2012 to 23.07 dm^3/(inhabitant·day) in 2017. The loss index decreased in recent years by over 50% compared to 2012 and is now at an average level compared to other Polish distribution systems. In the 334 Polish group water supply systems analysed by Bergel, this index ranged from 24.0 to 39.9 dm^3/(inhabitant·day) on average, while the analysis of Hotloś for 10 municipal waterworks indicated an average range of this index from 16 to 35 dm^3/(inhabitant·day) (Bergel 2012, Hotloś 2007).

The unit volume of water needed for the company's own purposes ranged from 1.13 to 5.45 dm^3/(inhabitant·day), whereas the amount of non-revenue water ranged from 24.90 to 54.02 dm^3/(inhabitant·day). A significant reduction in the unit non-revenue water index observed since 2016 confirms the effectiveness of the company's actions aimed to reduce water losses. Another analysed index was unit water loss index per kilometre of water supply system q_s. In the analysed years, it ranged from 0.26 in 2012 to 0.12 $m^3/(km \cdot h)$ in 2016-2018. According to the German criteria, this index is at a recommended level below 0.20 $m^3/(km \cdot h)$.

The analysis of water loss took into account the hydraulic load index for the network q_o, m^3/(km·day). This index shows the mean amount of water supplied per day in reference to unit length of a water supply network. The values of indices for individual companies are presented in Table 7.

Table 7. Summary of indices of individual hydraulic load of a water supply system (q_o), $m^3/(km \cdot d)$

2012	2013	2014	2015	2016	2017	2018
21.08	18.73	17.66	18.31	17.17	16.01	16.53

Water losses in a distribution system are often related to the hydraulic load of the network. In general, a reduction in the load to the network results in a decrease in water losses. In 2012-2018, the load to the analysed water supply network showed a slightly downward tendency despite the growing number of connections. This is probably due to the constantly decreasing water consumption.

6. Summary

The results of the analysis showed that with its comprehensive activities, the company has significantly reduced its water losses in recent years. The company has been actively managing water losses for several years. The basis for its activity is continuous monitoring of network flows and active leakage control and, consequently, the reduction of water losses. Implementation of monitoring allows for the control of flows and pressure levels. The decrease in the NRWB index in 2012-2018 from 29% in 2012 to ca. 18% in 2018, and the decrease of the ILI value in the respective years from 3.1 to 1.5-1.6 indicates the effective countermeasures used to limit water losses. Currently, the value of IMI according to strict IWA criteria suggests a very good condition of the network. RLB_2 is another indicator that fell sharply over the period analysed. In 2012, its value was more than twice as high as at present. On the other hand, the average condition of the network is indicated by the unit water loss index per capita, which amounted to 52.80 in 2012 and currently is about 23.07 dm^3/(inhabitant day).

In view of the specific nature of operation of each distribution system, the company developed its own programme for reduction of water losses. These solutions are adapted to local conditions, taking into account the causes of water losses and the company's potential. The particularly important problem addressed by the company is to monitor night flows, which allows for detecting excessive flows and water consumption resulting from failures or theft. Correct separation of metered zones allows for identification of the areas with high flows. Consequently, the area of searching for failure or uncontrolled water consumption is narrowed down, which accelerates location of leakages and reduces the amount of water lost. The company indicates the need for detailed monitoring and reduction of network pressures to optimal values. This reduces the amount of leakages in pipes, thus limiting water losses.

Further reduction of losses will be achieved by continuation of the regular control of dishonest water consumers, the use of water meters resistant to magnetic field, their regular verification, control and calibration of measurement devices. It is planned to install water meters with radio sensors. Replacement of water meters with visual reading into water meters with radio devices enables to read all water meters in a given building or a given zone at the same time. Installation of the meters and ensuring simultaneous measurement is necessary to eliminate apparent losses. Furthermore, the use of advanced leakage detection equipment is essential to reduce water losses, including geophones, stethophones or correlators.

7. Conclusions

1. A reliable assessment of the activities of Water and Sewage Company in Końskie in terms of reducing water losses requires preparation of a water balance and determination and analysis of water loss indices.
2. The analysed water loss indices for the tested water supply system are currently lower or comparable to the values obtained in other collective water supply systems in Poland and worldwide. At present, most indicators of water loss are at a very good or good level. In 2012, most of the water loss indices

were high or even very high and showed higher than national average water losses from the network. This shows that the company took effective measures to reduce water losses in the last few years of the study.

3. The values of the failure intensity for the tested water supply system indicate that the impact of failures on water losses is insignificant, assuming that the company responds quickly to remove identified leaks and there are no undetected failures.
4. The networks which had been built relatively recently and a low failure rate suggest that the operator should take measures to evaluate the percentage of apparent losses in the overall value of losses and to pay particular attention to uncontrolled water intake.
5. For the precise determination of the unavoidable real losses index, it is recommended to divide the network into measurement areas (zones). The URAL and ILI evaluation should be performed for separated zones.
6. It is advisable that the company continues to minimize water losses to the economic level of leakage specified for the operated distribution system. Determination of the economic level of leakages requires preparation of an economic analysis that takes into consideration the costs of water intake, treatment and distribution, the costs of active control and disposal of leakages.

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Abstract

The paper presents the analysis and evaluation of water losses in the distribution system used by the Water and Sewage Company in Końskie, Poland. The analysis of water losses was conducted based on the use of numerous indices that provide objective information on the condition of the water supply system. The method of the percentage water loss index was extended by the methods of determination of water losses according to the International Water Association (IWA). The data needed for the calculation of water losses, such as the amount of water supplied to the network, the water sold, water used for the company's own needs, the length of the network, the number and length of water supply connections, number of customers, mean pressure in the network, and number of failures was derived from Water and Sewage Company in Końskie , Poland. These data were used to calculate the amount of water losses in individual years, percentage water loss index (PWS), and the indices recommended by the International Water Association (IWA): Real Leakage Balance (RLB), Non-Revenue Water Basic (NRWB), Unavoidable Annual Real Losses (UARL), Infrastructure Leakage Index (ILI) and unit indices of loss per capita and per kilometre of network. Due to the likely relationships of the load and failure rate of the network with water losses, the failure intensity index and index of hydraulic load to the network.

The results of the analysis showed that with its comprehensive activities, the company has significantly reduced its water losses in recent years. Currently, most of the water loss indices have reached a level considered good compared to the national data and average according to the standards used in Western European countries. In 2012, most of the analysed loss indices were at a high or even very high level and showed higher than the national average loss of network water. The decrease of the NRWB index from 29% in 2012 to ca. 18% in 2018, and the decrease of the ILI value in the respective years from 3.1 to 1.5-1.6 indicate the effective countermeasures used to limit water losses. Currently, the value of IMI according to strict IWA criteria suggests a very good condition of the network. RLB2 is another indicator that fell sharply over the period analysed. In 2012, its value was more than twice as high as at present. On the other hand, the average condition of the network is indicated by the unit water loss index per capita, which amounted to 52.80 in 2012 and currently is about 23.07 dm3/(inhabitant day). Very low values of the failure intensity index of the water supply system indicate that the impact of failures on water losses is insignificant, assuming that the company responds quickly to remove identified leaks and there are no undetected failures.

The several years of analysis and evaluation of numerous indices of water loss presented in the paper reveals the effectiveness of the adopted strategies of reducing leakages in the distribution system. It should be noted that the company has been involved in comprehensive activities aimed at limitation of water losses for several years.

Keywords:
water losses, percentage water loss index, infrastructure leakage index,
unit water start index, failure intensity index

Analiza i ocena strat wody w wybranym wodociągu grupowym

Streszczenie

W artykule przedstawiono analizę i ocenę strat wody w systemie dystrybucji eksploatowanym przez Przedsiębiorstwo Wodociągów i Kanalizacji w Końskich. Analizę strat wody przeprowadzono w oparciu o liczne wskaźniki pozwalające na obiektywną informację o stanie sieci wodociągowej. Metoda procentowego wskaźnika strat wody rozszerzona została o metody określania strat według International Water Association (IWA). Niezbędne dane do obliczeń strat wody jak: ilość wody dostarczanej do sieci, wody sprzedanej, zużytej na potrzeby własne zakładu, długość sieci, ilość i długość połączeń wodociągowych, liczbę odbiorców, średnie ciśnienie w sieci, liczba awarii otrzymano z Przedsiębiorstwa Wodociągów i Kanalizacji w Końskich. Na ich podstawie wyznaczono: ilość strat wody w poszczególnych latach, procentowy wskaźnik strat wody (PWS), a także zalecane przez International Water Association (IWA) wskaźniki: Real Leakage Balance (RLB), Non-Revenue Water Basic (NRWB), Unavoidable Annual Real Losses (UARL), Infrastructure Leakage Index (ILI) oraz wskaźniki jednostkowe strat na mieszkańca i kilometr sieci. Z uwagi na możliwy związek obciążenia i awaryjności sieci

ze stratami wody wyznaczono wskaźnik intensywności uszkodzeń i wskaźnik hydraulicznego obciążenia sieci.

Wyniki przeprowadzonej analizy pozwalają stwierdzić, że dzięki wszechstronnym działaniom przedsiębiorstwo w ostatnich latach zdecydowanie obniżyło straty wody. Obecnie większość wskaźników strat wody osiągnęło poziom uznany za dobry na tle danych krajowych a średni w odniesieniu do standardów krajów Europy zachodniej. W 2012 roku większość analizowanych wskaźników strat była na wysokim a nawet bardzo wysokim poziomie i świadczyła o wyższych niż średnie krajowe ubytkach wody z sieci. Spadek wskaźnika strat NRWB z 29% w 2012 roku do ok. 18% w 2018, spadek wartości wskaźnika ILI w tym okresie z 3,1 do 1,5-1,6 świadczy o skutecznym przeciwdziałaniu stratom wody. Obecnie wartość ILI według rygorystycznych kryteriów IWA świadczy o bardzo dobrym stanie sieci. Kolejnym wskaźnikiem, który uległ w analizowanym okresie poważnemu obniżeniu jest RLB_2. W 2012 wartość jego była ponad dwukrotnie wyższa niż obecnie. Natomiast na średni stan sieci wskazuje jednostkowy wskaźnik strat wody na mieszkańca, który wynosił 52,80 w 2012 roku a obecnie ok. 23,07 dm^3/(mieszkańca·dobę). Bardzo niskie wartości wskaźnika intensywności uszkodzeń sieci wodociągowej wskazują na mało znaczący wpływ awarii na straty wody przy założeniu, że Zakład szybko reaguje i usuwa stwierdzone wycieki i nie występują awarie nieujawnione.

Analiza i ocena na przestrzeni lat licznych wskaźników strat wody przedstawiona w artykule świadczy o skuteczności przyjętych strategii ograniczania wycieków w systemie dystrybucji. Należy podkreślić, że przedsiębiorstwo od kilku lat prowadzi wszechstronne, kompleksowe działania zmierzające do ograniczania strat wody.

Słowa kluczowe:
starty wody, procentowy wskaźnik wody, infrastrukturalny indeks wycieków,
jednostkowe wskaźniki start wody,
wskaźnik intensywności uszkodzeń sieci wodociągowej

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Contents of Rare Earth Elements in Acidic Waters Linked to Mining of Coal and Lignite (Upper Silesia and Muskau Bend, Southern Poland)

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1. Introduction

A group of 15 elements of the periodic table with atomic numbers 57-71 (lanthanum La, cerium Ce, praseodymium Pr, neodymium Nd, promethium Pm, samarium Sm, europium Eu, gadolinium Gd, terbium Tb, dysprosium Dy, holmium Ho, erbium Er, thulium Tm, ytterbium Yb, lutetium Lu) is defined as Rare Earth Elements (REEs). Due to similar properties and ionic radii, which are close to those of Yb and Lu, also scandium Sc and yttrium Y (with atomic numbers 21 and 39, respectively) are included in REEs (International Union Of Pure And Applied Chemistry 1970). Except for Pm, which does not have stable isotopes and, practically, does not occur in natural environment, the remaining elements quoted above form a group with relatively similar characteristics (Henderson 1984, Kabata-Pendias & Szteke 2012). In the surface environment fourteen from among the above mentioned elements are in an oxidation state of +3, whereas Ce^{3+} redox can be oxidized to Ce^{4+} , and Eu^{3+} can be reduced to Eu^{2+}.

A characteristic feature of lanthanides is their ionic radius decrease with an increase of atomic number from 103 pm for La^{3+} to 86 pm for Lu^{3+} („lanthanide contraction"). This phenomenon manifests itself in a change of properties - from more to less alkaline, as well as in solubility decrease with the rise of atomic weight as the ionic radius increases. The differentiation of properties leads to the formation of light REEs (LREEs), containing elements from La to Eu, and heavy REEs (HREEs), containing elements from Gd to Lu, including yttrium. In some works also a third group is distinguished – medium REEs (MREEs) – including elements from Sm to Dy.

Despite considerable scattering of REEs, their average contents in Earth's crust is significant – 0.018% (Kabata-Pendias & Szteke 2012), being on a par with the contents of non-ferrous metals (Cu, Zn, Ga, Ge, As, Cd, In, Sn, Sb, Hg, Tl Pb, Bi) (Polański & Smulikowski 1969). In igneous rocks most REEs occur in granitoids and rhyolites, though REE ore deposits are related to alkaline or ultra-alkaline rocks (Ryka & Maliszewska 1991). In a hypergenic environment REEs can form resistant to wethering primary minerals and can be built in new amorphous or crystalline mineral phases (Minarik et al. 1998, Kokowska-Popławska 2016, Migaszewski et al. 2019, Migaszewski & Gałuszka 2019).

One of the processes leading to secondary activation of REEs is natural or anthropogenic acidification of their environment. Relatively high concentrations of REEs can be found in waters influenced by the acidic mine drainage (AMD) process, where a lowered pH of waters and their increased aggressiveness leads to a release of REEs from the REE-bearing minerals contained in the rock matrix or mining waste (Bozau et al.2004, Migaszewski et al. 2014, Sun et al. 2007, Varekamp et al 2009, Zhao et al. 2007).

The article presents the first results of initial investigations showing the contents of REEs in AMD waters from the south of Poland, related to coal mining and old lignite mining. No studies on REEs content in acidic mine waters from this region of Poland have been conducted so far, therefore the Upper Silesia Coal Basin and the Muskau Bend were identified as prospective sites for further investigations into factors differentiating the contents of REEs in acidic waters.

Total REE contents in the examined acidic waters as well as normalized contents using North American Shale Composite (NASC) (Haskin et al. 1968, Gromet et al. 1984) were compared with data from other sites, where the water environment acidification was found as processes related to coal, ore and hard rock mining.

It should be noted that the phenomenon of environment contamination in mining areas due to the AMD process is one of the major environmental problems, which needs to be investigated further also in the context of REEs fractionation depending on local geochemical conditions.

2. Site description

Investigations of the acidic runoff waters were conducted in the vicinity of an active coal mining wastes pile, located in the town of Libiąż, in the eastern part of the Upper Silesian Coal Basin (USCB) in the southern part of Poland (Fig. 1).

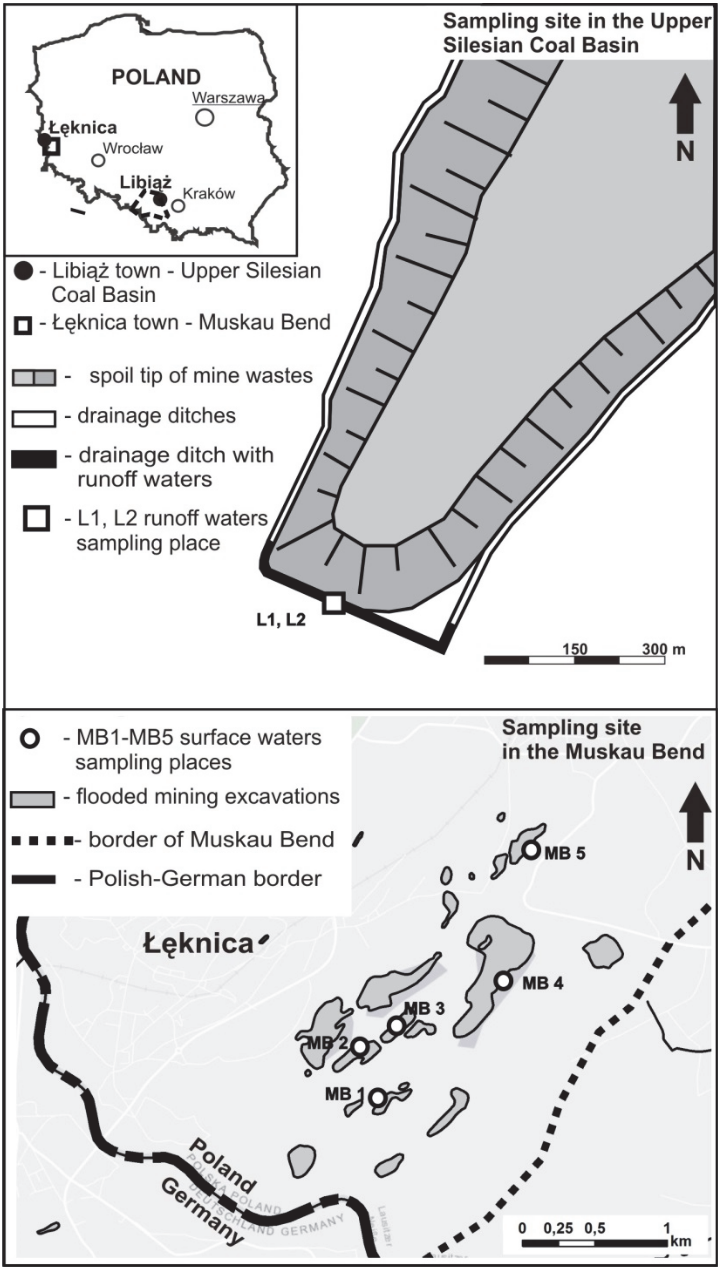

Fig. 1. Localization sampling sites in the eastern part of the Upper Silesia Coal Basin and post-mining lakes in the Muskau Bend

The pile, which has been functioning since the 1980s, contains mainly Carboniferous waste claystones as well as mudstones and sandstones, containing pieces of coal and pyrite (FeS_2), which were produced in the process of coal mining from the Łaziska and Libiąż beds (Westphalian C and D) of the Cracow Sandstone Series (Gabzdyl & Gorol 2008). Currently this facility takes an area of 33.5 hectares, at a relative elevation of 35 m. Acidic waters are retained in a surrounding drainage ditch having a length of 300 m, a width of 5 m and a depth of maximum 1.0 m. This ditch is an element of the acidic water neutralisation system and does not contact underground waters.

Detailed characteristics of the geochemical environment and the variability of AMD waters in Libiąż have been presented in the paper by Bauerek et al (2017). Acidic waters related to the influence of former lignite mining on the environment have been sampled from 5 flooded excavations in the former coal mine "Babina", located in Łęknica, on the territory of the Muscau Bend. Lignite deposits exploitation in this area was conducted during 1921-1974 and resulted in massive transformations of the landscape as well as the formation of several dozen deep (ranging from 5 to 22 m) anthropogenic reservoirs. Samples were taken from reservoirs characterized by the lowest pH of water, located in the area where mining works were finished at the latest (Jędrczak 1997, Lutyńska & Labus 2015, Skoczyńska-Gajda & Labus 2011).

The occurrence of Miocene lignite deposits directly near the surface is related to glaciotectonic deformations (slices, diapirs) of silty and sandy sediments of the Pliocene, Miocene and older Pleistocene Epoch in the area of terminal moraine of the glacier tongue of the Riss Glaciation (Haracz et al. 2012).

3. Materials and methods

3.1. Sampling and field measurements

In the summer of 2018 field measurements were done and samples were taken from acidic waters in anthropogenic reservoirs, related to active coal mining (the area of Libiąż, Upper Silesian Coal Basin) and abandoned lignite mining (the area of Łęknica, Muscau Bend). These works resulted in obtaining 2 samples of acidic runoff waters (L1 and L2) and 5 samples of waters filling the lignite mining excavations (MB1, MB2, MB3, MB4 and MB5).

Field measurements of such parameters as: pH, specific electrolytic conductivity, redox potential, dissolved oxygen and temperature were taken using a multifunctional WTW MultiLine 350i meter. Water samples for laboratory tests were taken in glass or plastic bottles, depending on the examined parameter (groups of chemical parameters), and delivered cooled to the laboratory. Except field measurements and acidity, the remaining parameters were determined in samples filtered in the field through a filter having a pore diameter of 0.45 μm.

3.2. Laboratory tests

Total and mineral acidity in the examined water was determined using the potentiometric titration method (hot, with hydrogen peroxide) according to the methodology of American Public Health Association (1998) with expanded uncertainty U (for coverage factor k = 2 and statistical significance 95%) reaching 20%. The concentration of chlorides (U = 8%) and sulphates (U = 10%) was determined by the ion chromatography method using a DIONEX ICS-5000 ion chromatograph. The concentrations of Ca, Mg, Na, K, Al, Fe_{tot} (U = 10%) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Perkin-Elmer Optima 5300DV spectrometer. The dissolved substances were determined by the weighing method (U = 10%). Iron Fe^{2+} was determined by the spectrophometric method using a SPEKOL 1200 spetrophometer (U = 10%). The concentration of Fe^{3+} was calculated as a difference between total iron (Fe_{og}) and Fe^{2+}.

Rare earth elements were determined by the method of inductively coupled plasma atomic emission spectrometry (ICP-MS, Nexion 300S, produced by Perkin Elmer, USA), in accordance with methodology described in the work of Cykowska et al. (2017). Determination of rare earth elements' contents in acidic waters was conducted with expanded uncertainty U = 15% (for Sc) and U = 10% (for the remaining REEs).

The ICP-MS instrument was optimized with a standard daily procedure. A set of solutions prepared from the Multielement Calibration Standard (CCS-1, Inorganic Ventures, USA) was applied. Influence of physical interferences was minimized with the use of Re (ICP-45W-1, AccuStandard, USA) as an internal standard. The Certified Reference Materials (CRM) used for measuring REE concentrations were NCS DC 70314 and NCS DC 73324. Standard addition tests for selected acid water samples were also carried out.

All chemical analyses were conducted (according to ISO/IEC 17025:2005) in the accredited Laboratory of Water and Wastewater Analysis (Central Mining Institute, Katowice, Poland).

3.3. REEs enrichments and ratios

Concentrations of particular REEs in the examined acidic waters, their total concentrations (ΣREEs La-Lu), concentrations of LREEs (La-Eu), HREEs (Gd-Lu) and MREEs (Sm-Dy) as well as LREE/HREE ratios have been presented in Table 2.

The results obtained from REE measurements were normalized to North American Shale Composite (NASC) (Haskin et al. 1968; Gromet et al. 1984). Calculations allowed to compare REE concentrations colected from different anthropogenic reservoirs and identify any individual REE anomalies.

In addition, the La_{NASC}/Yb_{NASC} and Sm_{NASC}^Yb_{NASC} ratios were computed to assess depletion or enrichment of REE subgroups: LREE (La), MREE (Sm), and HREE (Yb).

Ratios values below 0.8 are indicative of negative anomalies whereas those above 1.2 point to positive anomalies (Grawunder et al. 2014).

The depletion or enrichment of individual REE elements: Ce/Ce_{NASC}, Eu/Eu_{NASC}, Gd/Gd_{NASC}, Tb/Tb_{NASC} ratios in the USCB acidic waters were calculated from the Eq. (1) (Bau and Dulski 1996) and reported in Table 3:

$$Ce/Ce_{NASC} = Ce_{NASC} /(0.5La_{NASC} + 0.5Pr_{NASC}) \tag{1}$$

where:
Ce_{NASC} – a background concentration whereas La_{NASC} and Pr_{NASC} are the NASC-normalized La and Pr concentrations, respectively.

For the calculations of Eu/Eu_{NASC}, Gd/Gd_{NASC}, Tb/Tb_{NASC} ratios, the following modificated equations were applied:

$$Eu/Eu_{NASC} = Eu_{NASC} /(0.5Sm_{NASC} + 0.5Dy_{NASC}) \tag{2}$$

$$Gd/Gd_{NASC} = Gd_{NASC} /(0.5SSm_{NASC} + 0.5Dy_{NASC}) \tag{3}$$

$$Tb/Tb_{NASC} = Tb_{NASC} /(0.5SSm_{NASC} + 0.5Dy_{NASC}) \tag{4}$$

where:
$Eu/Gd/Tb_{NASC}$ – background concentrations whereas Sm_{NASC} and Dy_{NASC} are the NASC-normalized Sm and Dy concentrations, respectively.

Modification of equation (1) was needed because distinct enrichment of acidic waters from USCB in Eu, Gd and Tb excludes use of these elements in the calculation of the anomaly.

4. Results and discussion

4.1. Geochemistry of waters

The results of investigations of selected physicochemical parameters of AMD waters samples collected from the eastern part of the Upper Silesian Coal Basin and from selected reservoirs in the area of the Muscau Bend have been presented in Table 1.

Surface runoff waters which have been found in the vicinity of the waste pile containing coal waste belong to AMD waters. The pH values of waters represented by samples L1 and L2 are low, reaching 3.0 and 2.4, respectively. The hydrogeochemical character of the examined waters presented in Piper's rhomb diagram in Monition's modification (Bagińska & Macioszczyk 1986) indicates that water L1 belongs to the chloride-sulphate-sodium type (Cl-SO_4-Na), whereas water L2 – to the sulphate-chloride-sodium type (SO_4-Cl-Na) (Fig. 2).

The sum of dominant anions ($SO_4^{2-} + Cl^-$) expressed in milligram equivalent percentage is 99.4% mval and 98.7% mval, with the concentrations of sulphates reaching 41.8% mval and 67.2% mval, and the concentrations of chlorides – 57.6% mval and 31.4% mval in waters L1 and L2, respectively. The contents of sodium as the main cation are smaller, reaching 61.9% mval and 47.5% mval. The cation composition is complemented by magnesium, calcium and iron ions.

A very high acidity of water represented by sample L2 (3820 mg/l $CaCO_3$) and a high concentration of sulphates (5630 mg/l), iron Fe^{3+} (485 mg/l) and aluminium (227 mg/l) indicates that it is a stagnant water, which affected the silty sediments filling the surrounding drainage ditch over a long period of time (Bauerek et al. 2017). The acidic water represented by sample L1 is characterized by a distinctly higher pH (3.0) and lower concentrations of most ions: SO_4 – 3270 mg/l, Fe^{3+} – 174 mg/l, Al – 53.3 mg/l. An exception is the concentration of chlorides, which reaches 3330 mg/l and is higher than the concentration of sulphates.

The characteristics of acidic mine waters from this location, presented in the work of Bauerek et al. (2017) demonstrate that water L1 should be classified as transitional water – between shortly retained and stagnant water in the ditch over a long period of time (a few weeks to 1-2 months). Due to a higher pH and lower acidity, such waters are characterized by lower aggressiveness towards silty sediments filling the ditch, and, in consequence, a lower ability to decompose mineral phases and leach metals.

Waters sampled from anthropogenic reservoirs in the area of the former lignite mine in the Muscau Bend are characterized by a pH ranging from 2.6 to 3.5; a dominance of sulphates (from 148 mg/l to 1150 mg/l) in the water ionic composition and higher concentrations of iron, reaching 101 mg/l. The above mentioned features confirm that the chemical composition of these waters is shaped as a result of the AMD process. A much higher concentration of Ca^{2+} ion among cations, with very small contents of chlorides, causes that the examined AMD waters from Muscau Bend belong to the hydrogeochemical sulphate-calcium type (Fig. 2).

Table 1. Physico-chemical characteristics acidic waters

Parameter	Eastern part of the Upper Silesia Coal Basin		Southern part of the Muskau Bend				
	L1	L2	MB1	MB 2	MB 3	MB 4	MB5
pH	3.0	2.4	2.8	2.9	2.8	2.6	3.5
EC (µS/cm)	12 400	11 300	1 800	1 770	1 880	1 840	396
TDS (mg/l)	10 800	12100	1620	1690	1780	1480	218
Eh (mV)	510	547	496	546	544	567	396
Alkalinity (mg/l $CaCO_3$)	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Acidity tot. (mg/l $CaCO_3$)	1020	3820	650	483	578	750	103
Major ions (mg/l)							
Ca^{2+}	467	323	163	217	200	103	27.7
Mg^{2+}	340	417	29.6	35.7	33.8	21.2	5.71
Na^{+}	2250	1430	6.67	7.01	6.71	6.53	5.01
K^{+}	52.4	5.47	6.37	8.02	7.23	5.47	4.50
Cl^{-}	3330	1940	6.2	4.8	4.8	4.3	6.9
SO_4^{2-}	3270	5630	1040	1120	1150	1000	148
Fe^{2+}	23	15	39	1.2	3	2.4	1
Fe^{3+}	174	485	101	51.3	94.6	125.6	0.58
Al	63.3	227	3.96	28.0	18.4	24.8	4.85

Despite the features which are typical of AMD waters, the examined waters from the former lignite mine „Babina" are characterized by a relatively low concentration of total dissolved solids (from 218 mg/l to 1780 mg/l) and low acidity (from 103 mg/l $CaCO_3$ to 750 mg/l $CaCO_3$) compared to the acidic waters from the USCB.

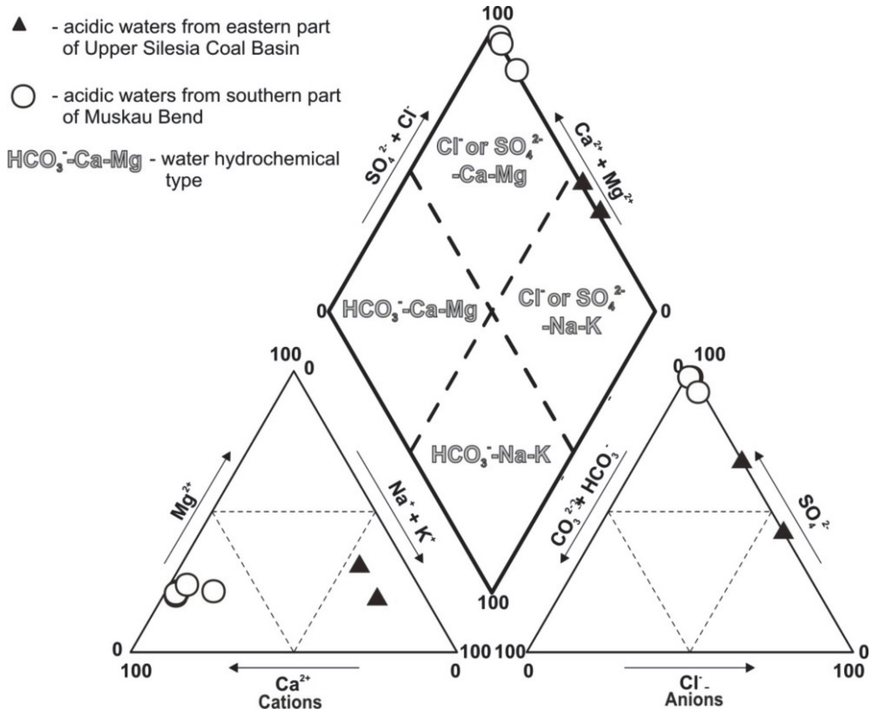

Fig. 2. Chemical composition of analyzed acidic waters from the eastern part of the Upper Silesia Coal Basin and the Muskau Bend

Low pH values of the waters subjected to investigations are related to the oxidation of pyrite contained in the waste shale of the Carboniferous in the coal mining waste pile in Libiąż as well as in Miocene loams, sands and pieces of lignite in the vicinity of water reservoirs of the Muscau Bend (Bozau et al. 2004, Bauerek et al. 2017). The first stage of water acidity occurs due to pyrite decomposition in the presence of atmospheric oxygen and water according to the following reaction (Lattermoser 2010):

$$FeS_2(s) + 3{,}5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

However, the major stage of water acidity takes place as a result of the bacterial oxidation of iron Fe^{2+} to Fe^{3+} with the participation of chemautotrophic acidicophilic microorganisms, e.g. *Acidicithiobacillus ferrooxidans* bacteria (Lattermoser 2010).

On the plots of dependencies between the concentrations of major parameters (SO_4, Al, Fe) and pH and acidity one can clearly see the separation of surface runoff waters from the eastern part of the USCB (Fig. 3). It is noteworthy that the use of acidity for differentiating the results allows us to more clearly separate waters from different locations than by using the pH parameter as a differentiating indicator. On charts showing the correlation between the concentrations of SO_4, Al, Fe_{tot} and acidity, points that represent samples of water from the Muscau Bend are grouped in a small area of relatively low contents of the parameters above mentioned. On the other hand, points representing acidic waters of the surface runoff from the area of the USBS confirm the results of previous investigations, indicating a high variability of water chemistry (Bauerek et al. 2017).

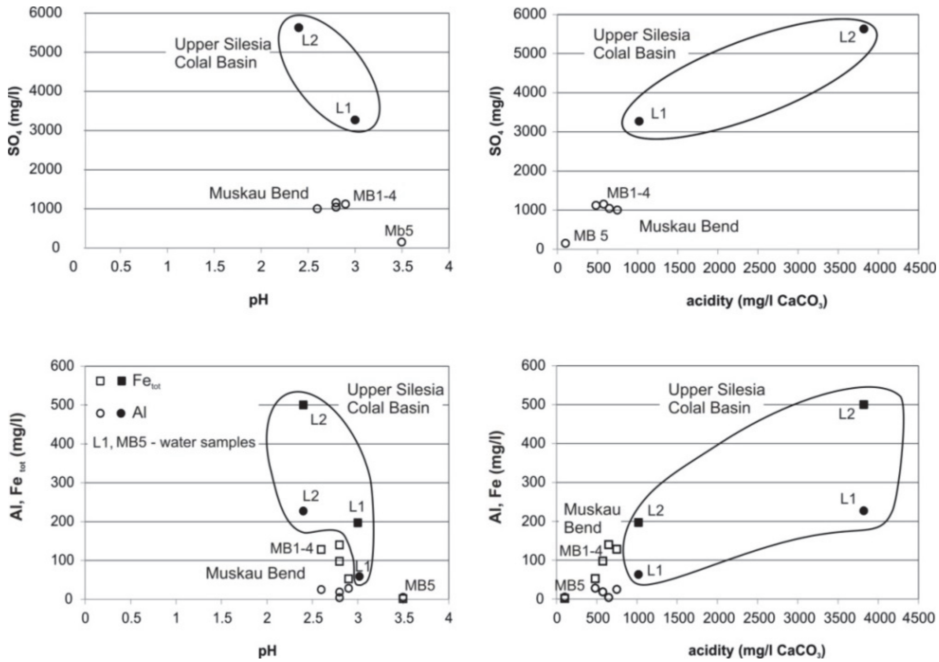

Fig. 3. Plots of SO_4, Al, Fe_{tot} concentrations versus pH and acidity of AMD waters

Concentrations of SO_4, Al. and Fe_{tot} grouped according to pH indicate that six out of seven water samples show a similar pH range, i.e. from 2.4 to 3.0, whereas sample MB5, which is characterized by the highest pH (3.5), clearly stands out from the remaining samples of waters collected from the Muscau Bend as it has the lowest concentration of SO_4 (103 mg/l) and Fe_{tot} (1.58 mg/l).

4.2. Measured concentration of REEs

Acidic runoff waters from the eastern part of USCB contain 3.3 to 93 times more REEs (contents of ΣREE for L1 is 478.53 µg/l and 1831.97 µg/l for L2) compared to waters filling the former lignite mining excavations (the contents of ΣREE ranges from 19.7 µg/l to 145.30 µg/l) (Table 2).

Table 2. Measured concentrations of REEs and ratios in the AMD waters of the Upper Silesia Coal Basin and the Muskau Bend

Parameter	Eastern part of the Upper Silesia Coal Basin		Southern part of the Muskau Bend				
	L1	L2	MB 1	MB 2	MB 3	MB 4	MB 5
	µg/l						
Light REE (La-Eu)							
La	65.0	209.1	5.10	14.10	15.20	31.00	15.00
Ce	181.0	687.7	8.60	22.00	24.00	64.00	26.00
Pr	24	95	0.80	1.70	2.00	6.40	2.50
Nd	107	416	2.80	5.50	6.50	24.00	9.20
Sm	25	103	0.50	0.80	0.90	4.30	1.60
Eu	5.3	23.6	0.10	0.20	0.20	0.90	0.40
Heavy REE (Gd-Lu)							
Gd	26.9	102.4	0.60	1.2	1.40	4.80	2.20
Tb	3.4	15.6	0.10	0.20	0.20	0.70	0.40
Dy	19.6	84.6	0.50	1.00	1.30	4.10	2.10
Ho	3.3	14.7	0.10	0.20	0.20	0.80	0.40
Er	9.1	39.8	0.20	0.50	0.60	2.20	1.20
Tm	1.2	5.0	0.05	0.10	0.10	0.30	0.10
Yb	7.2	31.0	0.20	0.30	0.30	1.60	0.80
Lu	1.0	4.2	0.05	0.05	0.05	0.20	0.10
ΣREE	478.53	1831.97	19.70	47.85	52.95	145.30	62.00
LREE	406.92	1534.68	17.90	44.30	48.80	130.60	54.70
MREE (Sm-Dy)	79.98	329.43	1.80	3.40	4.00	14.80	6.70
HREE	71.61	297.30	1.80	3.55	4.15	14.70	7.30
LREE/HREE	5.68	5.16	9.94	12.48	11.76	8.88	7.49

In the examined waters the content of HREEs is much lower compared to LREEs, but in the waters from the USBC it is two times higher (the average value of LREE/HREE is 5.4) compared to the waters from the Muskau Bend (the average value of LREE/HREE is 10.1) (Table 2, Fig. 4). In terms of contents of individual REEs, the examined waters are similar. In the acidic waters from the USBC and the Muskau Bend the dominant element is Ce, the contents of which reach 181.0 μg/l and 687.7 μg/l and from 8.6 μg/l to 64 μg/l, respectively. Nd (the contents 107 μg/l and 416 μg/l) and La (the contents 65 μg/l and 209.1 μg/l) have the second and third place in the USBC waters, while in the acidic waters from the Muskau Bend these elements occur in a reverse order: La (5.1-31 μg/l) prevails over Nd (2.8-24 μg/l).

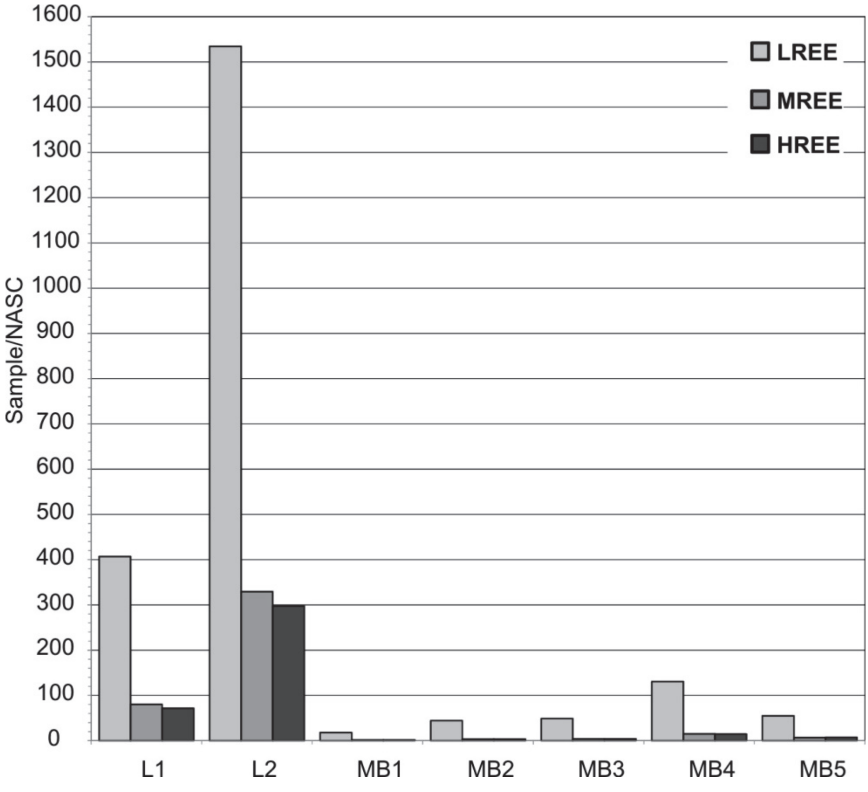

Fig. 4. Measured concentrations of LREEs, MREEs and HREEs in acidic waters

Concentrations of REEs in acidic waters sampled from the vicinity of coal waste pile are characterized by high variability, which probably results from different time of acidic water retention in the vicinity of silty sediments, being the carriers of REEs (Kokowska-Popławska 2012, Zhao et al. 2007). A comparison of shortly retained water, represented by sample L1, with stagnant waters, represented by sample L2, revealed that the acidic runoff waters were 4 times (from 3.2 to 4.5 times) richer in REEs, which was accompanied by a 3.7-fold increase in acidity, lowered pH – from 3.0 to 2.4, and an increased content of soluble components (Table 1).

A comparison of REEs contents in acidic waters L1 and L2 with the results of tests for AMD waters from other locations indicates that the waters from the eastern part of USCB have a relatively higher content of REEs. For example, water L1 has a higher total concentration of ΣREEs than in the natural standard reference water sample PPREE 1 (Animas River, Colorado, USA), where the value of ΣREEs reaches 457.73 μg/l (Verplanck et al. 2001). On the other hand, the acidic water represented by sample L2 is characterized by ΣREE concentration of 1831,9 μg/l, which is 4 times higher than that in the reference water. The total concentration of ΣREEs in the acidic runoff waters from the mining waste pile in the eastern part of USCB is higher than the values quoted for AMD waters pumped from Sitai coal mine (north China), where the average total value of ΣREEs is 61.2 μg/l (Zhao et al. 2007). The recorded total concentrations of ΣREEs in samples L1 and L2 are on a comparable level or higher than the total concentration of REEs in waters flowing from the former Zn-Pb mine (ΣREEs 1940 μg/l) in Montevecchio/Sardinia/Italy (Cidu et al. 2011) and in waters from lignite open pit mines in Lusatia/Germany (ΣREEs = 770 μg/l) (Bozau 2004). Whereas REEs concentrations in acidic runoff waters are much lower than in the waters from the former uranium mine in Thuringia/Germany (ΣREEs = 8150 μg/l) (Grawunder & Merten 2012), Osamu Utsumi uranium mine in Brazil (ΣREEs = 29 000 μg/l) (Miekeley et al. 1992).

REEs concentrations in acidic runoff waters from USCB are much lower comparing to the REEs concentrations in some shallow water bodies in Wiśniówka quaries in south-central Poland (pools: ΣREEs = 17 916 μg/l, dewatering ditch ΣREEs = 8519 μg/l). However periodically (depending on the residence time), the sum of REEs recorded in the ditches in vicinity of the coal waste pile (USCB) is higher than in waters from mine pit lakes (Podwiśniówka pit lake ΣREEs = 684 μg/l, Wiśniówka Duża pit lake ΣREEs = 219 μg/l) (Migaszewski et al. 2019). This may suggest that the two mentioned shallow water reservoirscontain more aggressive waters with greater leaching ability of REE-containing minerals.

AMD waters form the southern part of the Muskau Bend area affected by former mining of lignite – they are less rich in REEs due to dilution by ground waters. Concentrations of ΣREEs in waters from abandoned open pit mining excavations and depressions caused by mining subsidence varied from 19.7 to

145.3 µg/l. Such results are similar to REEs contents in streams and aquifers affected by AMD reported from Spain and USA (Olias et al. 2008, Verplanck et al. 2004).

4.3. NASC-normalized concentration of REEs

North American Shale composite (NASC), (Haskin et al. 1968, Gromet et al. 1984) was used for normalization of REEs concentrations in acidic waters. Plots of shale normalizing the REE patterns of AMD waters from the USCB and the Muskau Bend are presented in the Figures 5 and 6, respectively.

The REE NASC-normalized pattern of acidic runoff waters (L1 and L2) shows a positive anomaly of MREEs with Sm, Eu, Gd and Tb enrichment (Fig. 5), and depletion in LREEs. This is the reverse relationship when compared with measured REE concentration.

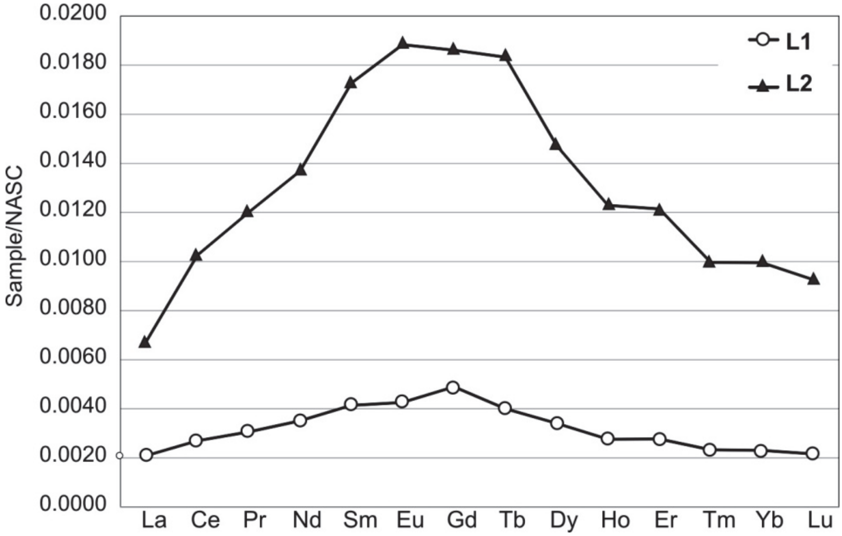

Fig. 5. NASC-normalized REE pattern in acidic runoff waters from the eastern part of the Upper Silesian Coal Basin

A similar roof-shaped NASC-normalized REE pattern was found in AMD pit waters located within Upper Cambrian quartzite in the Holy Cross Mountain and for acidic fresh water lake on Axel-Heiberg Island (northwest Canada) (Migaszewski et al. 2014, 2016, 2019), Johannesson & Lyons 1995).

Low values of La_{NASC}/Sm_{NASC} concentration ratios (0.39 and 0.5) in acidic runoff waters indicate LREEs depletion, while values of Sm_{NASC}/Yb_{NASC} ratios (1.73 and 1.80) point domination of MREEs group (Table 3).

The NASC normalized plots of waters L1 and L2 are very similar in shape but they are shifted relative to the axis of concentration. This suggests that processes which shape REEs concentrations are the same but at a different stage. Shortly retained water with a higher pH and lower acidity are less rich in REEs than aggressive, strong acidified waters, staying in a ditch for a relatively long time (weeks or even months).

Table 3. NASC normalized REEs concentrations ratios in AMD waters of the Upper Silesia Coal Basin and the Muskau Bend

Parameter	Eastern part of the Upper Silesia Coal Basin		Southern part of the Muskau Bend				
	L1	L2	MB 1	MB 2	MB 3	MB 4	MB 5
$LREE_{NASC}$/ $HREE_{NASC}$	0.80	0.75	0.89	1.09	1.10	0.94	0.79
La_{NASC}/ Yb_{NASC}	0.91	0.68	2.55	4.71	5.07	1.94	1.88
La_{NASC}/ Sm_{NASC}	0.50	0.39	1.96	3.39	3.25	1.39	1.80
Sm_{NASC}/ Yb_{NASC}	1.80	1.73	1.30	1.39	1.56	1.40	1.04
Ce/Ce_{NASC}	1.05	1.10	0.97	0.98	0.97	1.06	0.97
Eu/Eu_{NASC}	1.13	1.18	0.94	1.04	0.85	1.00	1.01
Gd/Gd_{NASC}	1.30	1.16	1.28	1.42	1.35	1.22	1.26
Tb/Tb_{NASC}	1.06	1.15	1.38	1.53	1.25	1.15	1.49

The NASC-normalized REE concentration patterns of acidic waters in post-mining lakes from the southern part of the Muskau Bend differs significantly from that determined for the acidic runoff waters in the USCB. Samples MB1-MB5 were characterized by two visible positive anomalies of the contents of LREEs, especially La and Ce, and enrichment with Gd, Tb and Dy, included in MREEs (Fig. 6). A similar NASC-normalized pattern of REE contents was found in the waters from artificial post-mining lakes, resulting from lignite exploitation, in the eastern part of Germany (Bozau et al. 2004).

NASC-normalized concentration ratios computed for acidic waters from Muskau Bend point strong positive anomaly of LREE enrichment (La_{NASC}/Yb_{NASC} ratios from 1.88 to 5.07). MREEs positive anomaly is marked by Sm_{NASC}/Yb_{NASC} ratios varied from 1.30 to 1.56 (Table 3).

Of the individual MREEs elements, only Gd and Tb, in acidic waters collected from the Muskau Bend, are significantly enriched (> 1.2), relative to NASC concentrations (Table 3). Gd/Gd_{NASC} and Tb/Tb_{NASC} ratios are from 1.22 to 1.42 and from 1.25 to 1.53, respectively.

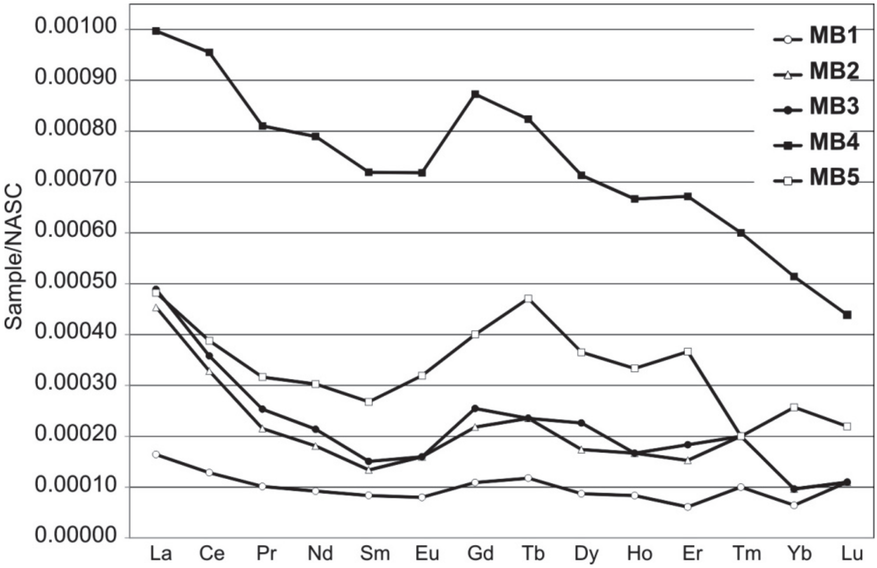

Fig. 6. NASC-normalized REE concentration patterns in acidic surface waters from the southern part of the Muskau Bend

Concentrations of three major REEs (La, Ce and Nd) in acidicic waters from two coal mining sites, grouped according to pH and acidity, have been presented in Fig. 7. Acidic waters from the eastern part of the USCB on the plot of La, Ce and Nd versus acidity are a clearly separate group, located in the range of relativley high REE concentrations, accompanied by high acidity (> 1000 mg/l $CaCO_3$).

Presentation of the concentrations of REEs grouped according to pH indicates that in the vicnity of the coal mining waste pile the process of REEs release from rock matrix in contact with acidic waters occurs with greater intensity. Due to higher water aggressiveness (acidity 1020 and 3820 mg/l $CaCO_3$), the concentrations of all REEs (ΣREE 478.53 µg/l and 1831.97 µg/l) in acidic runoff waters from the USCB are several times higher than in the flooded lignite mining excavations (ΣREE from 19.7 µg/l to 145.30 µg/l).

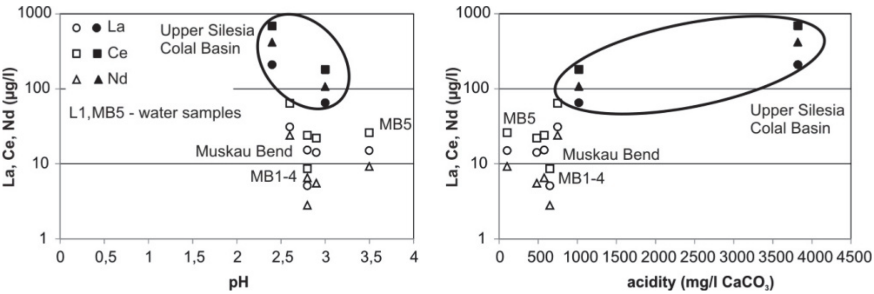

Fig. 7. Plots of La, Ce and Nd concentrations against pH and acidity in AMD waters from the USCB and the Muskau Bend

Considerable differentiation in REEs concentrations in the investigated acidic waters is probably also related to the local hydrodynamic system. Acidic water samples from the ditch surrounding the coal waste pile are slightly diluted with rainwaters, originating directly from precipitation. Most probably waters from the flooded lignite mining excavations are diluted with underground waters, as these reservoirs are not separated from the aquifer.

5. Conclusions

Acidic runoff waters from areas in the vicinity of coal waste piles (Upper Silesia Coal Basin-USCB) and flooded lignite mining excavations (Muskau Bend) are an example of AMD waters rich in rare earth elements (REEs). High concentrations of REEs in acidic waters from the USCB result mainly from the high aggressiveness of acidic waters in relation to loamy sediments filling the drainage ditch, which are the source of REEs, and increase as the water remains in the ditch.

A characteristic feature of acidic waters from the two sites is an evident dominance of the LRREs (La-Eu) over the fraction of the HREEs (Gd-Lu). In the USCB waters this disproportion is twice higher than in the waters from the Muskau Bend. NASC-normalized REE concentration pattern concentrations show that the waters from the USCB are rich in MREEs (Sm, Eu, Gd and Tb), while the waters from the Muskau Bend are characterized by a positive anomaly of LREEs (La and Ce) and a less marked anomaly of MREEs (Gd, Tb and Dy).

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Abstract

The aim of the research was comparison rare earth elements contents in acidic waters related to coal mining in the eastern part of the Upper Silesian Coal Basin (USCB), southern Poland, and the former lignite mining in the Polish part of the Muskau Bend. Acidic runoff waters flowing down from mine waste piles in the USCB are enriched with REEs (ΣREEs 478.5 and 1831.9 μg/l) compared to waters filling old lignite mining excavations (ΣREEs 19.7-145.3 μg/l). High concentrations of REEs in acidic waters from the USCB result from their high aggressiveness (acidity 1020 mg/l $CaCO_3$ and 3820 mg/l $CaCO_3$, pH 2.4 and 3.0) to loamy sediments being a source of REEs, and increase as the time of their contact increases. Concentrations of NASC-normalized REEs show that waters from the USCB are enriched in MREEs (Sm, Eu, Gd and Tb), while the waters from the Muskau Bend are characterized by a positive anomaly of LREEs (La and Ce) and a less marked anomaly of MREEs (Gd, Tb and Dy).

Keywords:
acid mine drainage (AMD), rare earth elements (REE), coal, lignite, acidity, sulfates

Zawartości pierwiastków ziem rzadkich w kwaśnych wodach związanych z górnictwem węgla kamiennego i węgla brunatnego (Górny Śląsk i Łuk Mużakowa, południowa Polska)

Streszczenie

Celem badań było porównanie zawartości pierwiastków ziem rzadkich w kwaśnych wodach związanych z wydobyciem węgla kamiennego, we wschodniej części Górnośląskiego Zagłębia Węglowego (GZW) oraz związanych z dawnym wydobyciem węgla brunatnego w polskiej części Łuku Mużakowa. Kwaśne wody spływu powierzchniowego z hałd odpadów górniczych GZW są wzbogacone w pierwiastki ziem rzadkich (REE) (ΣREE 478,5 i 1831,9 μg/l) w porównaniu do wód wypełniających stare wyrobiska górnicze węgla brunatnego (ΣREE 19,7-145,3 μg/l). Wysokie stężenia REE w kwaśnych wodach z GZW wynikają z ich wysokiej agresywności (kwasowość 1020 mg/l $CaCO_3$ i 3820 mg/l

$CaCO_3$, pH 2,4 i 3,0) względem ilastych osadów będących źródłem REE i rosną wraz z upływem czasu ich kontaktu z osadami. Stężenia pierwiastków ziem rzadkich znormalizowane do północnoamerykańskiego łupku złożonego (NASC) pokazują, że kwaśne wody z GZW są wzbogacone w pośrednie pierwiastki ziem rzadkich (MREE) (Sm, Eu, Gd i Tb), podczas gdy wody z Łuku Mużakowa charakteryzują się dodatnią anomalią stężeń lekkich pierwiastków ziem rzadkich LREE (La i Ce) i mniej wyraźnymi anomaliami pierwiastków pośrednich MREE (Gd, Tb i Dy).

Słowa kluczowe:
kwaśny drenaż górniczy, pierwiastki ziem rzadkich, węgiel, węgiel brunatny, kwasowość, siarczany

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Environmental Protection in the Aspect of Preventing Collisions with Wild Boar, Roe Deer, Red Deer Based on Selected Railway Lines in Wielkopolska

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1. Introduction

Development of road and railway infrastructure results in an increased landscape fragmentation. Due to economic considerations and a lack of adequately conducted ecophysiographic studies or environmental impact analyses new investments in the transport infrastructure transect habitats where forest animals feed and live (Burdzik & Wojtas 2016, Iwiński et al. 2019). Newly designed transport networks are being constructed while attempting to ensure the longest possible straight stretches of these routes, as a result of which ecosystems are directly divided even when it is attempted to compensate for the process of their defragmentation by installing passive protection measures against animal intrusion (Stolarski & Żyłkowska 2011). The intent to develop transport networks facilitating ever increasing maximum design speeds has led to a greater probability of collisions. Animals moving in the area of modernised railway tracks, on which trains travel at speeds reaching 160 km/h need much more time to respond, thus a higher percentage of animals collide with approaching trains. The incidence of collisions is limited by the application of various protection methods. These include passive measures such as animal passages, fencing or even noise barriers as well as active measures, e.g. successfully used wildlife protective devices such as UOZ-1 using sounds of frightened animals as a deterrent (Werka et al. 2013). Despite assurances on 100% effectiveness of passive protection methods against animals, collisions are an inevitable element of transport networks and account for a significant percentage of all delays and exclusion of vehicles from operation.

Events involving game animals are relatively difficult to identify and categorise. The primary problem is related with the determination of causes for animal migration in areas of transport infrastructure. This paper presents identified factors affecting the frequency of collisions of big forest mammals with trains over selected fragments of five railway lines located in the Wielkopolska region. Spatial and statistical analyses were used to determine what elements of landscape subjected to fragmentation affect the probability of such collisions.

2. Review of literature

Development of various elements of transport infrastructure provides several advantages both to the society and economy (Badyda 2010). However, introduction of new elements into the existing landscape leads to negative effects, suffered by animals living in a given ecosystem (Burdzik & Wojtas 2016). Ecological barriers produced as a result of construction and modernisation of transportation networks generate negative ecological effects such as e.g. collisions between means of transport and migrating animals (Czarnecka 2016).

The phenomenon of natural migration corridors being transected by road infrastructure may be limited thanks to the development of animal crossings along newly constructed or modernised fragments of transportation networks or along those fragments at the greatest risk of collisions. The high number of animal passages constructed in Poland for forest animals is unique on the European scale (Nowacka 2014). Obviously it has been the effect of the intention to preserve forests, meadows or wetlands relatively little transformed by human activity, constituting natural habitats and feeding grounds for animals (Burdzik & Wojtas 2016). Despite the considerable number of animal passages constructed in Poland (2300 such structures) (Nowacka 2014) it is still advisable to investigate the effectiveness of their use, since many of them remain unused, primarily due to the inadequate parameters of these facilities (Burdzik & Wojtas 2016).

Based on the results of analyses conducted in the area of railway tracks we may indicate basic causes for collisions between vehicles and forest animals. These may include the intensity of traffic, the width and speed of vehicles, mobility of animals and technical parameters of railway tracks. As it has been observed (Olkowska et al. 2015), the lowest number of collisions seems to be recorded for narrow-gauge single-track lines with low design speeds, because migrating animals adequately early receive the stimulus preventing a collision. Similar observations indicate that traffic intensity and migratory activity of animals are the primary factors determining the incidence of such collisions (Rolandsen et al. 2011). In fact migratory behaviour of individual species varies greatly, which results in the need to conduct separate analyses. Wild boars typically colonise areas located in the vicinity of urbanised regions (Merino et al. 2009).

Frequent foraging in areas inhabited by humans, mainly in the suburbs of cities, is associated with high activity of animals along transport routes, which leads to a greater number of collisions (Jansen et al. 2007). A factor resulting in an increased probability of collisions is connected with increasing populations of wild animals and the adaptation of wild animals to vehicle traffic along with their perception of vehicles as constituting no threat (Dodd et al. 2007). Observations of animal behaviour seem to indicate that transport routes are no longer barriers for wild boars, while they are a significant limitation for red deer and for roe deer (Kušta et al. 2017).

Due to the high intensity of vehicle traffic acting as a barrier, a large number of vehicles travelling within a given stretch of the transport network may act on animals as a deterring stimulus preventing them from crossing the pavement (Seiler 2005). Similarly as roads, railway lines have a negative impact on the natural environment and constitute a barrier to migration of forest animals. However, in view of the relatively low traffic intensity (in comparison to roads and motorways) they are very often a part of the habitat inhabited by animals, which cross such barriers several times a day or even forage in grassy stretches, which by being mowed by road maintenance services are an excellent substitute for pastures (particularly for roe deer and hares) (Stolarski & Żyłkowska 2011). Analyses of relationships between traffic intensity and maximum design speeds indicate that for railways we may point to the tracks as constituting a barrier. The highest number of recorded tracks of even-toed ungulates was found in the buffer zone along stretches of railway tracks with the lowest traffic intensity, while the smallest number of traces of animal life may be observed along intensively used fragments of the transport network (Olkowska et al. 2015). In the case of railway tracks a factor determining the number of collisions involving animals is connected with the train speed. As indicated by Kulińska et al. (2017), fragments of the stretches with speeds of 40-50 km/h are characterised by the lowest number of events, since animals are able to respond promptly enough. In contrast, at speeds exceeding 100 km/h the time needed by foraging animals to respond is too long, thus leading to collisions, since they do not manage to leave the tracks (Stolarski & Żyłkowska 2014, Kulińska et al. 2017).

3. Study area

The Wielkopolskie province is located in central-western Poland and covers an area of 29 826.50 km^2. The relief is the result of two glaciations: the Saalian II glaciation, which formed a relatively uniform southern part of the province devoid of lakes, and the Würm glaciation responsible for the formation of the Pomeranian, Poznań and Gniezno Lake Districts. The Wielkopolskie province lies in the basin of the Warta river (88% drainage) as well as the basins of the

Barycz, Krzycki Rów and the Obrzyca. The northern part of the province is dotted by almost 800 postglacial lakes. Climatic conditions in the Wielkopolska are mild, with an average annual temperature of 8.2°C and mean annual precipitation total ranging from 500 to 550 mm (Liberacki & Szafrański 2013). However, in the eastern part of the province we can observe progressing soil droughts commonly associated with the term of "steppe development" caused by deforestation and intensive operation of brown coal mines (Dzięciołowski 1979).

The primary function of land use in the Wielkopolska region is connected with agriculture, with agriculturally utilised areas covering 65% of the total area. The predominant soils in the Wielkopolska are rusty podsolic soils (60%), lessivé and brown soils (20%) and wetland soils. Almost 26% of the province area is covered by forests (766.2 thousand hectares as of 31.12.2012, according to Central Statistical Office). The main forest complexes include the Zielonka and Notecka Forests. Due to the urbanisation pressure and suburbanisation processes (Szczepański et al. 2013) almost 58% forests have been covered by various forms of legal protection (Zydroń & Bober 2013).

Selected fragments of railway tracks are lines varying in terms of their technical parameters, surrounding areas and the technological standard. Route 356 of the Poznań – Bydgoszcz line is a non-electrified segment of a single-track railway line of 128 km in length, since 2004 used only within the boundaries of the Wielkopolskie province. In 2011 it was modernised in the Poznań – Wągrowiec section (52 km) and it is used by the Koleje Wielkopolskie railways. The maximum design speed in that segment is 120 km/h. Line 356 runs in the vicinity of areas of considerable nature value (the Zielonka Forest, the Warta river valley) (Stachowski 2008). The line is used by passenger trains carrying approx. 3.6 thousand passengers daily. The Wielkopolska segment of railway line no. 351 is a railway trunk line within route E 59. It is a double-track, fully electrified railway route with maximum design speeds reaching 150 km/h. Its Wielkopolska segment runs through the Puszcza Notecka Forest and crosses the Warta river. Its larger part is located in agriculturally utilised areas. The analysed fragment of line 271 links Poznań with Wrocław. It is one of the most intensively used segments of the railway tracks in Poland. The double-track, fully electrified Wielkopolska segment, in recent years significantly modernised is located at a close distance to Poznań and runs through the buffer zone of the Wielkopolski National Park, along the Warta river and further through areas intensively utilised by agriculture. This line is characterised by maximum speeds reaching 160 km/h. A part of trunk line no. 3 links Warszawa and Kunowice divided into two sections (from Kunowice to Poznań called line 357 and from Poznań to Warszawa) for the purposes of the study. The travelling speeds reach 160 km/h. The line is a double-track and fully electrified segment equipped with passive wildlife protective measures such as overpasses and underpasses in the route. It runs mainly through intensively utilised agricultural areas.

Fig. 1. Map of analyzed railway lines with accident locations

4. Empirical material and research methods

Analysed empirical material comprised data recorded by services of the Polish Railway Lines on collisions between trains and animals, which rapidly entered the tracks or tried to cross them. The database collected from PLK PKP S.A covered 6 884 events in the period from 1.01.2007 to 15.06.2017. In view of the selected study area the data were subjected to a preselection process, which limited these events to those recorded for lines located within the Wielkopolskie province. The total number of collisions in the Wielkopolska region was 1269 events (18.5% all observations), for the final analysis a total of 602 events were selected, reported for 5 sections of the railway tracks being the transportation trunk for the Wielkopolskie province linking Poznań with neighbouring provincial capitals. The length of the analyzed sections was less than 503 km The empirical material was supplemented following the adopted methodology with attributes used in statistical analyses. Based on the available location data per 1 km^2 the following types were shown: forests, agriculturally utilised areas, surface waters and urbanised areas. The research methodology comprised two stages: spatial and statistical analyses. Spatial analyses were performed using GIS open-source software (QGIS ver. 2.12.2 Lyon). Vector information on the reported collisions

(PLK PKP S.A.) was integrated with open-layer data (OpenStreetMap, mapa.plk-sa.pl) concerning land use (forests, agriculturally utilised areas, surface waters, urbanised areas) and networks of railway tracks (WMS, vector data accessed from NaturalEarth). Using tools of spatial analyses (heating maps) it was decided to select for further analyses five segments of railway tracks linking the Poznań Main Station with the boundaries of the Wielkopolskie province (lines 3, 271, 351, 356). Based on the methodology proposed by Malo et al., (2004) the selected fragments of railway tracks were divided into equal segments of 1 km. Applying geoprocessing (QGIS, QChainage) the railway tracks were divided and buffer zones of 1 km^2 were established for them. Next the following attributes were determined for them: the number of events (ranging from 0 to 17, where n = 571), the presence of a specific land use function in the buffer zone: surface waters, forest complexes, agriculturally utilised areas and urbanised areas. The presence of a given element of landscape in the buffer zone was indicated in the dichotomic scale (1 when a given function was observed in the buffer zone, 0 when it was absent) using spatial nodes (QGIS, NNJoin) and the distances between vector layers were exported to the CSV file as source material for statistical analyses.

The independence of the variation in the levels of two quantitative variables may be verified using the chi-square test as a test of trait independence (Zydroń & Kayzer 2015). Let us assume that we are investigating independence of events in terms of differences in the number of incidents divided according to analysed animal species (roe deer, wild boar, red deer). Let us assume that events are assigned to separate groups in terms of the division into species. The obtained distribution of numbers forms the so-called four-fold table (Farreas et al. 2005). At such defined divisions verification was conducted for the hypotheses that in the analysed experimental sample the classification of events to investigated groups varies depending on the animal species. One of the aims of the analyses was to indicate whether a change in the frequency of events involving animals of individual species (wild boar, roe deer, red deer) is influenced by the distribution of populations in the levels of analysed factors. The distinguished factor is characterised by the size of the fraction of collisions involving animals in the investigated buffer zone (0 – the event was not recorded, 1 – the event was recorded).

5. Results

Analyses of the collected data on the events show that the greatest percentage of events 68% (391 events) are collisions involving roe deer. Slightly below 21% (118 events) were caused by collisions with wild boars. Red deer rapidly entering the tracks accounted for the lowest percentage share (11%, 62 events) in all the observed collisions.

Based on the results presented in the Table (Tab. 1) it was observed that the frequency of events involving the identified animal species is significantly influenced by buffer zones characterised by the presence of developed areas. It was found that 66% among all collisions with red deer, 77% involving roe deer and 83% with wild boars recorded in buffer zones comprising areas, in which buildings are found.

Table 1. Four-plot table including analyzed species

	forests		waters		developed areas		agricultural land	
	0	1	0	1	0	1	0	1
Wild boar	13	105	35	83	20	98	83	35
Red deer	7	55	21	41	21	41	46	16
Roe deer	45	346	110	281	90	301	259	132
total	65	506	166	405	131	440	388	183
χ^2	0.0224		0.880		0.659		1.94	
p	0.99		0.64		0.04		0.38	

When investigating the other factors no dependencies were found between their levels and the frequency of events involving animals of individual species. Approximately 89% all events with the participation of animals were recorded in the buffer zone comprising forested areas, 70% in the buffer zone with surface waters, while 30% in the buffer zone containing utilised agricultural areas (Table 1).

Analyses of events involving wild boars showed that the greatest number of collisions was recorded in the area of railway tracks located in forest complexes as well as developed areas and near surface waters. Analyses of collisions with wild boars given in four-fold tables identified pairs of variables, which are interdependent (Table 2). It was recorded that the number of collisions depends on the location connected with the simultaneous presence of forested areas and surface waters. It was observed that 67% collisions took place in the buffer zones, in which surface waters were simultaneously found with forests, while 22% events – in the case of the presence of forests and absence of surface waters. Additionally, at the absence of forests it was recorded that 8% events occurred in the situation when buffer zones contained no surface waters, while 3% – at the presence of surface waters.

The next pair of dependent variables was connected with the buffer zones with urbanised areas and surface waters. It was found that 55% events involving wild boars took place in the buffer zones comprising both surface waters and developed areas, while 28% events were reported in the buffer zones comprising urbanised areas and no identified surface waters. In turn, 15% observations were connected with the buffer zones with surface waters at the absence of building development (Table 2).

Moreover, when investigating the other pairs of buffer zones for events involving wild boars the results were not found to be significantly dependent on the interaction of both factors. Analyses of the results obtained for the buffer zones connected with arable fields and forests it was observed that the number of events is significantly higher for the presence of forests and absence of arable fields than at the simultaneous occurrence of both buffer zones.

Table 2. A contingency table for wild boar events

		waters		developed areas		agricultural land	
		0	1	0	1	0	1
forests	0	9	4	1	12	8	5
	1	26	79	19	86	75	30
	χ^2	10.96		0.889		0.542	
	p	0.001		0.34		0.46	
agricultural land	0	23	60	15	68		
	1	12	23	5	30		
	χ^2	0.510		0.251			
	p	0.45		0.62			
developed areas	0	2	18				
	1	33	65				
	χ^2	4.46					
	p	0.03					

Analysis of events involving roe deer indicated (Table 3) that the greatest number of collisions was recorded in the buffer zones containing forests (346), built-up areas (301) and waters (281).

Table 3. A contingency table for roe deer events

		waters		developed areas		agricultural land	
		0	1	0	1	0	1
forests	0	23	22	15	30	24	21
	1	87	259	75	271	235	111
	χ^2	13.3		3.05		3.79	
	p	<0.001		0.08		0.05	
agricultural land	0	76	183	62	197		
	1	34	98	28	104		
	χ^2	0.556		0.367			
	p	0.46		0.54			
developed areas	0	24	66				
	1	86	215				
	χ^2	0.124					
	p	0.72					

In the analyses of events involving roe deer variability related to the buffer zones with forested areas and surface waters as well as forested areas and arable land was observed to be interdependent. It was found that 66% all events with roe deer were reported at the simultaneous presence of forested areas and surface waters. In turn, at the presence of surface waters and absence of buffer zones related to forests the number of events with roe deer decreased by 2/3. Moreover, in the situation when surface waters and forests were not found simultaneously in the buffer zones or waters were found at the absence of forested areas the share of reported events was approx. 6% each. When investigating the other pairs of distinguished variables in terms of the frequency of events involving roe deer no interdependence was observed between their levels (Table 3.). Analyses of interactions between forests and fields showed the highest number of events for the buffer zones of forests at the absence of arable fields.

Events with the participation of red deer accounted for the lowest percentage of events involving large game. Only 7 such events were recorded when the buffer zones contained no forested areas (Table 4). Analyses of events caused by red deer indicated one pair of dependent variables, i.e. the presence of surface waters and forested areas in the buffer zones.

Table 4. A contingency table for red deer events

<table>
<tr><td></td><td></td><td colspan="2">waters</td><td colspan="2">developed areas</td><td colspan="2">agricultural land</td></tr>
<tr><td></td><td></td><td>0</td><td>1</td><td>0</td><td>1</td><td>0</td><td>1</td></tr>
<tr><td rowspan="4">forests</td><td>0</td><td>5</td><td>2</td><td>2</td><td>5</td><td>4</td><td>3</td></tr>
<tr><td>1</td><td>16</td><td>39</td><td>19</td><td>36</td><td>42</td><td>13</td></tr>
<tr><td>χ^2</td><td colspan="2">4.97</td><td colspan="2">0.094</td><td colspan="2">1.20</td></tr>
<tr><td>p</td><td colspan="2">0.03</td><td colspan="2">0.75</td><td colspan="2">0.27</td></tr>
<tr><td rowspan="4">agricultural land</td><td>0</td><td>16</td><td>30</td><td>17</td><td>29</td><td></td><td></td></tr>
<tr><td>1</td><td>5</td><td>11</td><td>4</td><td>12</td><td></td><td></td></tr>
<tr><td>χ^2</td><td colspan="2">0.066</td><td colspan="2">0.758</td><td></td><td></td></tr>
<tr><td>p</td><td colspan="2">0.75</td><td colspan="2">0.38</td><td></td><td></td></tr>
<tr><td rowspan="4">developed areas</td><td>0</td><td>8</td><td>13</td><td></td><td></td><td></td><td></td></tr>
<tr><td>1</td><td>13</td><td>28</td><td></td><td></td><td></td><td></td></tr>
<tr><td>χ^2</td><td colspan="2">0.253</td><td></td><td></td><td></td><td></td></tr>
<tr><td>p</td><td colspan="2">0.62</td><td></td><td></td><td></td><td></td></tr>
</table>

The largest number of events (63%) took place at the simultaneous presence of surface waters and forested areas in the buffer zones. A much higher number of collisions with red deer were recorded in the situation when the buffer zones contained forests at the absence of surface waters compared to the buffer zones containing no forests at the presence of surface waters. In the case when none of these land use types were found in the buffer zone as little as 8% collisions were recorded. No pairs of dependent variables were observed among the other variables (Table 4).

6. Discussion of results

The highest number of collisions in the areas of the analysed segments of railway tracks was observed for roe deer (391), with wild boars ranking second (118), while the lowest number of accidents was caused by red deer (62). The frequency of collisions with animals (with no division into species) on railroad tracks was influenced by the simultaneous presence of forest complex, developed areas and surface waters in these buffer zones. Obtained research results are partly consistent with those presented by Jansen et al. (2007) and Merino et al. (2009), who observed increased migration of wild boars in urbanised areas and areas affected by suburbanisation; however, their data did not concern deer species.

The simultaneous presence of two factors increases the probability of collisions. The presence of buffer zones including forested areas overlapping with buffer zones with surface waters, as well as built-up areas overlapping with surface waters results in an increased frequency of collisions involving wild boars. This is confirmed by studies by Malo (2004) and Seiler (2005), who observed an increased number of collisions in areas of high biodiversity, as well as an increased number of such observations in areas covered by forests. However, they stated that the presence of built-up areas reduces the frequency of such events. Collisions with roe deer and red deer are characterised by two and one pair of dependent variables. In those cases the highest number of events took place at the simultaneous presence of forests and surface waters in the distinguished buffer zones, while in the case of roe deer it was in the buffer zones where agriculturally utilised areas and forest complexes were simultaneously present.

Based on the conducted studies we may formulate a thesis that the locations where collisions involving forest animals are reported are dependent on the animal species. This may be observed between red deer and wild boars, with differences in the pairs of dependent variables. For this reason studies on factors affecting the frequency of events involving forest animals should be conducted for each species separately. Based on the conducted investigations it may be stated that spatial planning may reduce the frequency of collisions. Analyses of individual segments of the railway tracks using contingency tables we may specify, in which areas a higher frequency of events will be recorded and thus the application of passive and active methods preventing collisions with wild animals may be considered in these fragments of the railway lines.

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Abstract

Collisions with forest animals constitute a considerable percentage of all events recorded for railway lines. Due to the development of infrastructure and higher technical parameters of tracks, accidents involving forest animals cause considerable economic losses and lead to significant delays in railway service. Appropriate management of areas neighbouring transport networks as well as application of both active and passive methods preventing animals from suddenly entering the road may limit a further increase in the number of such events and reducing negative environmental effects due to animal mortality. The paper presents an analysis whether and if so, which elements of landscape affect the frequency of collisions involving forest animals and whether by properly managing and securing these areas there is a possibility to prevent animal intrusion on communication networks. Using spatial analyses in the GIS environment (spatial nodes, topological relationships) as well as statistical analyses (contingency tables) it was indicated which pairs of factors determine an increase in the frequency of events involving roe deer, red deer and wild boars. It was proposed to apply the 0.1 system to determine the incidence of observed collisions in the buffer zone characterised by a given management function (forested areas, surface waters, arable land, urbanised areas). When analysing the database on collisions of the Polish State Railways providing information on 561 collisions recorded in the years 2007-2016 as well as cartographic materials publicised as open-layers it was shown that an increase in the frequency of collisions involving animals treated jointly, with no division into individual species, is influenced by the presence of developed areas in the buffer zones adjacent to railway tracks. In turn, an analysis of animal species participating in these events shows a certain similarity in the case of deer (roe deer and red deer). For these species one identical pair of mutually dependent variables was observed, i.e. surface waters and forested areas. Additionally, for collisions with roe deer another pair of dependent attributes was found, i.e. forested areas and agriculturally utilised areas. For wild boars an increase was observed in the frequency of events in the buffer zones, where surface waters were found together with forests and connected with urbanised areas. In the case of analyses concerning collisions with roe deer an interdependence was observed between two pairs of variables – forested areas and surface waters, and forested areas and agriculturally utilised areas. Red deer accounted for the smallest percentage of all collisions and for them one pair of mutually dependent variables involved buffers comprising surface waters and forested areas. Results of these studies confirmed the need to conduct analyses for each species separately. It was observed that the character of sites, where collisions involving individual even-toed ungulate species were recorded, depends on the specific nature of a given species. Moreover, these studies showed that by appropriate management of areas adjacent to railway infrastructure provided by spatial planning, especially through the use of line protections we may reduce the frequency of collisions. It was observed that the proposed analytical methods (statistical and spatial) facilitate realisation of proposed research aims and can serve as a tool in planning the location of devices against the incursion of forest animals, which would reduce the negative environmental effects caused by animal mortality on railroad tracks.

Keywords:
spatial planning, ecological barriers, landscape fragmentation, railways, infrastructure and the environment

Ochrona środowiska w aspekcie przeciwdziałania kolizjom z udziałem zwierzyny leśnej na przykładzie wybranych linii kolejowych w Wielkopolsce

Streszczenie

Kolizje z udziałem zwierzyny leśnej stanowią znaczny odsetek wśród wszystkich zdarzeń obserwowanych na liniach kolejowych. Rozwój infrastruktury i wyższe parametry techniczne torów skutkują, że wypadki z udziałem zwierząt leśnych powodują znaczne straty ekonomiczne i są przyczynami znacznych opóźnień rozkładowych. Odpowiednie gospodarowanie terenami graniczącymi z sieciami transportowymi oraz stosowanie aktywnych i pasywnych metod ochrony przed wtargnięciem zwierzyny, może zapobiegać wzrostowi liczby zdarzeń i ograniczaniu negatywnych skutków środowiskowych spowodowanych śmiertelnością zwierzyny. W artykule poddano analizie czy i jakie elementy krajobrazu wpływają na częstość kolizji z udziałem zwierzyny leśnej oraz czy odpowiednio gospodarując i zabezpieczając te tereny istnieje możliwość zapobiegania wtargnięciom zwierzyny na sieci komunikacyjne. Wykorzystując analizy przestrzenne w środowisku GIS (złączenia przestrzenne, relacje topologiczne) oraz statystyczne (tablice kontyngencji) wskazano jakie pary czynników warunkują zwiększenie częstości zdarzeń z udziałem saren, jeleni i dzików. Zaproponowano wykorzystanie systemu 0,1 dla określania występowania zaobserwowanej kolizji w buforze charakteryzującym się daną funkcją zagospodarowania (tereny leśne, wody powierzchniowe, grunty orne, tereny zurbanizowane). Analizując bazę danych o kolizjach Polskich Linii Kolejowych zawierających 561 kolizji zaobserwowanych w latach 2007-2016 oraz materiały kartograficzne udostępniane na warunkach licencyjnych open-layers wskazano, że na wzrost częstości kolizji z udziałem zwierząt bez podziału na gatunki ma wpływ występowanie w buforze przylegającym do linii kolejowych terenów zabudowanych. Analizując gatunki zwierząt biorących udział w zdarzeniach, stwierdzono pewne podobieństwo dla jeleniowatych (sarny i jelenie). Wskazano dla nich jedną taką samą parę zmiennych zależnych od siebie w postaci terenów wód powierzchniowych i terenów leśnych. Dodatkowo dla kolizji z udziałem sarny zanotowano występowanie drugiej pary zależnych atrybutów w postaci terenów leśnych i gruntów użytkowanych rolniczo. Dla dzików zaobserwowano wzrost częstości zdarzeń w buforach, gdzie jednocześnie występowały wody powierzchniowe zestawione z lasami oraz połączone z terenami zurbanizowanymi. W przypadku analiz

dla kolizji z udziałem sarny, wskazano współzależność pomiędzy występowaniem dwóch par zmiennych – terenów leśnych i wód powierzchniowych oraz terenów leśnych i gruntów użytkowanych rolniczo. Jelenie stanowiły najmniejszy odsetek wszystkich kolizji i wskazano dla nich jedną parę zmiennych od siebie zależnych w postaci buforów zawierających wody powierzchniowe oraz tereny leśne. Wyniki badań potwierdziły konieczność prowadzenia analiz dla każdego gatunku z osobna. Zauważono, że charakter miejsc w jakim występują kolizje z udziałem poszczególnych gatunków parzystokopytnych zależy od specyfiki zwierzyny. Ponadto badania wskazały, że poprzez odpowiednie gospodarowanie terenami przyległymi do infrastruktury kolejowej w postaci planowania przestrzennego, a zwłaszcza poprzez stosowanie zabezpieczeń liniowych można ograniczać częstość występowania kolizji. Zauważono, że zaproponowane metody analiz (statystycznych i przestrzennych) umożliwiają realizację postawionych celów badawczych i mogą służyć jako narzędzie w planowaniu lokalizacji urządzeń przeciw wtargnięciu zwierzyny leśnej co pozwoliłoby na ograniczenie negatywnych skutków środowiskowych wywołanych śmiertelnością zwierząt na torach kolejowych.

Słowa kluczowe:
planowanie przestrzenne, bariery ekologiczne, fragmentaryzacja krajobrazu,
linie kolejowe, infrastruktura i środowisko

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The Analysis and the Evaluation of Municipal Waste Management in Voivodship Cities in Poland

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1. Introduction

The formation of municipal waste and further waste management is a civilization challenge for mankind. According to the principle of sustainable development, waste should be reused (recycled). It will be possible owing to the implementation of its common selective collection (Kłos 2012). Resource exhaustion (especially metals) and its connection to the increasing demand for production materials and a general increase in consumption are a serious threat to the whole world (Hotta & Aoki-Suzuki 2014, Billard 2019). Efficient waste management and recycling are the only ways to keep resources (Minelgaitė & Liobikienė 2019).

The promotion of the circular economy is the reply for the improvement of current municipal waste management. The main aim of this idea is to limit the consumption of resources, energy, and the amount of waste and the emission of harmful substances. The activities consist of closing the circle of materials and energy flow and using them economically. The aims can be reached in a long-term perspective by proper designing, conservation, repairs, reuse, re-production, renovation and recycling, as well as changing social awareness (Bondaruk et al. 2017). The term reverse logistics, used in the literature, also fits into this philosophy. It is the body of management processes of the circulation of created waste and information connected with the circulations, starting from the places waste is created to places of its destination, where some values are gained back from the waste (from renovation, recycling or conversion) (Green et al. 2012, Plewa et al. 2014). The activities are the base of such waste management in which selective collection is the primary stage of recycling the collected materials. Ferronato et al. (2019) published the results of research concerning the introduction of successful solid waste management strategy in developing countries (Romania and

Bolivia). In the monography, the authors indicated the benefits of being a member of the European Union (economic support, regulations) in developing the recycling systems.

According to the 2008/98/EC directive, the key legal document of the European Law in waste management, the creation of "the recycling society", which aim would be to avoid producing waste and using waste as resources, is being strived. The change of the directive of the 30^{th} May 2018 (Directive (UE) 2018/851) additionally encourages to save food (to collect unsold food products, food donations and other forms of redistribution), which consequently is supposed to reduce organic waste.

The data gained from the Central Statistical Office and cited in The National Waste Management Plan 2022 show that in Poland annually the percentage of stored municipal waste decreased from 94.21% in 2004 to 52.63% in 2014. Moreover, on the basis of the Marshals' report on the realization of their activities connected with waste management from 2013 and 2014, it is seen that the percentage of recycled waste increased (four fractions were assessed: paper, metals, plastic and glass) from 8.34% to 9.37% in total amount of collected municipal waste.

The regulation of the 13^{th} September 1996 on the maintaining cleanliness and order in municipalities imposes obligations on municipalities inter alia to reach a level of recycling and preparation for reusing the following fractions of municipal waste: paper, metal, plastic and glass (so-called 4 fractions) of at least 50% of total weight of municipal waste to the 31^{st} December 2020. Moreover, aims for other waste fractions were set. As one of the aims of municipal waste management, it was assumed that the amount of biodegradable waste and directed to storage will be limited so that not more than 35% of the waste produced in 1995 (the reference year) will be stored in 2020 (The National Waste Management Plan 2022). The regulation determines also the duty of selective collection of municipal waste.

To evaluate the municipal waste management one can apply rates that illustrate its accumulation, production, collection, selective collection and recycling per one inhabitant. The analyses are presented in works issued by the Central Statistical Offices. By comparing the calculated rates year to year in administrative units, one can evaluate the regularity of waste management.

The research set two aims. The first aim was to evaluate the condition of the management of municipal waste collected as mixed and municipal waste collected as separate (the mixed waste and the selected waste) with the use of modified rates created on the basis of Alankiewicz (2009). The second aim was to compare the selective collection of given fractions in particular voivodship cities in Poland (16 cities) with the use of spatial concentration coefficient and location quotient in order to assess the condition of municipal waste management. The monography concerns the possibility of using spatial planning tools to evaluate the condition of municipal waste management. The rates connected with the selective collection of waste for all voivodship cities in Poland were compared. Then, by using data from the Local Data Bank and theoretical assumptions on the concentration of spatial phenomena, the comparative assessment of the condition of the management of selectively collected waste was made.

2. The rules and methods for the evaluation of municipal waste management

The evaluation of the municipality's waste management depends to a large extent on an effective collection of waste and currently on a selective collection as well. De Feo et al. (2019) proposed a methodological approach useful in defining rates which can be used in communication campaigns organized in order to improve the effectiveness of selective municipal waste collection. For this reason, six economic-environmental indicators were determined. The methodology was used in collecting paper and cardboard in 12 cities of southern Italy. It was stated that the maximal amount of paper and cardboard that can be recycled from unsorted waste would bring back over 15 million Euro to Naples and Palermo. Moreover, maximal potential economic savings for every inhabitant was 25 Euro/capita per year. Catania was a city with the highest possible potential of saving carbon dioxide per inhabitant (> 60 kg CO_2eq./capita). The implemented innovative communicative method ("Greenopoli") assumes that school is the starting point for changing attitude as it enables direct access to potential and to the most important recipients (audience) of communication campaigns (De Feo et al. 2019).

The content of municipal waste depends to a large extent on the area urbanization degree from where the waste comes. Ying-Chu (2018) researched the influence of some urbanization indicators on the content of municipal waste using a linear regression model. The following rates were acknowledged as urbanization indicators: the household population, the area of urban planning, tap water penetration, sold electricity, number of operating factories, car density, education level and annual income. The five main elements of municipal waste were: paper, food waste, plastic, metal and glass. The results served as a valuable hint in evaluating changes in municipal waste content in relation to the urbanization indicators used in the research.

In China, the use of Aibolv mobile application, which realizes a new model of waste management "Internet + Recycling" and which enables easy access to selective collection systems for the producers and recipients, was suggested and checked. Owing to it, an individual can use various internet platforms to determine the date of waste collection. Then companies would take the waste from the person the given day. The "Internet + Recycling system allows units to have convenient access to formal systems of waste management. In the monography, the authors made a quantitative analysis of the balance of the waste mass and environmental results of recycling of some waste fractions (Gu et al. 2019).

Castillo-Giménez et al. (2019) estimated the efficiency and convergence in municipal waste treatment of the members of the European Union (27 countries) between 1995 and 2016. The efficiency rate (including waste storage, burning, recycling, composting and fermentation as waste treatment operation) was determined with Data Envelopment Analysis and Multi-Criteria-Decision-Making techniques at the national level. The convergence was evaluated using techniques suggested by Phillips and Sul (2007, 2009), and recently used by Kong et al. (2017). The highest results were gained by countries from Central Europe (Denmark, Germany, and Austria) and the worst results were given to Eastern Europe countries which joined the EU after 2000.

In Poland, to evaluate the level of waste management the segmentation evaluation method, which orders the criteria for the evaluation of the realization of the Municipal Waste Management Plan, was suggested. Making the plans is not required at present; however, the indicators worked out by the author can be used to evaluate the waste management led by the local government units (Alankiewicz, 2009). The rates include:

1. **Accumulation rate: $\mathbf{R_A}$** – the amount of produced waste for 1 inhabitant.
2. **Collection rate** – $\mathbf{R_C}$ – determining the degree to which inhabitants are included in the mixed waste collection system (since the 1st July 2013, 100% of municipality inhabitants should be included in the mixed waste collection system).
3. **Selective collection rate**: $\mathbf{R_{SC}}$ – determining the degree to which inhabitants are included in the selective collection system.
4. **Recovery rate: $\mathbf{R_R}$** – the amount of waste that underwent recovery.
5. **Storage rate: $\mathbf{R_S}$** – the amount of disposed waste.
6. **Cost rate: $\mathbf{R_{CO}}$** – costs for collecting waste, recovery and disposal that are ordered to be paid by inhabitants.

By using the suggested rates one can evaluate the realization of the rules that should be respected in a properly functioning waste management, i.e.:

- to evaluate the avoidance of producing waste – $\mathbf{R_A}$,
- to evaluate the reduction of waste – $\mathbf{R_C}$, $\mathbf{R_{SC}}$, $\mathbf{R_R}$,
- to evaluate the waste disposal that would ensure safety to people and the environment – $\mathbf{R_S}$,
- to evaluate "the polluter pays" principle – $\mathbf{R_{CO}}$.

Another attitude to the evaluation of waste management was suggested by Deluga (2018). To evaluate the way Koszalin inhabitants perceive waste management and also to show its condition, a survey method was used. It was stated that the majority of the inhabitants knows the rules for selecting waste. The necessity for the pro-ecological initiative was confirmed as the role of education about waste management is a key matter.

3. Materials and methods

To evaluate the condition of municipal waste management in voivodship cities, modified rates were suggested. The rates had been created under the influence of the assumptions of waste management by Alankiewicz (2009). To evaluate the level of municipal waste management (both mixed and selected), two rates were proposed:

$$W_1 = \frac{\mathrm{SW/1i}}{MW/1i} \tag{1}$$

where:
SW/1i – the mass of selected waste per 1 inhabitant,
MW/1i –the mass of mixed waste collected per 1 inhabitant.

$$W_2 = \frac{MW/1i - SW/1i}{SMW/1i} \tag{2}$$

where:
MW/1i and SW/1i – as in Formula 1),
SMW/1i – the mass of municipal waste collected (together mixed and selected) per 1 inhabitant.

W_1 rate can theoretically take the value in the <0,∞) range. Value 0 will be reached when SW/1i is 0, so there will be no waste selectively collected – the situation extremely undesirable. W_1 rate increases with the increase of the mass of selected waste and the decrease of the mass of mixed waste. $W_1 = 1$ value will mean that the mass of mixed waste per 1 inhabitant is the same as the mass of selected waste. The more above 1 the W_1 rate gets, the more effective the waste management is.

W_2 rate can take the value in the <-1,1> range. The value -1 reflects the perfect condition when all waste is selectively collected. The value 0 indicates the condition in which the mixed waste mass equals the selected waste mass. The value 1 is the extremely undesirable condition, i.e. when all the waste is collected as mixed.

Additionally, to evaluate a selective collection of waste, the concentration of spatial phenomena rate was used. In researching the spatial distribution of the phenomena, the aim is to determine the degree of the concentration of the analyzed phenomenon against a different phenomenon. From the comparison of the sets, one can notice to which degree the concentration of the analyzed phenomenon deviates from the concentration of the basic phenomenon. The concentration coefficient proposed by Florence is presented in the following formula (Kostrubiec 1972, Domański 1998):

$$C = \frac{\sum_{i=1}^{n}(x_i - y_i)}{100} \tag{3}$$

where:
C – concentration coefficient,
x_i – the percentage share of the *i* unit in the global value of the research phenomenon,
y_i – the percentage share of the *i* unit in the global value of the basic phenomenon,
n – the number of individual units.

The concentration coefficient is a unit-less measure and it stays in the <0,1> range. When the research phenomenon is distributed such as the basic phenomenon – full dispersion – the rate is 0. In the case when the rate equals 1, the research phenomenon is concentrated in one unit area – full concentration (Kostrubiec 1977, Senetra & Cieślak 2004). The Lorenz curve illustrates the value of the concentration coefficient. If the research phenomenon is distributed evenly, then we get a straight line inclined at the angle of 45° starting at the beginning of the coordinate system. Each inclination from the proportion makes the curve convex (Fig. 1). While creating the diagram, one collates the research units in the order according to the value of the location quotient, starting from the highest. The location quotient (LQ) is a quotient of the percentage share of the research phenomenon and the percentage share of the basic phenomenon. Then, the percentage values set for every series, in the order determined by LQ, are cumulated. The cumulated series are marked on the axes – the research phenomenon on the vertical axis and the basis phenomenon on the vertical one (Domański 1998, Senetra & Cieślak 2004). The graphical concentration measurement is the surface between the straight line inclined at the angle of 45° and Lorenz curve. The ratio of this surface to the total surface of the upper triangle equals the concentration coefficient (Fig. 1).

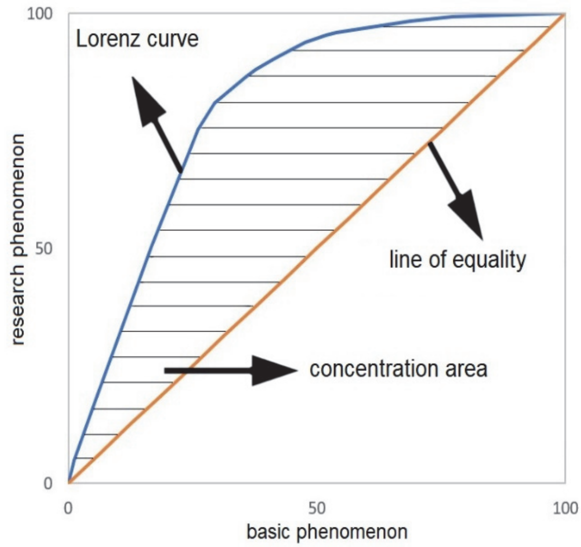

Fig. 1. Lorenz curve

For the need of the evaluation of the level of selectively collected waste in the total waste mass (mixed and selected) in particular cities, the authors used data applying to the general municipal waste and six fractions:

1. Paper and cardboard (PC).
2. Glass (G).
3. Plastic (P).
4. Waste electrical and electronic equipment (WEEE).
5. Bulky waste (BW).
6. Biodegradable waste (B).

The justification for choosing the fractions is their highest share in the mass of selective waste. Moreover, they are the most common waste selectively collected. In the first stage of the research, the concentration coefficient of all selectively collected waste in the research cities was calculated (Formulas 4, 5, 6) The basic phenomenon (BPH) was determined as the quotient of the sum of mixed waste and selected waste in every city, and the sum of the waste in all cities (4). The research phenomenon (RPH) was determined as the quotient of the amount of selected waste in every city and the sum of selected waste in all cities (5).

$$BPH = \frac{MSW\ in\ city\ i}{MSW\ in\ all\ cities} \tag{4}$$

where:
MSW – the mass of mixed and selected waste all together.

$$RPH = \frac{\text{SW in city i}}{\text{SW in all cities}} \tag{5}$$

where:
SW – the mass of selected waste.

The concentration coefficient (calculated according to Formula 3) takes the form presented with Formula 6.

$$Csw = \frac{\sum_{i=1}^{16}|RPH-BPH|}{100} \tag{6}$$

where:
$\sum_{i=1}^{16}|RPH - BPH|$–the sum of the absolute difference of the research phenomenon and the basic phenomenon.

For the evaluation of the degree of the concentration coefficient of the selectively collected waste in the division into six fractions, a similar methodological attempt was used. In this case the basic phenomenon (BPH) for all distinct fractions is the RPH value used in Formula 5 as the research phenomenon. The research phenomenon (RPH) for all selected fractions was defined in the following way:

1. Selected waste "paper and cardboard" – PC:

$$RPH_{PC} = \frac{SW_{PC}\text{ in city i}}{SW_{PC}\text{ in all cities}} \tag{7}$$

where:
SW_{PC} – the mass of selected waste PC.

2. Selected waste "glass" – G:

$$RPH_{G} = \frac{SW_{G}\text{ in city i}}{SW_{G}\text{ in all cities}} \tag{8}$$

where:
SW_{G} – the mass of selected waste G.

3. Selected waste "plastic" – P:

$$RPH_{P} = \frac{SW_{P}\text{ in city i}}{SW_{P}\text{ in all cities}} \tag{9}$$

where:
SW_{P} – the mass of selected waste P.

4. Selected waste "waste electrical and electronic equipment" – WEEE:

$$RPH_{WEEE} = \frac{SW_{WEEE}\text{ in city i}}{SW_{WEEE}\text{ in all cities}} \tag{10}$$

where:
SW_{WEEE} – the mass of selected waste WEEE.
5. Selected waste "bulky waste" – BW:

$$RPH_{BW} = \frac{SW_{BW}\text{ in city i}}{SW_{BW}\text{ in all cities}} \tag{11}$$

where:
SW_{BW} – the mass of selected waste BW.

6. Selected waste „biodegradable waste" – B:

$$RPH_{B} = \frac{SW_{B}\text{ in city i}}{SW_{B}\text{ in all cities}} \tag{12}$$

where:
SW_{B} – the mass of selected waste B.

4. Results and discussion

4.1. The evaluation of municipal waste management of mixed and selected waste in voivodship cities

For the evaluation, the data from the Local Data Bank (www.stat. gov.pl, access 17th December 2018) concerning municipal waste (mixed and selected waste) as well as information on the population in voivodship cities in Poland, were used. The value of W_1 and W_2 rates was calculated and presented in Table 1.

Table 1. The value of W_1 and W_2 rates in voivodship cities

No.	City	MW/1i	SW/1i	W_1	W_2
1	Wrocław	349.78	146.05	0.4175	0.4109
2	Bydgoszcz	238.92	94.72	0.3965	0.4322
3	Lublin	247.40	87.82	0.3550	0.4760
4	Zielona Góra	308.49	70.55	0.2287	0.6277
5	Łódź	260.58	100.39	0.3853	0.4438
6	Kraków	283.33	160.84	0.5677	0.2679
7	Warszawa	335.17	106.88	0.3189	0.5164
8	Opole	244.17	137.60	0.5635	0.2792
9	Rzeszów	270.57	107.13	0.3959	0.4327

Table 1. cont.

No.	City	MW/1i	SW/1i	W_1	W_2
10	Białystok	161.94	110.91	0.6849	0.1870
11	Gdańsk	295.18	112.59	0.3814	0.4478
12	Katowice	345.85	94.91	0.2744	0.5693
13	Kielce	261.51	80.72	0.3087	0.5283
14	Olsztyn	314.96	85.26	0.2707	0.5739
15	Poznań	299.14	115.86	0.3873	0.4417
16	Szczecin	317.09	88.04	0.2776	0.5654

The value of W_1 rate is the highest in the following cities: Białystok, Kraków and Opole, which means that in the cities there is a high percentage of selected waste. In the case of Białystok, the W_1 rate is high also because the city is characterized by a low amount of mixed municipal waste – 161.94 kg/inhabitant. The lowest rate occurred in Zielona Góra, Olsztyn, Katowice and Szczecin. A very low W_1 rate occurred in Zielona Góra due to the fact that there is a large percentage of mixed waste per inhabitant (308.49 kg) and a small amount of selected waste (70.55 kg/inhabitant). In none of the cities, the rate was above 1. The range of the W_1 value was divided into five even evaluation categories (Table 2). In two categories, which were marked with the lowest and low value (V and IV category), there are 12 voivodship cities. However, in I category, with the highest value, there is only one city – Białystok. That means that the majority of cities stay on the equally low level considering the evaluation of the relation of selected waste (per inhabitant) to the amount of mixed waste (per inhabitant).

Table 2. The range of evaluation of W_1 rate

Evaluation category	W_1 range	Cities
I – the highest	0.5938-0.6849	Białystok
II – high	0.5025-0.5937	Kraków, Opole
III – average	0.4113-0.5024	Wrocław
IV – low	0.3200-0.4112	Bydgoszcz, Lublin, Łódź, Rzeszów, Gdańsk, Poznań
V – the lowest	0.2287-0.3199	Zielona Góra, Warszawa, Katowice, Kielce, Olsztyn,Szczecin

In evaluating the condition of waste management with the use of W_2 rate, similar conclusions were drawn. The value of the rate did not reach results below zero, which means that there is more selected waste than mixed one in none of the analyzed cities. W_2 is the lowest in Białystok and Kraków, which proves the high percentage of selected waste in the total amount of municipal waste (both mixed and selected). The highest W_2 rate value was reached in Zielona Góra, Olsztyn, Katowice and Szczecin. It means that in the cities there is a large difference between the mass of mixed waste per inhabitant and the mass of selected waste per inhabitant. Similarly, like for W_1 rate, the range of W_2 rate was divided into five even brackets (Table 3).

In the case of W_2 rate, one can notice the similarities with the results of the W_1 evaluation. In IV category, in both cases, four out of six cities appeared in both studies: Zielona Góra, Katowice, Olsztyn and Szczecin. In I category, in both analyzed rates, the highest mark was received by Białystok.

Table 3. The range of evaluation of W_2 rate

Evaluation category	W_2 range	Cities
I – the highest	0.1870-0.2751	Kraków, Białystok
II – high	0.2752-0.3632	Opole
III – average	0.3633-0.4514	Wrocław, Bydgoszcz, Lublin, Łódź, Rzeszów, Gdańsk, Poznań
IV – low	0.4515-0.5395	Warszawa, Kielce
V – the lowest	0.5396-0.6277	Zielona Góra, Katowice, Olsztyn, Szczecin

In the next stage of the research, the selective collection of waste was evaluated with the use of the concentration coefficient. In this case, data concerning the amounts of mixed and selected waste in kilograms was used (not expressed per inhabitant, as it had been done while determining W_1 and W_2 rate). Table 4 presents the data for calculating the location quotient (LQ) for particular cities. According to methodological assumptions, the data was used in the following stages to calculate the concentration coefficient (C_{SW}) of the selected waste in the cities (Formulas 4, 5 and 6) (Tab. 5). Moreover, data from the Central Statistical Office was used as well (www.stat.gov.pl., access 17th December 2018).

A very low level of concentration coefficient (0.07) means that there are no units in which waste management is vividly inappropriate. On the basis of the calculated location quotients presented in Table 5, a graph of the curve of the space concentration of selected waste against all municipal waste in voivodship cities was created (Fig. 2).

Table 4. The data for calculating the location quotient and concentration coefficient of selected waste in voivodship cities in Poland

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
BPH	10.46	3.89	3.77	1.75	8.28	11.59	25.68	1.62	2.36	2.68	6.26	4.33	2.23	2.29	7.40	5.41
RPH	11.27	4.04	3.61	1.19	8.42	14.91	22.71	2.13	2.45	3.98	6.32	3.41	1.93	1.78	7.55	4.30
RPH-BPH	0.81	0.15	-0.16	-0.56	0.14	3.32	-2.97	0.51	0.09	1.30	0.06	-0.92	-0.30	-0.51	0.15	-1.11
RPH/BPH	1.08	1.04	0.96	0.68	1.02	1.29	0.88	1.31	1.04	1.49	1.01	0.79	0.87	0.78	1.02	0.79

Table 5. The location quotients, cumulated percentage share of the phenomena and the calculations of concentration coefficient

Cities according to LQ	10	8	6	1	9	2	15	5	11	3	7	13	12	16	14	4
LQ	1.49	1.31	1.29	1.08	1.04	1.04	1.02	1.02	1.01	0.96	0.88	0.87	0.79	0.79	0.78	0.68
RPH	3.98	6.11	21.02	32.29	34.74	38.78	46.33	54.75	61.07	64.68	87.39	89.32	92.73	97.03	98.81	100.00
BPH	2.68	4.30	15.89	26.35	28.71	32.60	40.00	48.28	54.54	58.31	93.99	86.22	90.55	95.96	98.25	100.00
$C_{SW} = 6.53/100 = 0.07$																

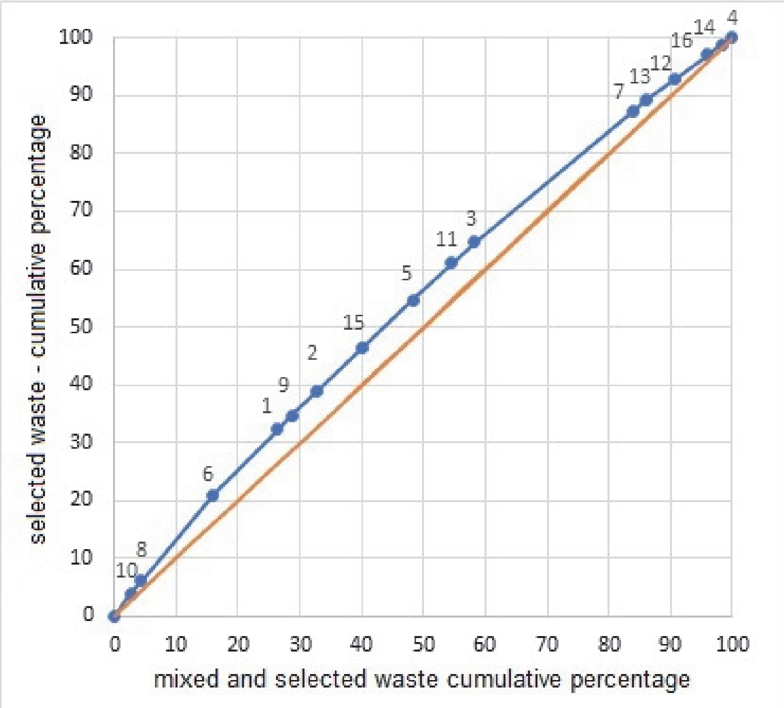

Fig. 2. The curve of the space concentration of selected waste against all municipal waste in cities

The concentration curve deviates from the straight line a bit which should be seen that the research phenomenon (the relation of selected waste mass in a city to the mass of all waste in all cities) is similarly concentrated to the basic phenomenon (the relation of mixed and selected waste mass in a city to the mass of all waste in the city). However, the best situation occurred in Białystok (the first object in Figure 2) and the worst situation was in Zielona Góra (the last object in Figure 2). The order of the cities on the graph is reflected by the height of the location quotient (LQ) for each of them. The quotient can be a convenient tool for evaluating the situation in every unit against all the analyzed units. The comparison of the order of the cities gained from the evaluation made with the use of W_1, W_2 rates and the location quotient (LQ) is shown in Table 6.

As a result of the evaluation made with the use of W_1 and W_2 rates, the same order of the cities occurred. It means that one can use one rate for the evaluation. The evaluation made using the theory of the concentration of spatial phenomena gave similar results. In ten cases (green color in Table 6), the same order was gained for all rates. In six cases (yellow color in Table 6), slight changes were observed (+/- one position).

Table 6. The comparison of W_1, W_2 rates and location quotients (LQ)

Cities order	W_1	W_2	LQ
1	Białystok	Białystok	Białystok
2	Kraków	Kraków	Opole
3	Opole	Opole	Kraków
4	Wrocław	Wrocław	Wrocław
5	Bydgoszcz	Bydgoszcz	Rzeszów
6	Rzeszów	Rzeszów	Bydgoszcz
7	Poznań	Poznań	Poznań
8	Łódź	Łódź	Łódź
9	Gdańsk	Gdańsk	Gdańsk
10	Lublin	Lublin	Lublin
11	Warszawa	Warszawa	Warszawa
12	Kielce	Kielce	Kielce
13	Szczecin	Szczecin	Katowice
14	Katowice	Katowice	Szczecin
15	Olsztyn	Olsztyn	Olsztyn
16	Zielona Góra	Zielona Góra	Zielona Góra

4.2. The evaluation of chosen fractions of the selected waste

Next, the evaluation of selected waste for six chosen fractions was made with the use of concentration coefficient. Tables 7 and 8 contain data necessary for calculating the location quotients (LQ) and concentration coefficients (Formulas 7-12). In Table 8, however, data necessary for preparing graphs for particular fractions selectively collected in research cities were presented (Figure 3).

Table 7. The data necessary for calculating the location quotient and the concentration coefficient of the selected waste

Cities	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
BPH	11.27	4.04	3.61	1.19	8.42	14.91	22.71	2.13	2.45	3.98	6.32	3.41	1.93	1.78	7.55	4.30
RPH																
PC	32.68	1.52	2.17	4.96	0.80	2.58	0.77	0.44	1.38	2.29	5.48	5.64	1.56	4.72	20.30	12.71
RPH_{PC}-BPH	21.41	-2.52	-1.44	3.77	-7.62	-12.33	-21.94	-1.69	-1.07	-1.69	-0.84	2.23	-0.37	2.94	12.75	8.41
LQ	2.90	0.38	0.60	4.17	0.10	0.17	0.03	0.21	0.56	0.58	0.87	1.65	0.81	2.65	2.69	2.96
[1])	**3**	**12**	**9**	**1**	**15**	**14**	**16**	**13**	**11**	**10**	**7**	**6**	**8**	**5**	**4**	**2**
G	14.00	7.15	1.79	1.72	3.05	10.88	16.31	2.31	2.55	4.51	6.54	3.43	3.32	1.83	14.12	6.49
RPH_{G}-BPH	2.73	3.11	-1.82	0.53	-5.37	-4.03	-6.40	0.18	0.10	0.53	0.22	0.02	1.39	0.05	6.57	2.19
LQ	1.24	1.77	0.50	1.45	0.36	0.73	0.72	1.08	1.04	1.03	1.03	1.01	1.72	1.03	1.87	1.51
[1])	**6**	**2**	**15**	**5**	**16**	**13**	**14**	**7**	**8**	**9**	**10**	**12**	**3**	**11**	**1**	**4**
P	1.20	1.47	1.83	8.47	3.97	6.40	1.95	0.63	3.05	6.40	6.77	2.46	7.18	7.15	31.32	9.75
RPH_{P}-BPH	-10.07	-2.57	-1.78	7.28	-4.45	-8.51	-20.76	-1.50	0.60	2.42	0.45	-0.95	5.25	5.37	23.77	5.45
LQ	0.11	0.36	0.51	7.12	0.47	0.43	0.09	0.30	1.24	1.61	1.07	0.72	3.72	4.02	4.15	2.27
[1])	**15**	**13**	**10**	**1**	**11**	**12**	**16**	**14**	**7**	**6**	**8**	**9**	**4**	**3**	**2**	**5**
WEEE	3.68	3.42	3.87	0.48	3.27	5.84	56.00	1.33	1.42	2.04	6.77	5.19	0.72	0.37	3.75	1.85
RPH_{WEEE}-BPH	-7.59	-0.62	0.26	-0.71	-5.15	-9.07	33.29	-0.80	-1.03	-1.94	0.45	1.78	-1.21	-1.41	-3.80	-2.45
LQ	0.33	0.85	1.07	0.40	0.39	0.39	2.47	0.62	0.58	0.51	1.07	1.52	0.37	0.21	0.50	0.43
[1])	**15**	**5**	**4**	**11**	**12**	**13**	**1**	**6**	**7**	**8**	**3**	**2**	**14**	**16**	**9**	**10**
BW	9.30	4.12	2.69	1.94	5.74	10.49	32.92	1.55	1.31	4.55	4.70	5.57	1.70	3.32	5.27	
RPH_{BW}-BPH	-1.97	0.08	-0.92	0.75	-2.68	-4.42	10.21	-0.58	-1.14	0.57	-1.62	2.16	-0.23	1.54	-2.28	0.53
LQ	0.83	1.02	0.75	1.63	0.68	0.70	1.45	0.73	0.53	1.14	0.74	1.63	0.88	1.87	0.70	1.12
[1])	**9**	**7**	**10**	**3**	**15**	**13**	**4**	**12**	**16**	**5**	**11**	**2**	**8**	**1**	**14**	**6**
B	10.53	6.01	4.04	0.05	11.96	16.35	11.50	2.67	0.82	3.25	13.56	2.69	1.40	1.15	9.18	4.84
RPH_{B}-BPH	-0.74	1.97	0.43	-1.14	3.54	1.44	-11.21	0.54	-1.63	-0.73	7.24	-0.72	-0.53	-0.63	1.63	0.54
LQ	0.93	1.49	1.12	0.04	1.42	1.10	0.51	1.25	0.33	0.82	2.15	0.79	0.73	0.65	1.22	1.13
[1])	**9**	**2**	**7**	**16**	**3**	**8**	**14**	**4**	**15**	**10**	**1**	**11**	**12**	**13**	**5**	**6**

[1]) – the order according to the location quotient (LQ)

Table 8. The location quotients, cumulated percentage share of the phenomena and the calculation of the concentration coefficient

Cities	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	K
Paper and cardboard – PC																	C_{PC}
[1])	**4**	**16**	**1**	**15**	**14**	**12**	**11**	**13**	**3**	**10**	**9**	**2**	**8**	**6**	**5**	**7**	
RPH_{PC}[2])	4.96	17.67	50.35	70.65	75.37	81.01	86.49	88.05	90.22	92.51	93.89	95.41	95.85	98.43	99.23	100.00	**0.52**
BPH[2])	1.19	5.49	16.76	24.31	26.09	29.50	35.82	37.75	41.36	45.34	47.79	51.83	53.96	68.87	77.29	100.00	
Glass – G																	C_G
[1])	**15**	**2**	**13**	**16**	**4**	**1**	**8**	**9**	**10**	**11**	**14**	**12**	**6**	**7**	**3**	**5**	
BPH_G[2])	14.12	21.27	24.59	31.08	32.80	46.80	49.11	51.66	56.17	62.71	64.54	67.97	78.85	95.16	96.95	100.00	**0.18**
BPH[2])	7.55	11.59	13.52	17.82	19.01	30.28	32.41	34.86	38.84	45.16	46.94	50.35	65.26	87.97	91.58	100.00	
Plastic – P																	C_P
[1])	**4**	**15**	**14**	**13**	**16**	**10**	**9**	**11**	**12**	**3**	**5**	**6**	**2**	**8**	**1**	**7**	
RPH_P[2])	8.47	39.79	46.94	54.12	63.87	70.27	73.32	80.09	82.55	84.38	88.35	94.75	96.22	96.85	98.05	100.00	**0.51**
BPH[2])	1.19	8.74	10.52	12.45	16.75	20.73	23.18	29.50	32.91	36.52	44.94	59.85	63.89	66.02	77.29	100.00	
Waste electrical and electronic equipment– WEEE																	C_{WEEE}
[1])	**7**	**12**	**11**	**3**	**2**	**8**	**9**	**10**	**15**	**16**	**4**	**5**	**6**	**13**	**1**	**14**	
RPH_{WEEE}[2])	56.00	61.19	67.96	71.83	75.25	76.58	78.00	80.04	83.79	85.64	86.12	89.39	95.23	95.95	99.63	100.00	**0.36**
BPH[2])	22.71	26.12	32.44	36.05	40.09	42.22	44.67	48.65	56.20	60.50	61.69	70.11	85.02	86.95	98.22	100.00	
Bulky waste – BW																	C_W
[1])	**14**	**12**	**4**	**7**	**10**	**16**	**2**	**13**	**1**	**3**	**11**	**8**	**6**	**15**	**5**	**9**	
RPH_{BW}[2])	3.32	8.89	10.83	43.75	48.30	53.13	57.25	58.95	68.25	70.94	75.64	77.19	87.68	92.95	98.69	100.00	**0.16**
BPH[2])	1.78	5.19	6.38	29.09	33.07	37.37	41.41	43.34	54.61	58.22	64.54	66.67	81.58	89.13	97.55	100.00	
Biodegradable waste – B																	C_B
[1])	**11**	**2**	**5**	**8**	**15**	**16**	**3**	**6**	**1**	**10**	**12**	**13**	**14**	**7**	**9**	**4**	
RPH_B[2])	13.56	19.57	31.53	34.20	43.38	48.22	52.26	68.61	79.14	82.39	85.08	86.48	87.63	99.13	99.95	100.00	**0.17**
BPH[2])	6.32	10.36	18.78	20.91	28.46	32.76	36.37	51.28	62.55	66.53	69.94	71.87	73.65	96.36	98.81	100.00	

[1]) order of the cities according to the location quotient (LQ); [2]) – cumulative percentage

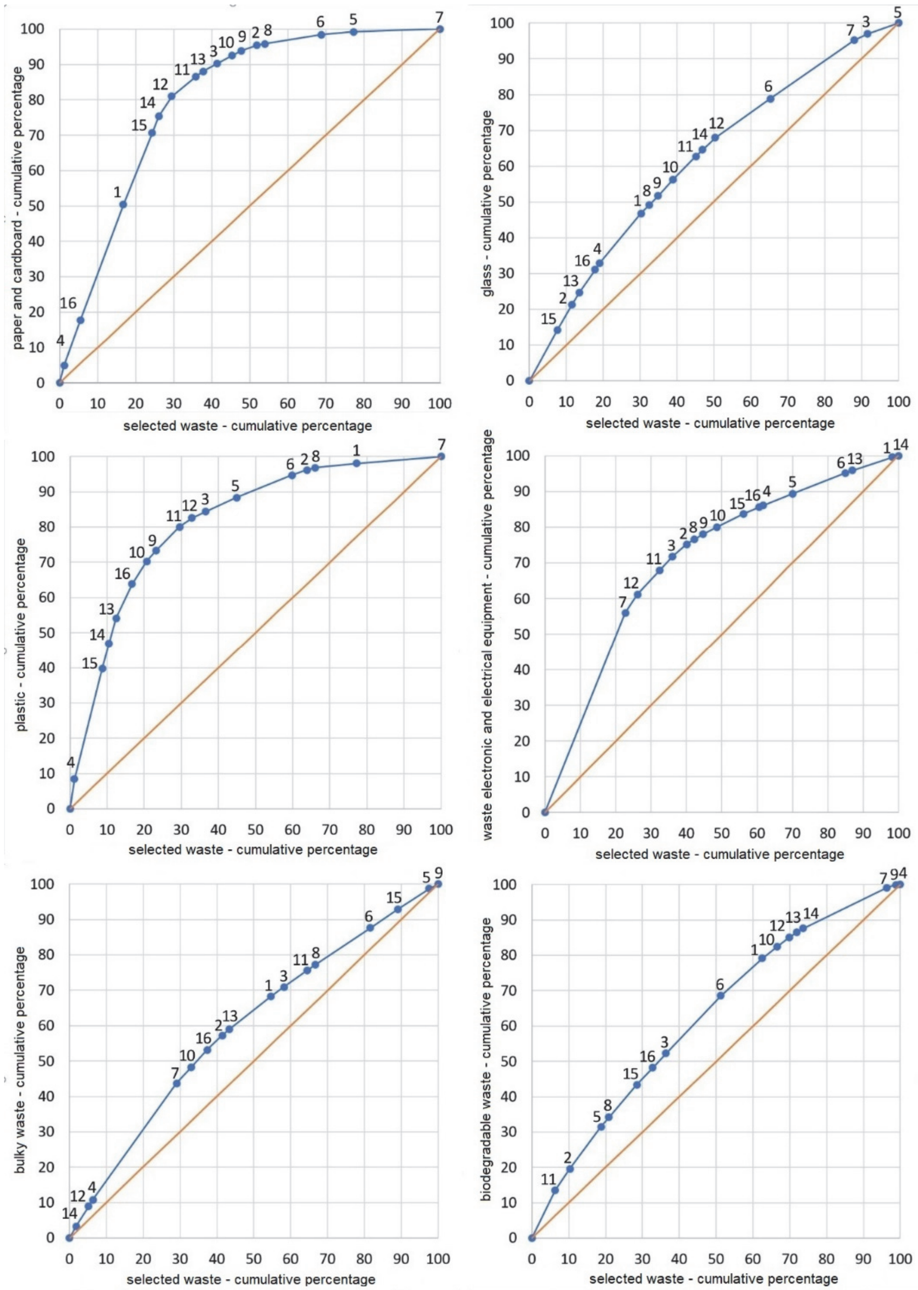

Fig. 3. The curves of space concentration of the research fractions of the selected waste against all selected waste in the cities

The analysis of location quotients (LQ), concentration coefficients and the graphs of space concentration of particular fractions of the selected waste against all selected waste shows that none of the fractions reached the concentration coefficient similar to the concentration coefficient of selected waste against all waste (mixed and selected), which was $C_{SW} = 0.07$. The highest concentration coefficient had paper and cardboard fraction ($C_{PC} = 0.52$), which means that the research phenomenon was concentrated in a few research cities. The graph of the concentration curve proves the fact. The curve is considerably deviated from the 45° starting from the beginning of the coordinate system (Fig. 3). The range of values of location quotients (LQ) of the fraction for every city (0.03-4.17) was broad. High location quotient indicates a high concentration of the phenomenon (selective collection of paper and cardboard) in the basic phenomenon (the relation of all selected waste in a given city to the amount of selected waste in all cities). It meant that in the city the selective collection is on a high level. A slightly lower concentration coefficient was calculated for plastic fraction ($C_P = 0.51$), and the location quotient stayed in the range (0.09-7.12). The lowest concentration coefficient occurred in three fractions: glass ($C_G = 0.18$), bulky waste ($C_{BW} = 0.16$) and biodegradable waste ($C_B = 0.17$). The low concentration coefficients indicate a similar level of collecting the waste fractions in all cities.

5. Summary and conclusions

The evaluation of the condition of the municipal mixed and selected waste management in voivodship cities in Poland with the use of suggested W_1 and W_2 rates and using the concentration of spatial phenomena, allowed for drawing the following conclusions:

1. W_1 rate does not reflect the real level of the collection of selected waste and the condition of waste management as W_1 rate value gets zero in each case when selected waste does not occur, regardless of the amount of collected mixed waste (also per one inhabitant). The rate can be used in a comparative assessment of administrative units or in evaluating the same unit in due time. The change of the rate shows the dynamics (tendency) of the relation of the amount of selected waste to mixed waste.
2. The second proposed rate (W_2) determines the differences between mixed waste and selected waste related to all selected municipal waste (both mixed and selected). In none of the evaluated cities, the relation was negative, which means that nowhere does the mass of selected waste exceed the mass of mixed waste. The rate, just like the previous one, can also be used in a comparative assessment or to show the dynamics of the phenomenon.
3. The evaluation made with the use of both rates gave similar results. The ranking of the cities determined on the basis of W_1 and W_2 rates was identical.

4. The research using the concentration of spatial phenomena and the concentration coefficient gave similar results as the evaluation made with W_1 and W_2 rates. In this case, the ranking of the cities is the same in ten cases and in the rest six cases it differs with only one position. It is worth to mention that the evaluation was made on the basis of data about waste mass (both mixed and selected) given in absolute units (kilograms). The populations of the cities were not considered.
5. The graphs of the concentration of research phenomena and the values of the location quotients (LQ) can be very useful and valuable tools not only for evaluating the condition of waste management. They can be fine hints for giving recommendations for particular spatial units. A low location quotient (LQ), in comparison to other units, indicates irregularities and necessity of intensifying activities in a given range. The rate can be treated as a kind of ranking for the whole considered system without making further calculations. Its changes in the following years inform about the changes in the level of the phenomenon and about taking or not taking corrective actions (recommendations). The tool can be used in constant monitoring and planning waste management from a global perspective for connected units and considered processes.
6. The evaluation of selected waste management, with the division into six fractions (paper and cardboard, plastic, glass, waste electrical and electronic equipment, bulky waste and biodegradable waste) was made only on the basis of the concentration of spatial phenomena. The concentration graphs, generated after calculations had been made, indicate the concentration of a particular fraction of selected waste.

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Abstract

Proper municipal waste management is one of the most important civilization challenges of a mankind in the light of the rules of sustainable development. The circular economy of waste management determines the improvement of current situation on condition that extracting resources and energy and the amount of the emission of harmful substances are limited. The reverse logistics is an important element of the management - the body of the processes of waste flow management and information connected with the flows, starting from the places where the waste is created to their place of destination in order to recycle various values (through reparation, recycling or conversion).

The research set two aims. The first aim was to evaluate the condition of the management of municipal waste collected as mixed and municipal waste collected as separate (the mixed waste and the selected waste) with the use of modified rates created on the basis of Alankiewicz (2009). The second aim was to compare the selective collection of given fractions in particular voivodship cities in Poland (16 cities) with the use of spatial concentration coefficient and location quotient in order to assess the condition of municipal waste management. The fractions are as follows: paper and cardboard, glass, plastic, waste electrical and electronic equipment, bulky waste and biodegradable waste. The justification of the choice of the fractions is their highest share in the mass of selected waste and the fact that they are the most common waste selectively collected. The research was conducted in all voivodship cities in Poland.

The gained results prove a vast diversification of the effectiveness of municipal waste selective collection in voivodship cities in Poland. For all rates the results were similar. Moreover, coincident results were gained in the research conducted with the use of spatial concentration and the location quotients, used for the first time in this kind of analyses. This proved that the methodology can be used in such research. The concentration graphs for research phenomena and the values of location quotients (LQ) can be valuable and useful tools not only in evaluating the condition of waste management. They can be valuable tips for working out the recommendations for particular spatial units. Low location quotient (LQ), in comparison with other units, signifies that there are abnormalities and that there is a necessity to intensify activities in a given range. The rate can be treated as a kind of a ranking for the whole considered system without the necessity of making further calculations. Its changes in the following years would inform about changes in the level of the phenomenon and about taking or not taking corrective actions (recommendations). The tool can be used in constant monitoring and planning waste management in a global perspective for related units and considered processes. In the case of the six research fractions of a selective collection of waste, the evaluation was made only with the use of the theory of spatial phenomena concentration. The reliable results were gained. The results were coincident with general trends set with the use of modified rates determined by Alankiewicz. That is the base for the evaluation of the effectiveness and recommendations for selective collection of waste in voivodship cities in Poland.

Keywords:
municipal waste, selected waste, mixed waste, spatial phenomena concentration

Analiza i ocena stanu gospodarki odpadami komunalnymi w miastach wojewódzkich Polski

Streszczenie

Prawidłowa gospodarka odpadami komunalnymi jest jednym z ważniejszych wyzwań cywilizacyjnych w świetle zasad zrównoważonego rozwoju. Gospodarka odpadami o obiegu zamkniętym jest warunkiem poprawy obecnej sytuacji. Jest to warunek ograniczenia zużycia zasobów i energii oraz ilości powstających odpadów i emisji szkodliwych substancji. Ważnym elementem tej gospodarki jest logistyka zwrotna – ogół procesów zarządzania przepływami powstałych odpadów i informacji związanych z tymi przepływami, poczynając od miejsc, w których one powstają do miejsc ich przeznaczenia w celu odzyskania z nich różnych wartości (poprzez naprawę, recykling lub przetworzenie).

W pracy założono dwa cele. Pierwszym celem była ocena stanu gospodarki zmieszanymi odpadami zebranymi i odpadami zebranymi selektywnie (w dalszej części opracowania nazywanymi: zmieszanymi i selektywnymi) za pomocą zmodyfikowanych wskaźników opracowanych na podstawie Alankiewicza (2009). Drugim celem było porównanie selektywnej zbiórki wybranych frakcji odpadów w poszczególnych miastach wojewódzkich Polski (16 miast) za pomocą współczynnika koncentracji przestrzennej oraz ilorazu lokalizacji. Frakcjami tymi są: papier i tektura, szkło, tworzywa sztuczne, zużyte urządzenia elektryczne i elektroniczne, odpady wielkogabarytowe, odpady biodegradowalne. Uzasadnieniem wyboru frakcji jest ich najwyższy udział w masie odpadów selektywnych, a także fakt, że są najpowszechniejszymi odpadami zbieranymi selektywnie. Badania przeprowadzono dla wszystkich miast wojewódzkich w Polsce.

Uzyskane wyniki potwierdzają znaczne zróżnicowanie efektywności selektywnej zbiórki odpadów komunalnych w miastach wojewódzkich w Polsce. Uzyskano podobne wyniki dla wszystkich zastosowanych wskaźników. Ponadto zbieżne wyniki uzyskane za pomocą koncentracji przestrzennej i ilorazów lokalizacji, zastosowane po raz pierwszy do tego typu analiz, potwierdzają możliwość stosowania tej metodyki. Wykresy koncentracji dla badanych zjawisk i wartości ilorazów lokalizacji (IL) mogą być bardzo przydatnymi i cennymi narzędziami, nie tylko do oceny stanu gospodarki odpadami. Mogą być cenną wskazówką do opracowania zaleceń dla poszczególnych jednostek przestrzennych. Niski iloraz lokalizacji (IL), w porównaniu z innymi jednostkami, świadczy o nieprawidłowościach i konieczności zintensyfikowania działań w danym zakresie.

Wskaźnik ten może być traktowany jako swoisty ranking dla całego rozpatrywanego systemu bez konieczności dokonywania dalszych kalkulacji. Jego zmiany w kolejnych latach informują o zmianach poziomu zjawiska oraz o podejmowaniu lub nie podejmowaniu działań naprawczych (zaleceń). Narzędzie to może służyć do stałego monitorowania i planowania gospodarki odpadami w ujęciu globalnym, dla powiązanych ze sobą jednostek i rozpatrywanych procesów. W przypadku sześciu badanych frakcji selektywnej zbiórki odpadów, oceny dokonano jedynie przy zastosowaniu teorii koncentracji zjawisk przestrzennych. Otrzymano wiarygodne wyniki zbieżne z ogólnymi trendami wyznaczonymi przy pomocy zmodyfikowanych wskaźników Alankiewicza. Jest to podstawą do oceny skuteczności i zaleceń w zakresie selektywnego zbierania odpadów w miastach wojewódzkich Polski.

Słowa kluczowe:
odpady komunalne, odpady zbierane selektywnie, odpady zmieszane,
koncentracja zjawisk przestrzennych

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Transport of Microbial Components in Coarse and Fine Particle Fractions in Office Buildings

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1. Introduction

Recent years continue to confirm the dynamic development of modern office space in Poland. In 2018, total office space reached the level of almost 10 million m^2, which makes it the largest office market in Central and Eastern Europe (Savills, 2019). In old and modern interiors, particular attention is focused on the air quality as one of major determinants of the well-being of occupants. Poor room ventilation and dampness can promote the growth of harmful microorganisms in buildings (Douwes et al., 2003; Hardin et al., 2003). Numerous studies tried to characterize airborne microbiota in indoor environments, e.g. schools, offices, shopping centers, libraries etc. (Gołofit-Szymczak & Górny, 2010; Harkawy et al., 2011; Mentese et al., 2012; Frączek et al., 2019). In the air, biological particles can be present as single vegetative bacterial cells or spores, fungal conidia as well as aggregates formed by bacterial/fungal cells and dust particles (Macher, 1999). If inhaled, they may be responsible for various adverse health outcomes in the exposed individuals. Numerous studies indicated that exposure to high concentration of (1-3)-β-D-glucans (a component of the fungal cell wall) and endotoxins (a part of the outer membrane of Gram-negative bacteria) may have important impact on human health. Both these compounds can be associated with the development of asthma, airway inflammation and occurrence of non-specific symptoms (headache, dry cough, nasal and eye irritation) (Rylander, 1999; Ross et al., 2000; Bouillard et al., 2005; Ławniczek-Wałczyk et al. 2010; Akpinar-Elci et al., 2013; Park et al., 2018). In the scientific literature, there are very few studies on the airborne transport of such microbial particles in both occupational and non-occupational environments. These available data show that such immunologically reactive components are usually carried on small dust particles (Górny & Dutkiewicz, 1999; Madsen & Nielsen, 2010; Balasubramanian et al., 2012). The $PM_{2.5}$ (particulate matter with a diameter of less than 2.5 μm) is of primary concern as it can reach lower parts of the human respiratory system (Li et al., 2017). The noted adverse health effects of $PM_{2.5}$ exposure include respiratory (respiratory irritation, asthma, chronic bronchitis, decreased lung functions, exacerbating existing asthma or chronic obstructive pulmonary disease – COPD, promotion of lung cancer) and cardiovascular (stroke, heart disease, hypertension, atherosclerosis) diseases (Butler et al., 2016). Knowing the sizes of aerosol particles is important as they determine their place of deposition in the human respiratory system and the associated adverse health outcomes. It should be noted, that learning about the ways of transport of microbial particles and factors affecting their spread in the indoor environment can be crucial for the introduction of appropriate measures solutions to minimize their spread and prevent infections and others disorders. In this context, the concentration of biological factors in the indoor air cannot be investigated separately but considerate also evaluation of non-biological particles carrying them. Hence, from the exposure assessment perspective, a detailed characteristic of airborne microbial components carried on dust particles could be of high importance. The aim of this study was to determine the concentrations of endotoxins, (1-3)-β-glucans and culturable microorganisms in coarse, fine and aerosol fractions collected in two office buildings.

2. Materials and methods

2.1. Sampling strategies

The measurements were carried out in summer season in two air-conditioned office buildings in Warsaw, Poland. Two bioaerosol as well as two particulate aerosol samples were taken at each of 12 studied office premises. The studied offices were divided into two groups: open space (for at least 10 workers) and double rooms. The area of examined rooms ranged from 15 m^2 (the smallest) to 64 m^2 (the largest). Additionally, the so-called background samples were taken outside the buildings to determine the outdoor level and to control a possible migration of microbiological contaminants into the indoor environment.

2.2. The culturable microorganisms

A sampling of viable microorganisms was carried out using a six-stage Andersen impactor (model 10-710, Andersen Instruments, Atlanta, GA, USA) at a flow rate of 28.3 l/min for 5 min. The samples were collected on nutrient media (BTL, Łódź, Poland): blood trypticase soy agar for mesophilic bacteria, EMB was applied for Gram-negative rods and malt extract agar for fungi. After incubation (for bacteria: 1 day at 37°C, followed by 3 days at 22°C and 3 days at 4°C; for fungi: 4 days at 30°C followed by 4 days at 22°C), the bacterial and fungal concentrations were calculated as colony forming units per m^3 (CFU/m^3). To obtain the bioaerosol concentration in coarse and fine fractions, concentrations from stages I-IV (> 7-2.1 µm) and IV-VI (2.1 -< 0.65 µm) were summed, respectively. The isolated bacterial colonies were identified to the genus and/or species level based on their morphology, microscopic structure and biochemical reactivity (using API tests; bioMérieux, Marcy-l'Etoile, France). The isolated fungal colonies were directly identified under stereo (SteREO Discovery V.12,Carl Zeiss, Göttingen, Germany) and light microscopes (Eclipse E200, Nikon, Tokyo, Japan) based on their macro- and micro-morphological characteristics. The analysis of yeasts was additionally supplemented by biochemical API tests (bioMérieux).

2.3. Particulate aerosol, endotoxins and (1-3)-β-D-glucans

The concentrations of particulate aerosol were measured using Sioutas impactor (SKC Ltd., Eighty Four, PA, USA) at a flow rate of 9 l/min for 240 min. Particles were separated in five aerodynamic particle diameter ranges: <0.25 (stage E), 0.25-0.5 (stage D), 0.5-1.0 (stage C), 1.0-2.5 (stage B) and 2.5-10µm (stage A). Particles were collected on 25-mm (stage A-D) and 37-mm PTFF filters (stage E) with 0.5 µm and 2 µm pore sizes, respectively (SKC Ltd.). The mass concentrations of particulate matter in all samples were gravimetrically determined before and after sampling following in both cases a 24 h equilibration period of filters at constant air temperature and humidity. PM_{10}, $PM_{2.5}$ and PM_1 values from stages A-E, B-E and C-E were summed, respectively. After gravimetric analysis, each filter was transferred into a 50-ml, pyrogen-free tubes (Lonza, Basel, Switzerland) with 10 ml of sterile pyrogen-free water and extracted for endotoxins and (1-3)-β-D-glucans. A detailed description of analytical procedures has already been presented by Ławniczek-Wałczyk et al. (2013). The concentrations of (1-3)-β-D-glucans and endotoxins were quantify using Glucatell (Associates of Cape Cod, East Falmouth, MA, USA) and Kinetic-QCL LAL (Lonza) assays, respectively. The concentration of airborne endotoxin was expressed in EU/m^3, whereas the (1-3)-β-D-glucans concentrations in ng/m^3.

2.4. Statistical analysis

The collected measurement data were subjected to the analysis of variance (ANOVA) supplemented with a post-hoc (Scheffe) test and correlation analysis using the STATISTICA software package version 7.1 (StatSoft, Inc., Tulsa, USA), assuming p values below 0.05 as statistically significant.

3. Results and discussion

3.1. The concentrations of culturable microorganisms

The concentrations (mean, standard deviation) of culturable microorganisms in examined offices are presented in Figure 1.

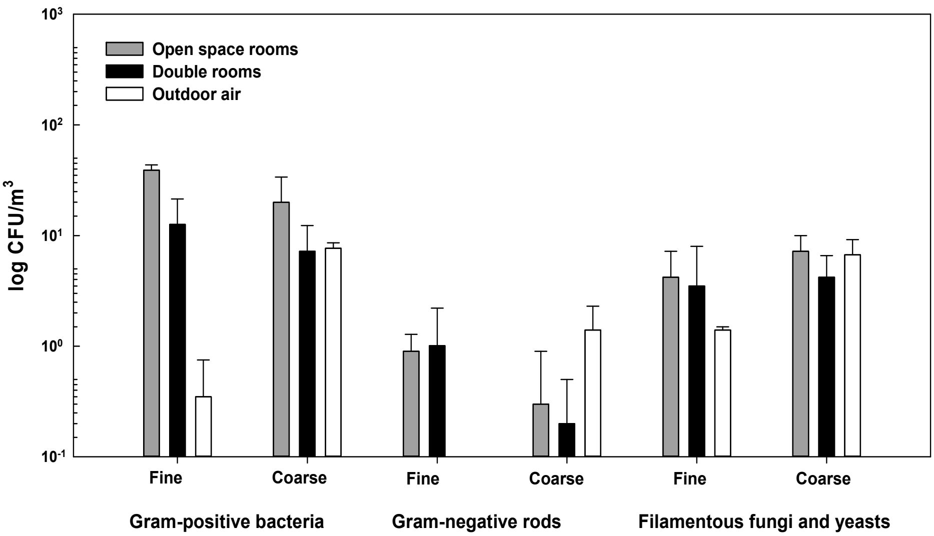

Fig. 1. The microbial fine and coarse concentrations (arithmetic mean, standard deviation) in the air of the examined offices and outdoor air

In both types of examined rooms, the higher levels of bacteria were observed in fine bioaerosol fraction (average: $3.9 \cdot 10^2$ CFU/m^3) than in coarse ($p < 0.01$). Moreover, the concentrations of Gram-positive bacteria in fine and coarse fractions recorded in open space rooms were significantly higher than in double rooms and outdoor background ($p < 0.05$). The higher levels of fungi in both groups of studied offices were observed in coarse bioaerosol fraction (average: of $5.6 \cdot 10^1$ CFU/m^3). For outdoor background, higher bacterial and fungal aerosol concentrations were observed in coarse fractions ($p < 0.01$). The comparison between indoor and outdoor concentrations of Gram-positive bacteria and fungi showed that their indoor concentrations only in open space rooms were higher than in outdoor air ($p < 0.05$). In case of Gram-negative bacteria, the higher concentrations in coarse fractions were noted in outdoor background than in indoor spaces. It is well known that people are the main active source of bacterial aerosol in the indoor environments. These microorganisms are emitted in a great number into the air during talking, coughing, sneezing or peeling of skin scales, whereas fungal aerosol particulates (such as intake spores, mycelium fragments, etc.) can be released into the air from the colonies growing on dead organic matter, plants, soil as well as other organic and inorganic substrates. Hence, an infiltration of outdoor air into the building envelope seems to be the major mechanism responsible for fungal contamination in studied offices. Hospodsky et al. (2012) noted that human activities may increase the total aerosol mass and bacterial concentration in PM_{10} and $PM_{2.5}$ size fractions in classrooms.

The one of the mechanisms increasing microbial concentration in coarse fraction of air in homes, classrooms, and buildings is resuspension. It was also shown that resuspension from the carpet was significantly higher compared to a smooth floor (Fromme, 2012; Hospodsky et al., 2012). In both types of examined offices, the most common organisms were Gram-positive mesophilic bacteria (37-70% of all identified isolates) followed by fungi (constituting 20-34% of the total microbiota) (Figure 2). Gram-positive bacteria from *Micrococcus*, *Staphylococcus*, *Enterococcus*, *Streptococcus* and *Kocuria* genera dominated in both types of studied offices. They belong to the normal human skin microbiota, but also can be commonly found in the outdoor environment (soil, water, etc.). Such non-pathogenic species present in the air may become an opportunistic pathogen under certain conditions (for example when they are in extremely high concentrations) (Hospodsky et al., 2012). It is well known that e.g. peptidoglycan, the major component of Gram-positive bacterial cell wall, could have a negative effect on human and animal health and if inhaled may contribute to adverse health processes such as infection, endotoxemia and other systemic inflammations (even with organ failure) (Poole et. al., 2012). Gram-positive bacilli and non-sporing rods of the *Microbacterium* genus, which naturally inhabit plants and soil, were also present in the studied premises. Among Gram-negative rods prevailed species from genera: *Sphingomonas*, *Pseudomonas* and *Klebsiella.* In the observed levels, they should not pose a threat to human health. The most frequently isolated fungi belonged to *Penicillium*, *Aspergillus*, *Cladosporium* and *Acremonium* genera. These fungi are naturally present in soil, plants and polluted water, and usually, they do not pose a threat to humans. When analyzing the presence of fungi in enclosed spaces, it should be remembered that their spores can persist for a long time on interior furnishings, offices equipment and elements of heating installations. Due to their allergenic properties, they may pose a potential threat to people staying inside buildings; therefore, the efficient operation of the ventilation system in these interiors is an extremely important issue. In the collected air samples, there was also a small number of yeast of the genera *Candida* and *Rhodotorula*. They inhabit human skin, and in people with dermatological problems may be the reason of mycosis (Flannigan et. al., 2011).

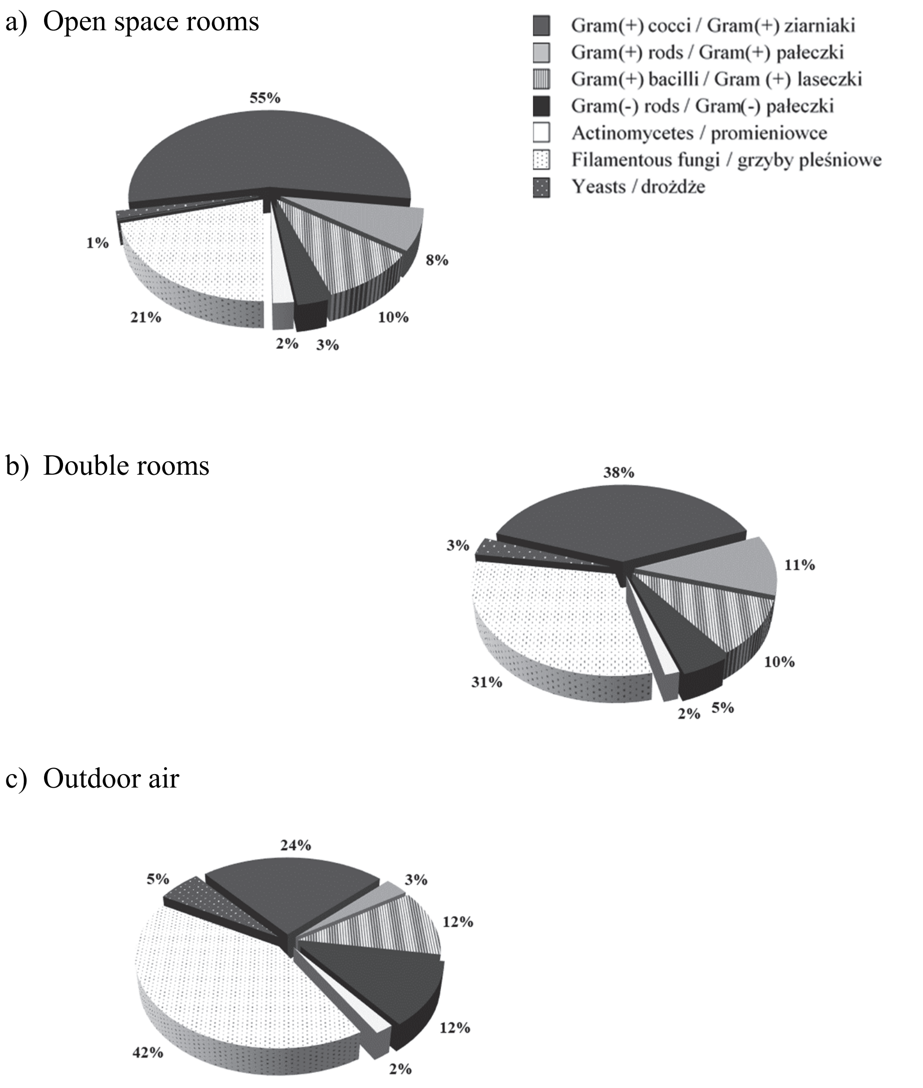

Fig. 2. The percentage contribution of microbial groups to the total isolated microbiota in indoor and outdoor air

To assess the exposure of office workers to harmful microbiological agents presented in the air, the regulation contained in European Directive 2000/54/EC on the protection of workers from risk related to exposure to biological agents at work were applied. In the studied premises, 8 bacterial (*Actinomyces* spp., *Corynebacterium* spp., *Klebsiella pneumoniae, Klebsiella* spp., *Staphylococcus aureus*, *Streptomyces* spp., *Streptococcus* spp., and *Streptococcus pyogenes*) and 1 fungal (*Aspergillus fumigatus*) species were classified to risk group 2 according to the Directive 2000/54/EC and based on that might be recognized as hazard to workers' health. However they, that concentrations were relatively low and did not exceed their levels normally observed in this environment. Nowadays, there is a lack of commonly approved criteria for the assessment of exposure to airborne bacteria and fungi as well as health-based guideline or threshold limit values for airborne microbial contaminants. In Poland, however, such threshold limit values (TLV) were proposed by the Interdepartmental Commission for Maximum Admissible Concentrations and Intensities for Agents Harmful to Health in the Working Environment. For bacteria and fungi in the air of residential and public utility premises as well as in outdoor air in all cases the TLV is equal $5.0 \cdot 10^3$ CFU/m^3. The obtained bacterial and fungal concentrations in offices and in outdoor air were below the Polish TLV (Górny et al., 2011).

3.2. PM Concentrations

The PM levels are often monitored as parameters determining a degree of air pollution in the office buildings. The concentrations of particulate aerosol in the examined offices are presented in Figure 3. It was found that PM concentrations varied between the studied rooms. In open space offices the mean concentrations of PM_1, $PM_{2.5}$ and $PM_{2.5\text{-}10}$ were at the level of 24, 35 and 7.5 μg/m^3, respectively, and were significantly higher than in double rooms (1.9, 4 and 1.8 μg/m^3, respectively) ($p < 0.01$). The obtained results showed that the concentrations of fine particle fraction ($PM_{2.5}$) were higher than coarse ones ($PM_{2.5\text{-}10}$). During this study, indoor PM_1 accounted for 67% and 65% of the $PM_{2.5}$ fraction in the open space and double rooms, respectively.

The comparison between indoor and outdoor particulate aerosol concentrations showed that outdoor PM concentration in the all measured fractions was significantly higher than those observed in double rooms ($p < 0.05$). The concentration of PM_1, $PM_{2.5}$ in open space offices were higher than in outdoor background, but the differences were not significant. It was noted, that outdoors PM_1 and $PM_{2.5}$ concentrations were higher than $PM_{2.5\text{-}10}$.

The PM measurements carried out by other researchers show that concentrations of PM_{10}, $PM_{2.5}$ and PM_1 in public buildings are usually in the range of $1.1 \cdot 10^1$-$1.8 \cdot 10^2$ μg/m^3, and $0.4 \cdot 10^1$-$6.7 \cdot 10^1$ μg/m^3, and $0.4 \cdot 10^1$-$3,4 \cdot 10^1$ μg/m^3, respectively (Reynolds et al., 2001; Gemenetzis et al., 2006; Menetrez et al., 2009; Balasubramanian et al., 2012; Szigeti et al., 2014; Morawska et al., 2017). The mean concentrations of studied fractions obtained in double rooms were lower or close to those observed by other researchers, and lower than 24 h WHO recommended values of 50 μg/m^3 and 25 μg/m^3, respectively for PM_{10} and $PM_{2.5}$ (WHO, 2006). The high values of $PM_{2.5}$ observed in open space rooms may be related to the occurrence of internal emission sources (e.g. emission from office devices), increased activity of people, and insufficient ventilation of the rooms (Morawska et al., 2017; Butler et al., 2016).

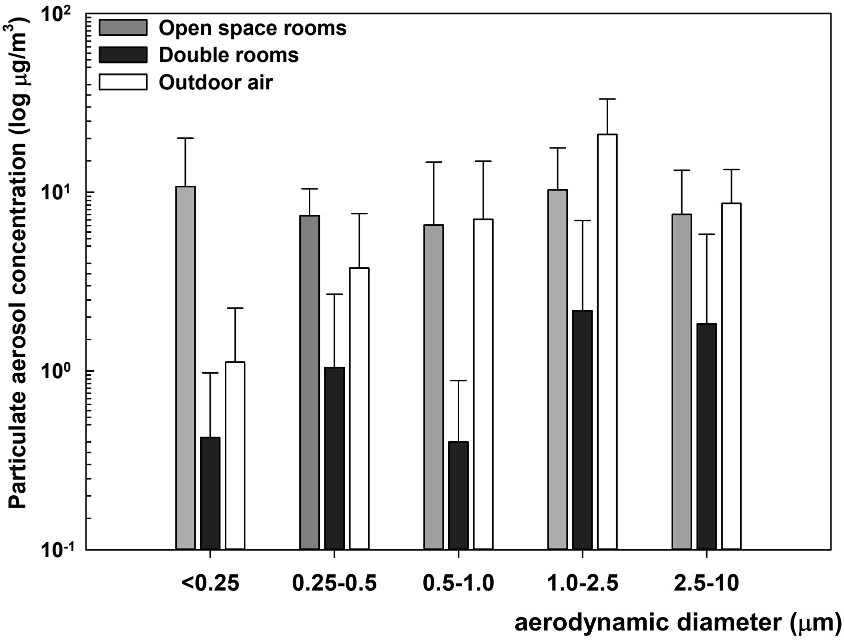

Fig. 3. The concentration (arithmetic mean, standard deviation) of particulate aerosol fractions in the examined offices

3.3. The concentrations of endotoxins and (1-3)-β-glucans

The PM concentrations of endotoxins in the studied offices are presented in Figure 4. In open space offices, the mean concentrations of endotoxins in PM_1, $PM_{2.5}$ and $PM_{2.5\text{-}10}$ were at the level of 9.9, 14.4 and 2.2 EU/m^3, respectively, and were higher than in double rooms (2.6, 3.8 and 2.1 EU/m^3, respectively) ($p < 0.01$). It was found that the concentrations of endotoxins in fine fraction were significantly higher than in coarse ones ($p < 0.01$). The concentrations of endotoxins in outdoor samples of PM_1, $PM_{2.5}$ $PM_{2.5\text{-}10}$ (2.7, 4.2 and 4 EU/m^3) were lower than in open space rooms ($p < 0.05$), but higher than in double rooms. However, this last-mentioned difference was not significant. A few studies conducted in public buildings have reported that concentrations of endotoxins in total dust and $PM_{2.5}$, may be in the ranges of 0.1-9,2 and 0.05-90 EU/m^3, respectively (Menetrez, et al., 2009; Balasubramanian et al., 2012; Bródka et al., 2012). The measurements carried out in homes have shown that endotoxin concentrations in the $PM_{2.5\text{-}10}$, $PM_{2.5}$, and PM_1 dust fractions can be at the level of 0.01-0.08; 0.01-39, 0.1-2.5 EU/m^3, respectively (Górny et al., 1999; Chen & Hildemann, 2009; Singh et al., 2011b; Balasubramanian et al., 2012; Yoda et al., 2017). The endotoxin concentrations obtained in this study were similar (double rooms) or higher (open space offices) than those hitherto reported in the scientific literature. Based on these observations, it can be assumed that the air-conditioning system did not properly reduce endotoxins and PM levels in studied open space offices.

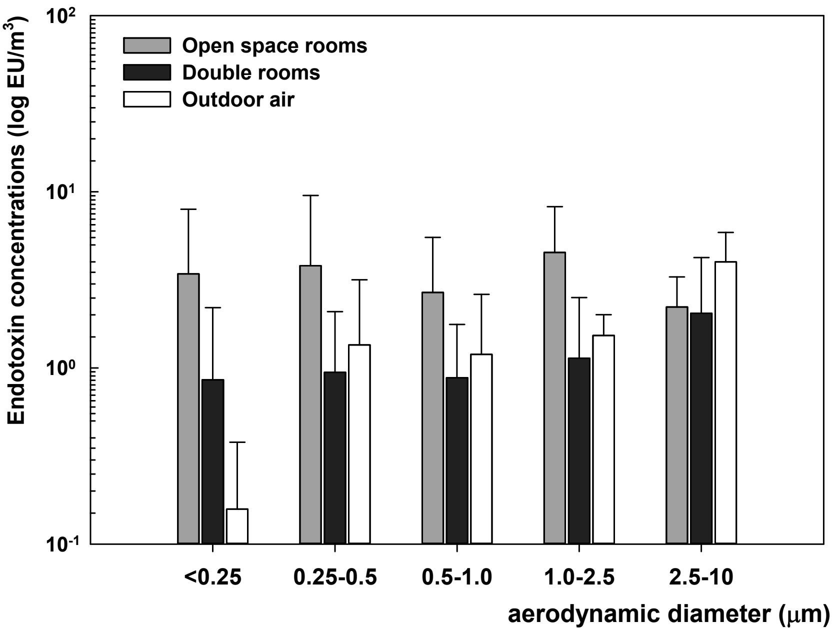

Fig. 4. The concentrations (arithmetic mean, standard deviation) of endotoxins of particulate aerosol fractions in the examined offices

The concentration of (1-3)-β-D-glucans in the examined offices are presented in Figure 5. There were no significant differences in (1-3)-β-D-glucans levels between examined offices. Their mean concentrations in PM_1, $PM_{2.5}$, and $PM_{2.5\text{-}10}$ were at the level of 6.7, 13.1 and 2ng/m^3 in open space rooms, and 5.4, 12.7 and 2.8 ng/m^3 in double rooms, respectively. It was also observed, that the concentrations of β-glucans in fine fraction were significantly higher than in coarse ones ($p < 0.001$). It was noted, that outdoors β-D-glucans concentrations in PM_1 (1.8 ng/m^3) and $PM_{2.5}$ (3.4 ng/m^3) were lower than in studied rooms, while their load in $PM_{2.5-10}$ (10 ng/m^3) were significantly higher in outdoor than indoor samples ($p < 0.5$). Recent investigations conducted in homes in urban areas by Chen & Hildemann (2009) have shown that β-D-glucan concentrations in the PM_{10}, $PM_{2.5}$ may reach 0.1 · 9 ng/m^3 and 0.1 · 1.4 ng/m^3, respectively. In Singh et al. studies (2011a,b) carried out in rural homes, (1-3)-β-D-glucan levels in PM_1 were in the range between 0.01-29 ng/m^3. A very wide range of (1-3)-β-D-glucan concentrations in the air of office buildings 0.4-52,5 ng/m^3 (TSP) was also obtained by Madsen et al. (2010) and Bródka et al. (2012). Taking into account the above-mentioned values, it can be concluded that the concentrations of (1-3)-β-D-glucans in the air of studied office buildings were characteristic for this type of premises.

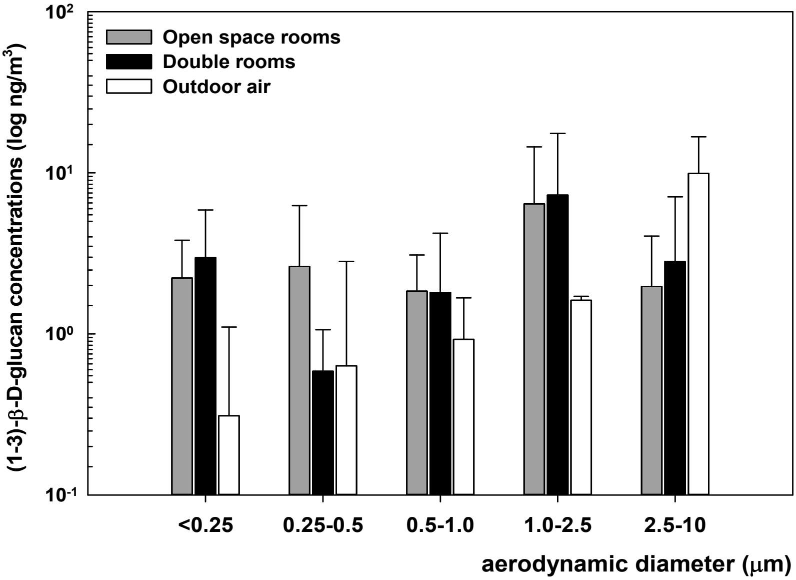

Fig. 5. The concentration (arithmetic mean, standard deviation) of (1-3)-β-D-glucans in particulate aerosol fractions in the examined offices

It was also found that endotoxin and (1-3)-β-D-glucan levels in PM_1 and $PM_{2.5}$ in both types of studies offices were higher than measured in homes (Singh et al., 2011a; Yoda et al., 2017). Moreover in our study, fine fractions (< 2.5 and < 1 μm) from offices had a significantly higher content ($p < 0.01$) of endotoxin and

(1-3)-β-D-glucans compared to outdoor samples. The concentrations of endotoxins showed a strong positive correlation with PM_1 ($r = 0.61$, $p<0.05$) and $PM_{2.5}$ levels ($r = 0.76$, $p < 0.05$) as well as with Gram-negative rods in fine bioaerosol fraction ($r = 0.75$, $p < 0.05$). The concentrations of (1-3)-β-D-glucans showed positive correlation with $PM_{2.5}$ ($r = 0.54$, $p < 0.05$) and $PM_{2.5\text{-}10}$ ($r = 0.28$, $p > 0.05$). The concentrations of (1-3)-β-D-glucans in $PM_{2.5}$ showed a positive correlation with fungi in fine bioaerosol fraction ($r = 0.59$, $p < 0.05$). Considering the above-mentioned relations, it can be concluded that the main source of endotoxins in the offices were Gram-negative rods. The sources of (1-3)-β-D-glucans were probably both fungal conidia and their fragments of aerodynamic diameters < 2.1 μm. All endotoxins and (1-3)-β-D-glucans levels in each of measured PM fractions showed a weak positive correlation with their outdoor levels. This observation can be explained by the fact that smaller particles may remain suspended in the air of indoor premises for longer period of time. Different human activities (walking, cleaning, etc.) can also cause aerosolization of microorganisms and their fragments into the air of indoors (Fromme et al., 2017; Salimifard et al., 2017).

In this study, the use of Andersen and Sioutas impactors allowed to describe the forms, in which the microbial particles are present in the air of studied office premises as well as their potential depth of penetration in the human respiratory system. The analysis of bioaerosol size distribution confirmed that bacteria occurred in the form of single cells and fungi occurred in the form of small conidia and fungal-dust aggregates. It was also found that the main carriers of endotoxins and (1-3)-β-D-glucans in this work environment were fine aerosol fractions with particle diameters < 2.5 μm. Such particles can penetrate the lower parts of the human respiratory system posing a health risk for exposed people (Ruzer & Harley, 2012). This study is among few investigations evaluating endotoxin and (1-3)-β-D-glucan concentrations in fine and coarse fractions. On the world scale, there are currently no widely accepted guidelines regarding interpretation of such measurement data (Ławniczek-Wałczyk & Górny, 2010; Górny et al., 2011). However in Poland, the TLV for occupational exposure to endotoxins in the environments polluted with organic dust (2000 EU/m^3) and in non-industrial (public buildings, dwellings) indoor environments (50 EU/m^3) were proposed (Górny et al., 2011). It should be emphasized that these values are related to the endotoxin concentration in total dust only. According to these proposals, the levels of endotoxins measured in studied offices were below proposed TLV of 50 EU/m^3. Nowadays, there are only a few studies concerning exposure to (1-3)-β-D-glucans in offices. The results of (1-3)-β-D-glucans' measurement conducted in the present study are similar to those reported by other authors (Rylander, 1997; Madsen et al., 2010), however, they focused on (1-3)-β-D-glucan levels in total dust only. So far, there are no TLV proposals for (1-3)-β-D-glucans. Research carried by Rylander (1997) indicated that exposure to 5ng/m^3

may be associated with the occurrence of many non-specific health problems such as headache, irritation of the throat and nose, and general fatigue. In this light, the obtained results suggest that exposure of office workers to (1-3)-β-D-glucans may increase the incidence of above mentioned adverse health effects. Hence, the measurements of (1-3)-β-D-glucans can be a useful tool supporting the hygienic quality assessment in office as well as in public utility premises.

4. Conclusions

- The concentrations of particulate matter, endotoxins, (1-3)-β-D-glucans and microorganisms in the air of open space rooms were higher than those noted in double rooms.
- This study demonstrated that endotoxins and (1-3)-β-D-glucans are mainly associated with fine fractions of aerosol particles in office buildings. Such particles can penetrate the lower parts of the human respiratory system posing a health risk for exposed people.
- The main source of endotoxins in the offices were Gram-negative rods. The sources of (1-3)-β-D-glucans were probably both fungal conidia and their fragments of aerodynamic diameters < 2.1 μm.
- The concentrations of airborne endotoxins, bacterial and fungal microorganism in offices were within the range normally observed in this type of facilities and did not exceed the proposed TLV for them.
- The measured airborne (1-3)-β-D-glucan concentrations exceeded 5 ng/m^3. Such exposure of office workers to airborne fungal components may increase the incidence of adverse health effects.
- Qualitative analysis of bioaerosols enabled to identify bacterial and fungal strains from the risk group 2 (according to the Directive 2000/54/EC), which might pose a health hazard to workers. However, these microorganisms in the observed low concentrations should not pose a threat to the health of employees.
- The constant monitoring of the hygienic condition of studied rooms is suggested, including regular cleaning and replacement of air filters in the air-conditioning system. This should prevent microbiological contamination of the offices in the future.

This paper has been based on the results of a research task carried out within the scope of the fourth stage of the National Programme "Improvement of safety and working conditions" partly supported in 2017-2019 – within the scope of research and development – by the Ministry of Science and Higher Education/National Centre for Research and Development. The Central Institute for Labour Protection – National Research Institute is the Programme's main co-ordinator.

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Abstract

In old and modern interiors, particular attention is focused on the air quality as one of major determinants of the well-being of occupants. Exposure to microbiological contaminants in such close indoor space may be associated with the occurrence of various adverse health outcomes in the exposed individuals. Because the size of inhaled particles determines their place of deposition in the human airways and the associated adverse health outcomes, a detailed characteristic of airborne microbial components carried on fine dust particles in office buildings is needed. The aim of this study was to determine the concentrations of endotoxins, (1-3)-β-D-glucans and culturable microorganisms in coarse, fine and aerosol fractions collected in two office buildings in Warsaw. The concentrations of particulate aerosol were measured using Sioutas impactors in PM_1, $PM_{2.5}$, and $PM_{2.5-10}$. Kinetic-QCL LAL and Glucatell assays were used to detect endotoxin and (1-3)-β-D-glucan concentrations, respectively. The bioaerosol samples were taken using six-stage Andersen impactor as coarse (> 7-2.1 μm) and fine (< 2.1 μm) fractions, as well.

The mean concentrations of particulate aerosol, endotoxins and (1-3)-β-D-glucans in all studied offices were: in PM^1 – 6 μg/m^3, 4 EU/m^3 and 5 ng/m^3; in $PM_{2.5}$ – 11 μg/m^3, 6 EU/m^3 and 10 ng/m^3; and $PM_{10-2.5}$ – 3.5 μg/m^3, 2 EU/m^3 and 2.5 ng/m^3, respectively. The concentrations of endotoxins and (1-3)-β-glucans in $PM_{2.5}$ were significantly higher than in $PM_{10-2.5}$ ($p < 0.01$ and $p < 0.001$, respectively) and accounted for 71% and 84% of their total load in PM_{10}. The airborne bacteria occurred mostly in fine fraction (average $3.9 \cdot 10^2$ CFU/m^3, $p < 0.01$), while fungi in coarse fraction of aerosol ($5.6 \cdot 10^1$ CFU/m^3). The concentrations of endotoxins showed a positive correlation with PM_1 ($r = 0.61$, $p < 0.05$) and $PM_{2.5}$ levels ($r = 0.76$, $p < 0.05$) as well as with Gram-negative rods in fine fraction ($r = 0.75$, $p < 0.05$). The concentrations of (1-3)-β-D-glucans showed positive correlation with $PM_{2.5}$ ($r = 0.54$, $p < 0.05$) and fungi in fine fraction ($r = 0.59$, $p < 0.05$).

This study demonstrated that endotoxins and (1-3)-β-D-glucans are associated mostly with fine fraction of aerosol particles. Such particles can penetrate the lower parts of the human respiratory system posing a health risk for exposed people. The main source of endotoxins in the offices were Gram-negative rods. The sources of (1-3)-β-D-glucans were probably both fungal conidia and their fragments of aerodynamic diameters <2.1 μm. The noted concentrations of endotoxins and microorganism were within the range normally observed in this type of facilities. Nevertheless, constant monitoring of the hygienic condition is suggested, including regular cleaning and replacement of air filters in the air-conditioning system.

Keywords:
offices, endotoxins, (1-3)-β-D-glucans, PM_1, $PM_{2.5}$, $PM_{2.5-10}$, bioaerosol

Transport cząstek pochodzenia mikrobiologicznego w drobnej i grubej frakcji aerozolu w budynkach biurowych

Streszczenie

Zarówno w starych, jak i nowoczesnych wnętrzach budynków biurowych szczególną uwagę zwraca się na jakość powietrza, która jest wyznacznikiem dobrostanu mieszkańców. Narażenie na zanieczyszczenia mikrobiologiczne w takich zamkniętych pomieszczeniach może być związane z pojawianiem się różnych niekorzystnych efektów zdrowotnych u narażonych osób. Ponieważ wielkość wdychanych cząstek determinuje ich miejsce osadzania w drogach oddechowych człowieka i związane z tym problemy zdrowotne, potrzebna jest szczegółowa charakterystyka frakcji cząstek pyłowych transportujących cząstki pochodzenia mikrobiologicznego w budynkach biurowych. Celem niniejszego badania było poznanie zakresów stężeń endotoksyn, (1-3)-β-D-glukanów i mikroorganizmów w drobnej i grubej frakcji aerozolu ziarnistego w dwóch budynkach biurowych w Warszawie. Stężenia aerozolu ziarnistego zmierzono przy użyciu impaktorów Sioutas we frakcjach PM_1, $PM_{2.5}$ i $PM_{2.5\text{-}10}$. Testy Kinetic-QCL LAL i Glucatell zastosowano odpowiednio do detekcji endotoksyn i β-D-glukanów. Próbki biaerozolu pobrano przy użyciu sześcio-stopniowego impaktora Andersena we frakcji gruboziarnistej (> 7-2,1 µm) i drobnej (< 2,1 µm).

Średnie stężenia aerozolu ziarnistego, endotoksyn i β-D-glukanów w wszystkich badanych biurach wynosiły odpowiednio: w PM_1 – 6 µg/m^3, 4 JE/m^3 i 5 ng/m^3; w $PM_{2.5}$ – 11 µg/m^3, 6 JE/m^3 i 10 ng/m^3 i w $PM_{10\text{-}2.5}$ – 3.5 µg/m^3, 2 JE/m^3 i 2.5 ng/m^3. Stężenia endotoksyn i β-D-glukanów w $PM_{2.5}$ były znacznie wyższe niż w $PM_{10\text{-}2.5}$ (odpowiednio $p < 0.01$ i $p < 0.001$) i stanowiły 71% i 84% frakcji PM_{10}. W badanych pomieszczeniach, bakterie występowały głównie w drobnej frakcji aerozolu ($3.9 \cdot 10^2$ JTK/m^3, $p < 0.01$), podczas gdy grzyby izolowano najczęściej z frakcji gruboziarnistej aerozolu ($5.6 \cdot 10^1$ JTK/m^3). Stwierdzono pozytywną korelację pomiędzy stężeniami endotoksyn a stężeniami pyłu PM_1 ($r = 0.61$, $p < 0.05$) i $PM_{2.5}$ ($r = 0.76$, $p < 0.05$), jak również Gram-ujemnymi pałeczkami ($r = 0.75$, $p < 0.05$). Stężenia β-D-glucans wykazały korelację z $PM_{2.5}$ ($r = 0.54$, $p < 0.05$) oraz grzybami w drobnej frakcji ($r = 0.59$, $p < 0.05$).

Niniejsze badania wykazały, że głównym nośnikiem endotoksyn i (1-3)-β-D-glukanów w pomieszczeniach biurowych były drobne frakcje aerozolu ziarnistego. Cząstki te mogą przenikać do dolnych dróg oddechowych powodując niekorzystne skutki zdrowotne u narażonych osób. Stwierdzono, że głównym źródłem endotoksyn były Gram-ujemne pałeczniki. Źródłami (1-3)-β-D-glukanów były głównie fragmenty strzępek grzybni (lub spor) o aerodynamicznych średnicach <2,1 µm. Odnotowane stężenia endotoksyn i mikroorganizmów w biurach mieściły się w zakresie normalnie obserwowanym w tego typu obiektach. Niemniej jednak sugerowane jest stałe monitorowanie stanu higienicznego tych pomieszczeń, w tym regularne czyszczenie i wymienianie filtrów powietrza w instalacji klimatyzacyjnej.

Słowa kluczowe:
biura, endotoksyny, (1-3)-β-D-glukany, PM_1, $PM_{2.5}$, $PM_{2.5\text{-}10}$, bioaerozol

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Airborne Microorganisms of Hypogenic Maze Caves Based on the Example of the Zoloushka Cave, Ukraine-Moldova

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1. Introduction

The cave environment, due to its specificity (stable microclimate, high humidity, abundance of organic material, etc.), greatly facilitates the occurrence and growth of various types of microorganisms. They occur in all sub–environments of the underground: in the air, water, sediments, speleothems, at the bottom of the lakes, on the surface of the walls etc. Numerous studies conducted in recent decades by geo-microbiologists resulted in discovering extraordinary richness and diversity of the microbial life in caves, and led to a number of interesting discoveries referring to a geochemical role of microorganisms in the accumulation of mineral (biomineral) compounds in the caves (Wang et al. 2010, Muhammad 2018).

Among various geomicrobiological studies in caves, the greatest attention (and numerous publications) has been devoted to microorganisms related to the mineral substrate of the cave environment (walls and ceiling, speleothems) and deposits (silt), whereas very little attention has been paid to microorganisms present in the waters of cave reservoirs and the condensate. However, research on airborne microorganisms in caves is most limited. There are several reasons for that. Firstly, the cave air as an object of study does not arouse as much interest as sediments or water because it is believed that it is generally clean and in comparison with other elements of the cave environment does not contain any interesting microorganisms. Secondly, sample collection for the determination of airborne microorganisms in caves presents more severe methodical and technical difficulties than sampling sediments or water (Monte & Ferrari 2000, Wang et al. 2010, Porca et al. 2011, Ghosh et al. 2017).

In view of the above, the present knowledge of the microorganisms in the cave air is superficial and scarce. The literature on this subject comprises the works by Nakaew et al. (2009) exploring rare strains of *Actinobacteria* in Thai caves, the paper by Wang et al. (2010) presenting mycological research in Chinese caves, the works by Bastian et al. (2009) exploring pathogenic bacteria and protozoa in the Lascaux Cave in France, the works by Mulec et al. (2012) showing the airborne microflora of eutrophic caves in Slovenia and Slovakia and the works by Mulec & Oarga (2014) showing airborne bacteria, yeasts and moulds in Cuban cave the Great Cavern of Santo Tomás.

Among a few domestic works dealing directly with this subject, one can mention research carried out in the limestone caves of the Ojców National Park (ONP) (Wojkowski 2013) and in the Bear Cave in Kletno (Ogórek & Leyman 2013). Both of them showed that the airborne microflora of caves is diverse and may contain more microorganisms than the outer atmospheric air, especially in relation to specific groups of microorganisms. The studies also pointed to the relation of the abundance of microorganisms in the cave air with the intensity of the air exchange with the outside, which constitutes the type of the cave microclimate. Several studies were also carried out in the artificially created underground environment, i.e. mines (Pusz et al. 2018, Frączek et al. 2013).

This paper presents the results of studies conducted in a cave which is totally different from the aforementioned limestone caves, which are relatively small and generally characterised by a strong air exchange with the outside environment. The cave being the object of this study is the Zoloushka Cave (Eng. Cinderella Cave), which belongs to the group of caves in Western Ukraine making up the world's largest complex of gypsum caves. The major aim of this research was to determine the number of selected groups of microorganisms present in the air filling the halls and chambers of the Cave. These groups of microorganisms included: heterotrophic bacteria, *Actinobacteria* and fungi. The microbiological studies were accompanied by measurements of microclimate parameters to determine thermal conditions, humidity and circulation occurring in the Cave.

2. Study area, materials and methods

Zoloushka Cave is a large maze cave with a huge total length of corridors (over 90 km) located at a considerable depth below the surface (20-60 m). It is characterised by extremely poor (hindered) air exchange with the outside atmosphere (Andreychouk 2007). The cave is located in the southern part of Western Ukraine, in the district of Chernivtsy (historically – Northern Bukovina), at the place where the borders of three countries (Ukraine, Moldova and Romania) meet (Fig. 1).

Fig. 1. Location of the Zoloushka Cave (black badge) on the background of the Western Ukraine gypsum karst area: 1 – gypsum karst area

One of the borders – between Ukraine and Moldova runs directly above the cave thus dividing it into two parts: the western (Ukrainian) and eastern (Moldovan) (Fig. 2). The greater part of the cave labyrinth is located on the Ukrainian side (about 2/3). The borders of Ukraine and Moldova with Romania are situated within the distance of 0.8-1.3 km to the south of the cave and run along the border river of Prut. The entrance to the cave is located on the Moldovan side. The nearest settlements are: a Ukrainian village of Podvirne (800 m from the entrance) and a Moldovan village of Criva (1.5 km).

The cave was artificially exposed during the exploitation of the gypsum quarry founded in the late '40s of the last century. The discovery of the cave was made in 1977 by speleologists from Chernivtsy, who also carried out its first exploration. Due to the mining activity, a considerable part of the cave labyrinth was destroyed. As a result of the intervention of speleologists and scientific communities in the late '80s the cave was put under the protection by law (it was given the status of a natural monument) on both the Ukrainian and Moldovan sides, and mining operations were altered. The western part of the quarry with the cave holes in the gypsum wall was filled with loose material of dumps, while at the same time a 28-meter high concrete shaft with ladders was built into the ground, thus enabling entering the cave.

Until the cave labyrinth was opened by the quarry, the underground system of cavities had been almost completely filled with water and constituted a natural part of the rich in water karst aquifer. In order to facilitate the exploitation of gypsum, the quarry was being gradually deepened and the water present in gypsum was pumped out. This resulted in creation of a depression cone around the quarry and dehydration of the underground labyrinth, which has allowed its penetration by speleologists and conducting research in the cave.

Since the late '80s of the last century, the cave has been a "training ground" for a variety of research – geological, geochemical, hydrogeological, geotechnical, microclimatic, speleogenetic and others. The value of these studies arises from the fact that the cave became exposed while being at the stage of its active formation, and its artificial dehydration enabled researchers to observe the ('accelerated') course of various processes associated with the transition of the caves from the watered (freatic) stages to vadose and dry. These studies have led to the acquisition of a number of regularities in the development, and also some discoveries. The results have been published in numerous papers, including a synthesizing monograph of one of the discoverers of the cave (Andreychouk 2007).

In the '80s of the last century geo–microbiological research was also carried out in the cave. It was focused on the prevalence of microorganisms in the cave sediments, their typological diversity and their role in the creation of iron–manganese formations (Andreychouk & Klimchouk 2001). These studies indicated a very wide distribution and high biochemical (metabolic) activity of microorganisms in the sediments and on the surface of the walls, which is facilitated by a unique microclimate of the cave and the abundance of organic matter in clay sediments. However, the study did not examine microorganisms in the cave air. Nevertheless this issue appeared to be very interesting due to the specific nature of the cave environment (dehydrated and dried from water but still moist, with very stable climatic conditions) and the presence of a large number of microorganisms in solid sub-environments (on rocks, in sediments, including the bottom sediments of underground reservoirs etc.) which may potentially be a source of airborne microorganisms.

To resolve the issue of the origin of microorganisms in the air of the cave ('exogenous' source – the outer atmosphere or 'endogenous' one – the cave environment), the stability of its microclimate in the course of the year is of considerable importance. Stable microclimate conditions may constitute a background reflecting both external and internal factors. Therefore it is vital to recognise the exact characteristics of the cave microclimate.

Microclimate and microbiological analyses were carried out in measurement series of a few days in two seasons: in winter (2-3.03.2017) and in summer (22-23.06.2017). Fixed measurement sites were established in selected locations of the cave (Fig. 2).

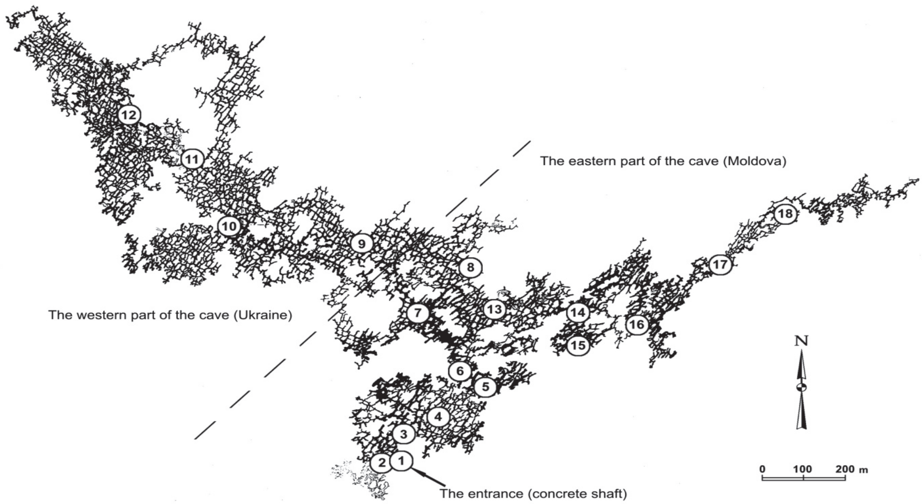

Fig. 2. The distribution of measurement sites within the field of the cave

Air samples for microbiological examination were collected by employing the method of collision detection with the MAS Merck air sampler. At each measurement site the device was placed at a height of about 1.0 m above the cave bottom and air samples were collected in triplicates. The bacterial aerosol was tested on tryptic–soy agar (TSA), *Actinobacteria* – on Gauze agar, and fungi on malt extract agar (MEA). TSA plates were incubated for 24 hours at 37°C, followed by 3 days at 22°C, and for the next 3 days at 4°C. Gauze plates were incubated at 28°C for 7 days, while MEA plates for 4 days at 30°C, then for 4 days at 22°C and for the next 3 days at 4°C. Prolonged incubation of bacterial cultures occurring in the air of caves has allowed the growth of strains growing slowly in the lower temperature range (Jensen & Schafer 1998, Ghosh et al. 2017). After the incubation of the plates, quantitative analysis of the grown microorganisms was performed – the number of grown colonies were counted and the bioaerosol concentration was expressed as the number colony forming units per one cubic meter of the air ($cfu \cdot m^{-3}$). Identification of isolated *Actinobacteria* cultures (Fig. 6) was prepared on the basis of macro- and microscopic morphological features and their biochemical properties based on Bergey's Manual of Determinative Bacteriology (1974).

Microclimate measurements were performed with Assman aspiration psychrometer at a height of 1.0 m above the bottom of cave corridors. Additionally, the temperature and relative humidity at a height of 1.0 m above the cave bottom were automatically recorded with StowAway miniature electronic sensors. The error of the temperature recorder was ±0.2°C, whereas of the relative humidity ±5%. The applicability of the recorders in environmental research, and the accuracy of their measurement were examined in the Department of Meteorology and Climatology of the University of Agriculture in Krakow (Wojkowski & Olechnowicz-Bobrowska 1997).

Microclimate measurements were also performed in the vertical profile of the shaft being the entrance to the cave at noon 23.06.2017 and at midnight 22/23.06.2017.

3. Results

3.1. The main features of the cave microclimate

The following brief characterisation of the cave microclimate is based on previous studies (Korzhyk & Andreychouk, 1981, Andreychouk 2007), and on research conducted by the authors of this article in 2012-2017. According to the nature of air exchange with the outer atmosphere, Zoloushka Cave belongs to static caves, characterised by a stable time course of basic meteorological elements such as pressure, temperature and humidity of the air. Owing to the characteristics of the cave such as a large area of the underground system, its location under impermeable (to water and air) overlying rocks (mostly clay deposits) of a considerable thickness, and connection with the surface through a vertical shaft of a small ventilation cross-section, stable microclimate conditions (static zone) occur in a larger part of the labyrinth (9/10), and these conditions undergo daily and seasonal changes (dynamic zone) only in the vicinity of the entrance (Fig. 3). The border between the zones runs, depending upon the season, at the distance of 30-100 m from the entrance opening (shaft).

The measurements of basic meteorological elements carried out in the cave in recent years show that the air temperature in the static zone is stable and fluctuates, regardless of the season, within the range of 10.8-11.2°C, whereas the relative humidity reaches almost always 100%. However, the latest research conducted by the authors in 2017 point to a minor difference (of 1.0°C) between the temperatures of the cold and warm period (Table 1). At this stage, we are not able to state clearly whether these observed differences really occur, or are the result of systematic measurement errors resulting from technical reasons. Nevertheless the microclimate stability within the major part of the cave is a clear and established fact, which is important for the air circulation in the cave, i.e. the velocity of the exchange of the cave air with the external atmosphere. The observations carried out in recent years have indicated that this exchange is weak. Due to a very slow movement of the air in the static part of the cave it is not possible to measure its velocity using conventional methods, for example with anemometers.

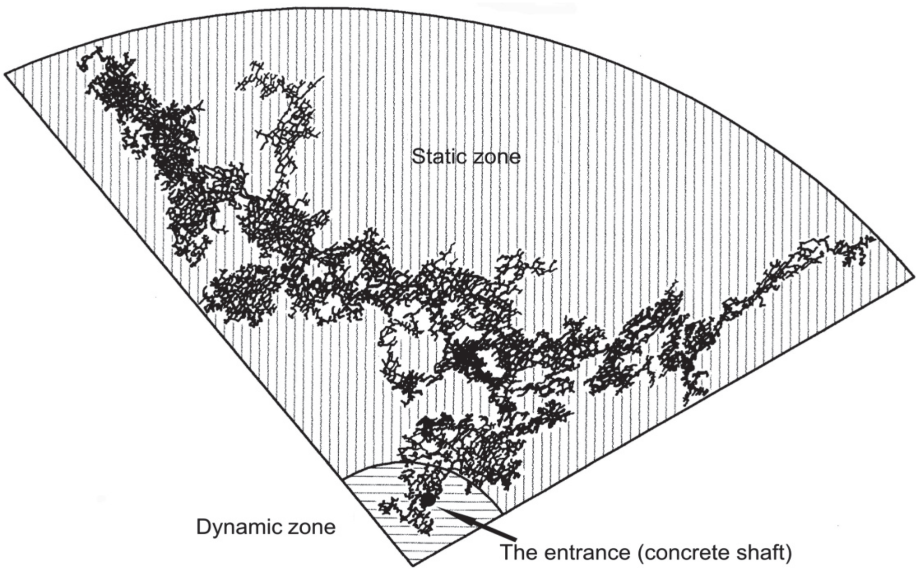

Fig. 3. Microclimatic zones of the Zoloushka Cave (Andreychouk 2007)

Initially, the velocity of the air flow was attempted to be estimated by employing the method of 'smoke' which consists in burning a smoky and fragrant substance, such as incenses flavoured with oils, and observing the spread of smoke in the cave (measurement of how quickly the smoke moves between the specified sites). Repeated observations and measurements performed with the aforesaid method showed that the air in the static part of the cave moves within a distance of approximately 30-100 m per hour, which is equivalent to a velocity of 0.01-0.03 $m \cdot s^{-1}$.

The velocity of the air flow estimated with the method of "smoke", however, contains a serious error. A much more accurate method for measuring the velocity of the air flow turned out to be a katathermometric method. A silver-plated Hill katathermometer was used to measure the cooling quantity of the air, and then the velocity of the air movement was calculated on the basis of empirical formulas (Bradtke and Liese, 1958). The measurements carried out with the katathermometric method showed that in the static part of the cave the velocity of the air movement ranges between 0.05 and 0.08 $m \cdot s^{-1}$ (Table 2). The air movement slightly accelerates on its approaching the dynamic area of the cave.

The general direction of the air movement is always towards the zone around the entrance hole, and in particular towards the area of the cave D-System, which probably has a connection through the rock fissures with the quarry.

Table 1. The results of microclimatic measurements in the Zoloushka Cave during winter and summer periods (italics – measurement sites situated in a dynamic zone, near the entrance)

Measurement sites		Air temperature (°C)		Relative humidity (%)	
		Winter period	Summer period	Winter period	Summer period
1	Outside	4.2	27.5	94	63
2	*Lower part of entrance shaft*	*9.1*	*14.0*	*97*	*97*
3	*The Hall of Kobylanska Prospect*	*11.0*	*13.1*	*98*	*99*
4	The Window	11.0	12.4	100	100
5	The Hall of Perspectives	11.0	12.4	100	100
6	The Overture	–	12.2	–	100
7	The Hall of the Speleologists of Chernivtsy	10.8	12.3	100	100
8	The Stalactitic Couloir	11.2	–	100	–
9	The Western Crossing	11.0	12.4	100	100
10	The Torchs	10.8	12.1	100	99
11	The Cellars	11.0	12.3	100	100
12	The Transition Geochim-Bukovina	11.2	–	100	–
13	The Metro	10.9	12.3	100	100
14	The Dinosaur Hall	10.9	12.3	100	99
15	The Colorado Labyrinth	10.9	12.4	99	99
16	Wet Well	10.8	12.3	99	100
17	The Far Eastern region (beginning)	10.5	–	99	–
18	The Far Eastern region (end)	11.3	–	99	–

Table 2. The results of measurements of air velocity ($m \cdot s^{-1}$)

Measurement sites		Air velocity ($m \cdot s^{-1}$)
1	Outside	0.96
4	The Window	0.05
5	The Hall of Perspectives	0.06
7	The Hall of the Speleologists of Chernivtsy	0.07
9	The Western Crossing	0.05
10	The Torchs	0.06
14	The Dinosaur Hall	0.08

Weak intensity of the exchange of the cave air with the outside atmosphere generally leads to a stagnating regime of the air circulation within a greater part of the cave. This results, among others, in the accumulation of significant amounts of carbon dioxide (CO_2) (1-5%) in the air (Fig. 4). An increase of its content towards deeper parts of the cave reflects weakening of the circulation activity in areas situated further away from the entrance and from the area of D-System ventilating the cave.

In the dynamic zone around the entrance hole, the exchange of the air is much more active. When approaching the bottom of the shaft, a gentle current of air is felt on the face. It is also indicated by a clear seasonal variation of temperature and humidity of the air in this part of the cave (Table 1).

A concrete shaft itself nowadays constitutes an important element of the microclimatic system of the cave enabling its ventilation. The role of the slot ventilation through the quarry still has to be explained. Figures 4 and 5 show that the microclimatic conditions in the shaft, particularly temperature, undergo stratification, especially within the first 10 metres of the shaft, pointing to its buffer (compensating) role in relation to the interior of the cave.

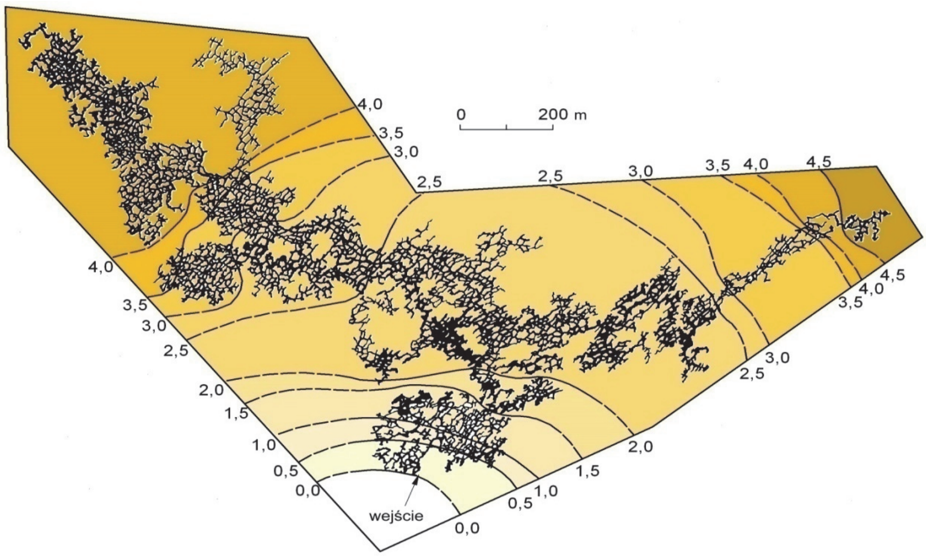

Fig. 4. The content of carbon dioxide (CO_2) in the air of the Zoloushka Cave (Andreychouk et al. 2011)

In the context of the evaluation of air exchange in the cave, extremely important are measurements of the velocity of its movement in the shaft entrance. The performed measurements (Fig. 5) show that it changes within the range of 0.1-1.3 $m \cdot s^{-1}$. Maximum values of the velocity appear on the bottom of the shaft, which results from a distinct narrowing of the transitional opening (< 0.5 m^2) – from the bottom of the shaft to the interior of the cave (the cross section of the shaft is approximately 4 m^2). These data are important for determining the velocity of the exchange of the cave air. Unfortunately, a proper quantitative balancing of the air circulation between the cave and the external environment requires data from a continuous annual monitoring, because the velocity of the exchange is highly variable over time, both in a seasonal course and daily.

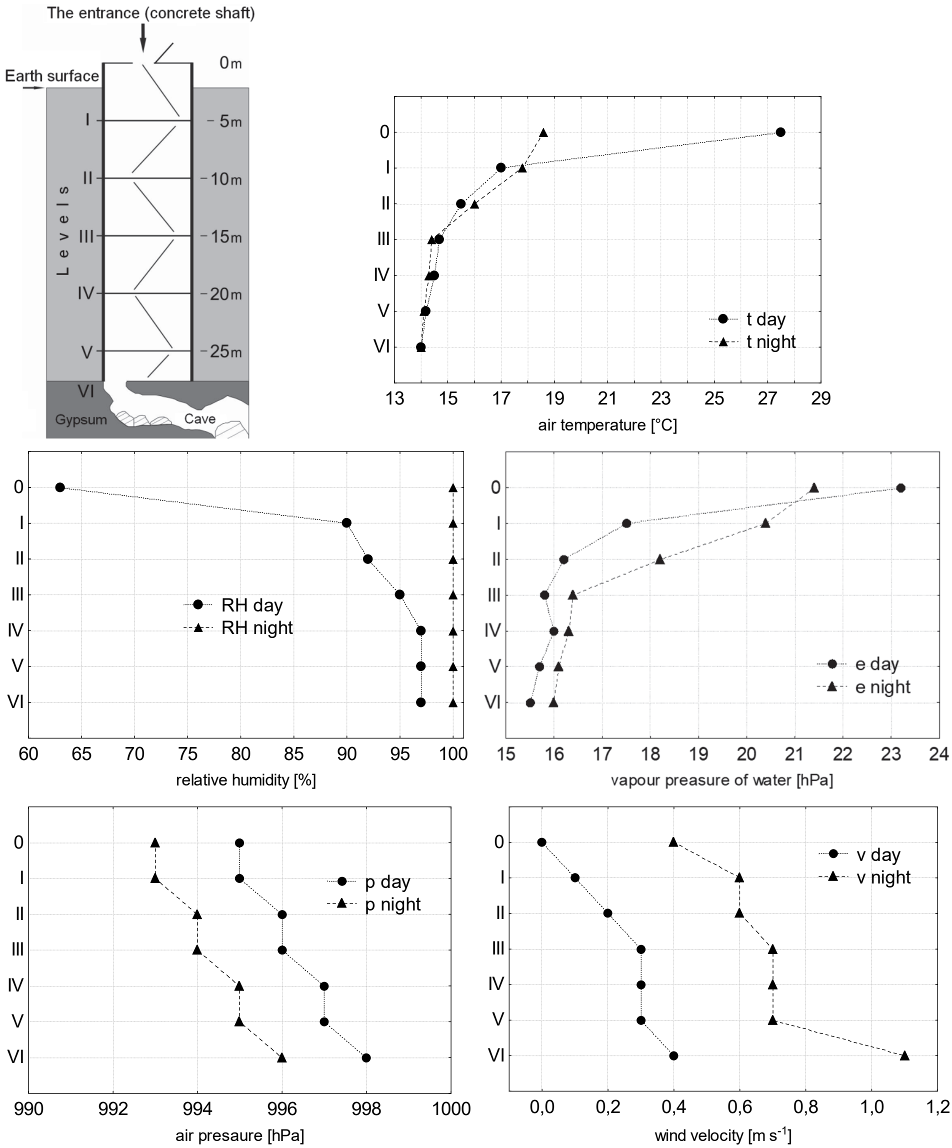

Fig. 5. Selected meteorological elements in the vertical profile of the shaft entrance of the Zoloushka Cave during the daytime and night-time

Periodic observations show, however, that this velocity generally ranges from 0.0 to 1.5 m $\cdot$ s^{-1}. Basing on these values, an attempt may be made to determine the time necessary for a complete exchange of the air in the cave. Given the capacity of the cave – 650 000 m^3, the ventilation opening of 0.5 m^2, and assuming the average value of the velocity of the air flow of 0.7 m $\cdot$ s^{-1}, a complete air exchange in the cave labyrinth may take 21-22 days (about 30 000 m^3 per day).

Nevertheless these calculations should be considered very carefully due to the lack of data from regular year-long measurements. Most likely, however, the total time of the air exchange is much longer because of the peculiarities of the internal circulation of the air in the cave – a stagnating circulation regime in areas distant from the entrance, and more active movement of the air in the area in the vicinity of the opening.

3.2. Microorganisms content in the cave air

The study of airborne microorganisms in the cave atmosphere was conducted in 16 sites under the ground, more or less evenly distributed within the cave field, on the surface of the earth above the cave, and in the entrance shaft to the cave (Fig. 2). The measurements have shown that the total number of the studied groups of microorganisms in the air of the cave varies in the course of year within the following ranges: heterotrophic bacteria 48-2,630 cfu·m^{-3}, fungi 80-3,395 cfu·m^{-3}, and *Actinobacteria* 5-51 cfu·m^{-3} (Table 3). Mean values of the microbial aerosol concentrations with respect to the entire cave are: heterotrophic bacteria – 353 cfu·m^{-3}, fungi – 974 cfu·m^{-3}, and *Actinobacteria* – 17 cfu·m^{-3}.

Based on the analysis, it has been found that the microbial aerosol levels vary greatly between the examined seasons. In general, there is a regularity of an increase in their concentration during the warm period: 3-5 times higher values for bacteria (48-764 cfu·m^{-3} in winter and 175-2630 cfu·m^{-3} in summer), 4-5 times for fungi (80-990 cfu·m^{-3} in winter and 390-3395 cfu·m^{-3} in summer), and 0-1 times for *Actinobacteria* (0-51 cfu·m^{-3} in winter and 5-55 cfu·m^{-3} in summer) (Table 3). In comparison to the external environment, in winter the concentration of microbial aerosol the air of the cave is generally similar in the case of all groups of microorganisms. For heterotrophic bacteria the value recorded outside was – 133 cfu·m^{-3}, while the mean for the cave was 199 cfu·m^{-3}, for fungi the concentration for the outdoor air was 559 cfu·m^{-3} compared with the mean value for the case of 497 cfu·m^{-3}, and for *Actinobacteria* – it was 13 cfu·m^{-3} (outside) and 16 cfu·m^{-3} (mean for the cave). In summer, the picture becomes more diverse, especially in relation to fungi and *Actinobacteria*. The content of fungi in the cave air shows a 4-fold increase from 390 cfu·m^{-3} outside to 1668 cfu·m^{-3} in the cave, whereas the content of *Actinobacteria* decreases from 55 cfu·m^{-3} outside to 15 cfu·m^{-3} inside the cave.

As regards the difference in the concentration of individual groups of microorganisms within the cave field, it should be noted that there are no clear patterns. Similarly low and high levels of airborne microorganisms may occur in the parts of the cave located both closer to the entrance and away from it. Only in the case of *Actinobacteria*, an increase in their concentration can be observed (both in summer and winter) in the part of the cave labyrinth near the entrance hole (measurement sites 2-5 in accordance with the Tables 1-2). As to other groups of microorganisms, what is characteristic for them is their high variability within the cave and their 'abnormally' high amount at certain sites. For example, the content of the heterotrophic bacteria at the measurement site at Wet Well (measurement site No. 16) reaches 764-2630 cfu$\cdot$m^{-3}, which significantly exceeds the mean value for the cave, both in winter (199 cfu$\cdot$m^{-3}) and summer (497 cfu$\cdot$m^{-3}). In the case of fungi, a similar anomaly is characteristic for measurement sites 14-16 in the eastern part of the cave, especially in summer. During a cold period, an increased amount of fungi was noted in the part of the cave located closer to the entrance at the measurement sites No. 3-5 (Table 3).

4. Discussion

Seasonal variability is a very important factor affecting the microbiological quality of cave air (Wang et al. 2010). The aforementioned regularities in the occurrence of microorganisms indicate a rather complex nature of the phenomenon. Seasonal variability of the number of microorganisms in the cave air (and external air), namely an increase in their number in summer, clearly points to a close relationship with the external environment, characterised by a similar trend. This leads to a general conclusion that a majority of population (if not all) of airborne microorganisms in the cave originates from an exogenous (external) source. It seems that this is a natural phenomenon and results from the infiltration of external air carrying an additional load of microorganisms (Kummer & Thiel 2008, Ghosh et al. 2017). However, fungi are an exception as their numbers in summer substantially exceed the external values. Similar results were observed in studies conducted in caves in another part of the world (Wang et al. 2010). The reason for this phenomenon is not yet understood, given the stability of the cave microclimate throughout the year (which is somewhat contradicted by the data from the recent measurements of the microclimate) and relatively low values of the amount of fungi in the external atmospheric air. It is possible that the 'enrichment' of the cave atmosphere with fungi in summer time is not only related to the variability or stability of ecological conditions conducive to the existence of fungi in the cave. Perhaps during the summer period other factors grow in importance: physical (weaker or more active air circulation, drying out or moistening of clay substrate etc.) or biological (the peculiarities of the development cycle and metabolism of fungi). It seems that the widespread presence and dominance of fungi in the air of caves may be conditioned by the fungal production of very numerous spores, as well as their extremely modest nutritional and environmental requirements. Optimal growth conditions for these microorganisms are high air and substrate humidity, although many species are characterised by the ability to survive in very dry conditions (Wang et al. 2010, Porca et al. 2011, Ghosh et al. 2017). This topic, interesting for ecologists concerned with caves, requires more extensive research.

Table 3. Concentration of microorganisms (cfu·m^{-3}) in the air of Zoloushka Cave during winter and summer periods (*italics* – measurement sites situated in a dynamic zone, near the entrance)

Measurement sites		Bacteria (except *Actinobacteria*) (cfu·m^{-3})		Fungi (cfu·m^{-3})		*Actinobacteria* (cfu·m^{-3})	
		Winter period	Summer period	Winter period	Summer period	Winter period	Summer period
1	**Outside**	**133**	**710**	**559**	**390**	**13**	**55**
2	*Lower part of entrance shaft*	171	360	404	1120	9	42
3	*The Hall of Kobylanska Prospect*	100	262	695	1355	29	20
4	The Window	221	230	668	1610	32	20
5	The Hall of Perspectives	116	370	990	1865	51	25
6	The Overture	–	318	–	725	–	12
7	The Hall of the Speleologists of Chernivtsy	131	775	403	1305	13	15
8	The Stalactitic Couloir	118	–	100	–	14	–
9	The Western Crossing	167	535	158	765	16	12
10	The Torchs	225	175	100	1175	8	12
11	The Cellars	48	232	98	1270	0	10
12	The Transition Geochim-Bukovina	106	–	80	–	0	–
13	The Metro	87	187	80	2125	17	5
14	The Dinosaur Hall	232	197	88	3395	20	5
15	The Colorado Labyrinth	169	185	384	2570	11	12
16	Wet Well	209	2630	285	2410	10	5
17	The Far Eastern region (beginning)	317	–	729	–	10	–
18	The Far Eastern region (end)	764	–	488	–	12	–
Mean values:		**199**	**497**	**359**	**1668**	**16**	**15**

The spatial diversity of the microbial concentration within the cave also reflects the influence of certain environmental ‘endogenous’ (internal) factors which causes both the variation in their abundance and is responsible for the occurrence of local (or regional) anomalies. Analyses of this type carried out by other researchers also confirm the large diversity of microorganisms in this type of environment, mainly depending on the specific characteristics of each of the studied caves (the size of caves, availability of nutrients) (Wang et al. 2010, Porca et al. 2011, Ghosh et al. 2017, Muhammad 2018).

In the case of fungi, a potential relation with the character of the clay substratum of the cave corridors is revealed. In areas where the ground is drier (especially measurement sites No. 2-6 located closer to the entrance hole, and sites No. 17 and 18), the values are higher, whereas in more humid areas they are relatively lower.

As regards several other anomalies, they may be related to local conditions. A very high (relatively) number of fungi in the Hall of Perspectives (measurement site No. 5) may (hypothetically) be the effect of storing up various kinds of tools used by cavers during the exploration work, which comprise wooden elements. Increased levels of both fungi and bacteria are also noted in places where speleologists stay longer (especially in summer), for example, in the Hall of the Speleologists of Chernivtsy (measurement site No. 7) or in the Dinosaur Hall (measurement site No. 14).

An ecological relationship with the external environment may be indicated by elevated values of *Actinobacteria* in the part of the cave located closer to the entrance, although in the winter their high concentration was also observed in the Perspective Room (measuring site No. 5), where the previously mentioned tools are stored. It cannot be ruled out that the source of *Actinobacteria* may also be present in a cave environment, especially in the winter, when the concentration of *Actinobacteria* outside the cave is 2-4 times smaller than within the cave. In the near-hole area of the cave, where they are observed in the greatest abundance, these microorganisms easily colonize the roof projections (Fig. 6).

It should be emphasized that this is a group of bacteria occurring relatively often in the environment of caves, which probably results from the fact that they occur always where there is a large amount of minerals and organic matter. In addition, these bacteria are able to form spores characterised by high resistance to stress caused by dehydration and remarkable metabolic activity (Lacey 1997, Górny 2004).

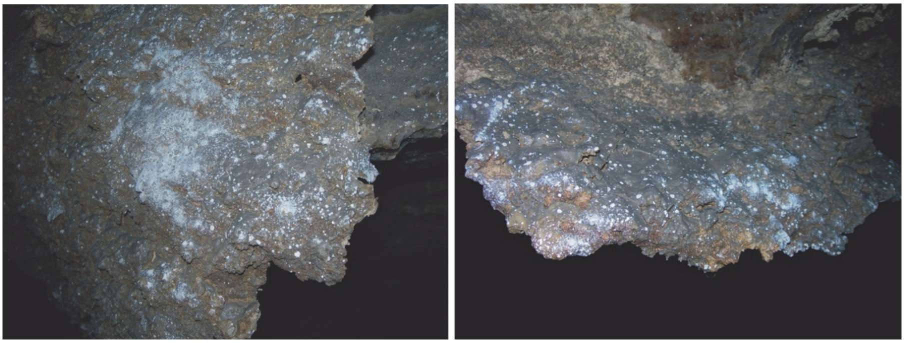

Fig. 6. Colonies of *Actinobacteria* covering the ceiling of the Hall of Kobylanska Prospect (measurement site No. 3), located near the entrance well (photo V. Andreychouk)

The results of the study show that the air of Zoloushka maze cave is characterised by a fairly high content of microorganisms, mainly bacteria and fungi, and lower of *Actinobacteria*. This is consistent with the data presented in the literature, which shows that *Actinobacteria* constitute usually about 5% of bacteria isolated from the air (Libudzisz et al. 2009). Nevertheless, when compared with the results of studies carried out in caves of a more dynamic exchange of air (Wojkowski 2013), the number of microorganisms in Zoloushka Cave is much lower (Table 4).

Table 4. Comparison of the mean concentrations of airborne microorganisms ($cfu \cdot m^{-3}$) in the air of caves of the Ojców National Park and Zoloushka Cave

Cave	Bacteria (except *Actinobacteria*) ($cfu \cdot m^{-3}$)	Fungi ($cfu \cdot m^{-3}$)	*Actinobacteria* ($cfu \cdot m^{-3}$)
Jama Ani	2245	206	251
Okopy Górna	1287	260	86
Sąspowska	2720	268	146
Zoloushka	**348**	**1013**	**16**

Fungi, whose amount in the air of Zoloushka Cave is almost 4 times higher, are an exception. In the case of the Ojców National Park caves, there was an average of 82% of bacteria (except *Actinobacteria*), 11% of fungi and 7% of *Actinobacteria* in the total number of microorganisms. In Zoloushka Cave the proportions were 25%, 74% and 1%, respectively. This may imply that the stable microclimate and humid environment of Zoloushka Cave is more favourable for the existence and growth of fungi (taking into account their 'explosion' in summer) than the dynamic climate and less humid environment of the Ojców National Park caves. The relative humidity and temperature measurements can be used to identify conditions that promote the growth of microorganisms in the cave environment. (Porca et al. 2011).

5. Conclusions

The study shows that there is a significant number of airborne microorganisms: bacteria, *Actinobacteria* in particular, and fungi in the large labyrinth caves, such as the studied Zoloushka Cave. The number of microorganisms is, in varying degrees, subject to seasonal fluctuations, and is characterised by a distinct spatial variability (within the cave field) culminating in the occurrence of specific 'anomalies' (high number of microorganisms significantly different from the mean).

The seasonal variability of microorganisms in the cave air points to the impact of external factors. The stability of the microclimate (ecological) conditions in the cave in the course of the year allows the conclusion that most of the microorganisms come from the outside and enters the cave during the exchange of the air with the external environment. Nevertheless, the environment of the cave does not remain passive – it makes the air contents spatially (within the cave field) diverse and, in some cases, it determines them (in places of significant anthropogenic pollution of the cave, which probably facilitates the growth of fungi). It should be emphasised, however, that the issue of the role of the external and internal environments in the migration and infiltration of microorganisms into the cave air may be settled more or less unambiguously only after having examined the qualitative (species) composition of microorganisms, and having understood their ecology.

The study does not indicate that the cave is a clear 'trap' for microorganisms, as might be inferred from microclimatic assumptions (stagnating regime of the air circulation). Only a high content of fungi in the air during the summer period still remains unclear. The fact that the numbers of microorganisms in the cave air and in the outside are generally comparable interferes with the established fact for ONP caves that there is a relative 'accumulation' of microorganisms in the environment of the cave (Wojkowski 2013). It is possible that ecological factors prevailing in the Zoloushka Cave are unfavourable for the existence of microorganisms in the air, for example, a particularly high concentration of carbon dioxide, poor circulation or rather low air temperature.

In comparison with the caves of a dynamic air exchange, Zoloushka maze cave of 'stagnant' microclimate is characterised by lower concentrations of microorganisms and its atmosphere is generally more pure. Both cases, however, point to a critical role of the external environment in supplying microorganisms into the cave atmosphere.

The research carried out in the Zoloushka Cave, as well as the authors' studies in other caves, still do not allow drawing generalizing conclusions on the presence of microorganisms in the air of caves. It should be emphasized that in addition to microbiological tests, the microclimate study turns out to be equally important which may be helpful in interpreting the results and explaining the observed regularities. For now, it has been concluded that the microbial aerosol concentration of the cave air is individual and different, depending on specific characteristics of the cave. Conclusions of a generalizing character will be possible only after a considerably larger number of cases will have been analysed and tests in caves of various genetic, morphological and microclimate types will have been conducted.

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Abstract

The article presents the results of microbiological and microclimatic research carried out in a large maze Zoloushka Cave (Ukraine-Moldova). The cave was artificially exposed during the exploitation of the gypsum quarry founded in the late '40s of the last century. Until the cave labyrinth was opened by the quarry, the underground system of cavities had been almost completely filled with water and constituted a natural part of the rich in water karst aquifer. The cave became exposed while being at the stage of its active formation, and its artificial dehydration enabled researchers to observe the ('accelerated') course of various processes associated with the transition of the caves from the watered (freatic) stages to vadose and dry.

Microbiological analyses aimed to determine the number of microorganisms (heterotrophic bacteria, *Actinobacteria*, and fungi) present in the air of the cave in two seasons – summer and winter. Microclimatic study aimed to determine the thermal, humidity and circulation characteristics of the cave microclimate The rules of occurrence of microorganisms in temporal and spatial (within a cave) cross-sections and the relative role of external and internal (cave) factors in shaping of the microbiological "image" of cave air were established.

The stability of the microclimate (ecological) conditions in the cave in the course of the year allows the conclusion that most of the microorganisms come from the outside and enters the cave during the exchange of the air with the external environment. Nevertheless, the environment of the cave does not remain passive – it makes the air contents spatially (within the cave field) diverse and, in some cases, it determines them (in places of significant anthropogenic pollution of the cave, which probably facilitates the growth of fungi). The measurements have shown that the total number of the studied groups of microorganisms in the air of the cave varies in the course of year within the following ranges: heterotrophic bacteria 48-2,630 cfu·m^{-3}, fungi 80-3,395 cfu·m^{-3}, and *Actinobacteria* 5-51 cfu·m^{-3}. Mean values of the microbial aerosol concentrations with respect to the entire cave are: heterotrophic bacteria – 353 cfu·m^{-3}, fungi – 974 cfu·m^{-3}, and *Actinobacteria* – 17 cfu·m^{-3}. In general, there is a regularity of an increase in their concentration during the warm period: 3-5 times higher values for bacteria (48-764 cfu·m^{-3} in winter and 175-2630 cfu·m^{-3} in summer), 4-5 times for fungi (80-990 cfu·m^{-3} in winter and 390-3395 cfu·m^{-3} in summer), and 0-1 times for *Actinobacteria* (0-51 cfu·m^{-3} in winter and 5-55 cfu·m^{-3} in summer).

Keywords:
airborne microorganisms, cave microclimate, hypogenic cave,
Zoloushka Cave (Ukraine-Moldova)

Mikroorganizmy w powietrzu labiryntowych jaskiń hypogenicznych na przykładzie Jaskini Zołuszka, Ukraina-Mołdowa

Streszczenie

Artykuł prezentuje wyniki badań mikrobiologicznych i mikroklimatycznych przeprowadzonych w dużej labiryntowej Jaskini Zołuszka (Ukraina-Moldowa). Jaskinia została odkryta podczas eksploatacji gipsowego kamieniołomu założonego pod koniec lat 40-tych ubiegłego wieku. Przed otwarciem labiryntu jaskiniowego system próżni podziemnych był prawie całkowicie wypełniony wodą i stanowił naturalną część zasobnego w wodę wodonośca krasowego. Otwarcie jaskini na etapie jej aktywnego formowania się oraz sztuczne jej odwodnienie stworzyło okazję do obserwacji (w trybie „przyśpieszonym”) przebiegu różnorakich procesów, towarzyszących przejściom jaskiń ze stadiów zawodnionych (freatycznych) do wadycznych i suchych.

Badania mikrobiologiczne zmierzały do określenia liczebności mikroorganizmów (bakterii, grzybów i promieniowców) występujących w powietrzu jaskini w dwóch kontrastowych porach roku, latem i zimą. Badaniom mikrobiologicznym towarzyszyły pomiary mikroklimatyczne, które miały na celu ustalenie termicznych, wilgotnościowych i cyrkulacyjnych charakterystyk mikroklimatu jaskini. Ustalono prawidłowości występowania mikroorganizmów w przebiegu czasowym oraz przestrzennym (w obrębie jaskini), a także względną role czynników zewnętrznych i wewnętrznych (jaskiniowych) w kształtowaniu „obrazu” mikrobiologicznego powietrza jaskiniowego.

Stabilność warunków mikroklimatycznych (ekologicznych) w jaskini w przebiegu rocznym pozwala wnioskować, że większość mikroorganizmów pochodzi z zewnętrz i trafia do jaskini w trakcie wymiany jej powietrza ze środowiskiem zewnętrznym. Nie mniej jednak, środowisko jaskiniowe nie pozostaje bierne, lecz różnicuje przestrzennie (w polu jaskiniowym) te zawartości, a w niektórych przypadkach również je warunkuje (w miejsca o znacznym antropogenicznym zanieczyszczeniu jaskini, sprzyjającym prawdopodobnie rozwojowi grzybów). Pomiary wykazały, że ogólna liczba badanych grup mikroorganizmów w powietrzu jaskini waha się w przebiegu rocznym w następujących przedziałach: bakterie 48-2630 jtk·m^{-3} (rozrzut ponad 50-krotny), grzyby 80-3395 jtk·m^{-3} (rozrzut ponad 40-krotny), promieniowce 5-51 jtk·m^{-3} (rozrzut ponad 10-krotny). Średnie liczby zawartości mikroorganizmów w odniesieniu do całej jaskini wynoszą: bakterie 353 jtk·m^{-3}, grzyby 974 jtk·m^{-3} i promieniowce 17 jtk·m^{-3}. Na ogół występuje prawidłowość wzrastania ich ilości w okresie ciepłym: dla bakterii 3-5 razy (48-764 jtk·m^{-3} zimą i 175-2630 jtk·m^{-3} latem), dla grzybów 4-5 razy (80-990 jtk·m^{-3} zimą i 390-3395 jtk·m^{-3} latem) i promieniowców 0-1 razy (0-51 jtk·m^{-3} zimą i 5-55 jtk·m^{-3} latem).

Słowa kluczowe:
mikroorganizmy, mikroklimat jaskiń, jaskinia hypogeniczna,
Jaskinia Zołuszka (Ukraina-Mołdowa)

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Removal of Organic Matter from Water During the Biofiltration Process – a Full Scale Technological Investigation

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1. Introduction

Increasing requirements for drinking water quality and the constantly depleting resources of high quality water make it necessary to intake and treat water polluted by many substances, including organic compounds. Currently one of the major challenges of water treatment technology is the effective removal of colloidal or dissolved organic pollutants from water. Particular attention is given to the removal of biodegradable organic matter fractions that are ubiquitous in aquatic ecosystems. This fraction includes a heterogeneous mixture of organic compounds with different physicochemical properties, including humic and fulvic substances, proteins, amino acids, lipids, polysacharides and biopolimers (Huber et al., 2011; Gibert et al., 2013; Gibert et al., 2015; Pruss, 2015; Pruss and Pruss, 2016). The presence in the water of a biodegradable fraction of organic matter can cause the secondary development of microorganisms in the water supply network and thus worsen the organoleptic characteristics of water directed to the consumer (Shaw et al., 2014; Szuster-Janiaczyk, 2016; Prest et al., 2016;). Biodegradable organic carbon is also a precursor of harmful disinfection byproducts (Włodyka-Bergier and Bergier, 2011; Rosińska and Rakocz, 2013; Wolska, 2014; Włodyka-Bergier et al., 2016). One of the methods of removing biodegradable organic carbon from the water which reduces the doses of disinfectants and ensures biological stability of water in water distribution systems, is the filtration of water through the beds of biologically active carbon filters (Zimoch and Szostak, 2006; Seredyńska-Sobecka et al., 2006; Simpson, 2008; Lu et al., 2013;

Tian et al., 2014; Outi et all., 2015; Prest et al., 2016; Papciak et al., 2016; Holc et al., 2016; Kołaski et al., 2017, Liu et al., 2017, Holc et al., 2018; de Vera et al., Domoń et al.,2018, Wolska et al., 2019). For microorganisms colonizing biologically active filter beds, a biologically active source of carbon and energy is biodegradable dissolved organic carbon (BDOC). Removal of organic matter from water is a result of oxidation in the respiratory processes of microorganisms and the increase of their biomass. Decrease in oxygen concentration and following increase in carbon dioxide concentration in the treated water indicates the development of microorganisms in the filter bed (Laurent et al., 1999; Mołczan, 2006; Pruss et al., 2009; Liao et al., 2012; Holc et al., 2016; Elhadidy et al., 2017; Kołaski et al., 2018). Biocenosis that inhabits biologically active carbon filters are mainly bacteria, fungi, and flagetes, ciliates and crawlers. Bacteria colonizing the filter beds are mainly psychrophilic, both auto- and heterotrophic, but only the heterotrophic bacteria are responsible for the decomposition of organic compounds adsorbed on the surface of activated carbon grains. Among the bacteria predominate are bacteria of the genus *Pseudomonas sp. (Maltophila, P. cepacia, Ps. Acidoverans) and Acinetobacter sp., Flavobacterium and Bacillus sp.* (Olesiak and Stępniak, 2014). The colonization of filters by microorganisms has vertical stratification. This is due to the difference in oxygen concentration and nutrient content at different depths of the filter bed (Simpson, 2008; Velten et al., 2011; Gerrity et al., 2018). The biological activity of the filter bed is related to the presence of microorganisms in the water and consists of forming of the biological layer on the surface of the filter grain. This process lasts from several to several weeks and depends on many factors such as: water temperature, type and concentration of organic compounds, oxygen concentration and type and granulation of the filter material. The pH of the incoming water, the type of pollutants and the concentration of toxic substances are also important (Pruss et al., 2009; Kołwzan, 2011; Liao et al., 2013; Lautenschlager et al., 2014; Olesiak and Stępniak, 2014; Kaarela et al., 2015; Oh et al., 2018). The rate of biological layer development also depends on the amount and type of bacteria and other microbes present in the water. Under natural conditions biofilm forming takes a lot of time. It takes several weeks for this to develop, but this time may be shortened if favorable conditions for the development of microorganisms, such as the supply of sufficient organic substances (Holc et al., 2016), are provided. Studies show that in waters with a small amount of organic compounds, the process of filter bed adaptation took much more time (Kiedryńska, 2004). The longer filters are operating the thicker the biological layer becomes and the more intense the microbial growth is. This happens until the filter bed is backwashed. Backwashing the filter results in partial scouring of the biological layer, so after the backwashing the microbial activity of the filter bed is reduced (Pruss et al., 2009). The development of microorganisms on the surface of the bed should be controlled to prevent clogging of the filter bed, but also because of the risk of pathogenic microorganisms growth (Liao et al., 2012; Lin et al., 2014; Kaarela et al., 2015; Oh et al., 2018).

The aim of the study was to assess the impact of the microbiological activity on the efficiency of organic compounds removal from water treated on recently launched carbon filters of analyzed Water Treatment Plant. In addition to traditional culturing methods, the metabolic activity assay (FDA method) was used to evaluate the microbiological activity of the filter bed. The test is fast, simple and inexpensive, so it can be an effective tool in the routine control of biodegradation of organic matter in biofilter beds.

2. Materials and methods

The research was carried out on the full scale Water Treatment Plant. Treated water is characterized by a high content of organic pollutants. In order to eliminate them from water and ensure the biological stability of water in the water supply network, in January 2015 a second stage of water treatment was launched, based on integrated ozonation and filtration through carbon filter beds. Every month between January and May 2016, water and a filter bed samples were collected from four activated carbon carbon filters operating in the same technological line of WTP. The filtration velocity varied between 2.5 to 3.0 m/h, contact time varied between 40 to 48 min.

2.1. Drinking water treatment plant and characteristics of GAC filters

The Water Treatment Plant (WTP) is supplied with a mixture of groundwater and infiltration water. Maximum capacity of water production is 150 000 m^3/d. The treatment technology is based on typical technological processes such as aeration, I° filtration through anthracite-quartz filter bed, chemical oxidation with ozone, II° filtration through activated carbon filter bed and disinfection. Aeration and simultaneous degassing of water takes place in system of 30 cascades. The aerated water flows into the reaction chambers located under the cascades and then into the II° reaction chambers, where, in a situation of deterioration of water quality, there is a possibility of dosing powdered activated carbon (PAC). Another technological process is the chemical oxidation with ozone. Gas ozone is produced from technical oxygen in three ozonators and is dosed into the water. Static mixers placed in water pipes provide complete mixing of water with ozone. The required contact time of water with ozone is provided by labyrinth reaction chambers. After the ozonation process, the water is degassed and then the water is pumped into the carbon filters building. The carbon filters building consists of 24 filter chambers, each filled with 2 m of active carbon, the filtration area of one filter is equal to 39.33 m^2. The filtration chambers are filled with WG-12 activated carbon (manufacturer: Gryfskand Sp. z o.o., Hajnówka, Poland) made of special, low-ash coal, connected by a binder and activated by water vapor (iodine quantity 1,100 mg/g, methylene blue adsorption 30 g/100 g; total surface area B.E.T 1,100 m^2/g; particle size 1.5-0.75 mm). The maximum hydraulic load of filtration equals 9.0 $m^3/m^2 \cdot h$. Carbon beds are backwashed every 24 days with both air and water. Filter water backwashing intensity is equal to 35-50 $m^3/m^2 \cdot h$, air backwashing intensity is equal to 60 $m^3/m^2 \cdot h$. The backwash water is drained by the wash troughs. Each filter chamber has 3 backwash troughs. The filter chambers were equipped with a panel underdrain system which enabled the filter chambers to be filled without the gravel bed (Pruss et al., 2011). Because of the restrictions for carbon filters, the chambers are separated from the rest of the water treatment plant.

Before the treated water flows to the water distribution system it is disinfected. Disinfection is carried out with chlorine dioxide in the suction piping and with sodium hypochlorite in discharge piping. Carbon filter exploited on the analyzed WTP were first launched in January 2015. In the initial phase of their exploitation efficiency of organic matter removal from treated water was high and process of chemisorption was dominating. Over time, the effectiveness of the TOC removal gradually decreased until it stabilized. By the end of March 2015, the biosorption process began.

A detailed description of the WTP is presented in earlier publications (Kołaski et al., 2017; Kołaski et al., 2018; Wołowiec et al., 2019).

The scheme of the Water Treatment Plant was presented in Figure 1.

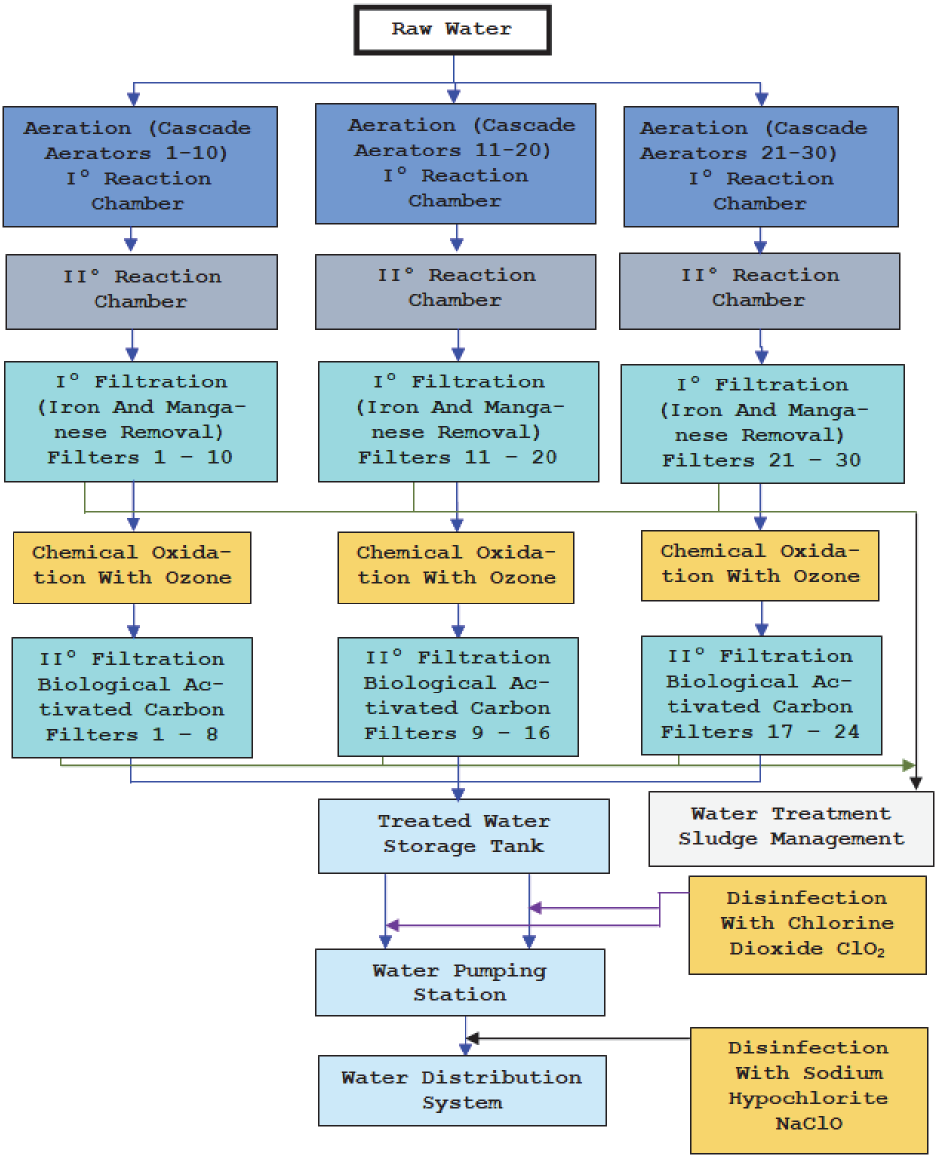

Fig. 1. The scheme of the Water Treatment Plant

2.2. Sampling

Granular activated carbon samples were collected from five specific sampling points on the bed surface – three points located along the filter side and two points between the wash troughs. Figure 2 illustrates the location of the bed sampling points.

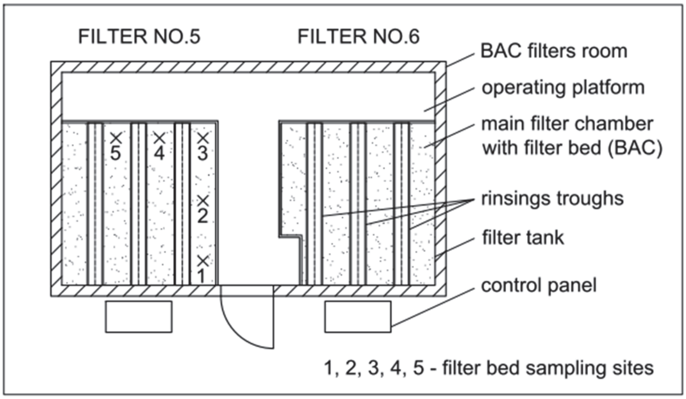

Fig. 2. Location of the sampling points: 1-5 – filter bed sampling points

2.3. Water and filter bed analyses

Water samples were collected directly from above the filter bed and from the outflow from the filter. In these samples pH, dissolved oxygen concentration, temperature and total alkalinity were determined directly after the samples had been collected. After transporting samples to the laboratory, the total organic carbon, oxygen consumption, microbial activity and total bacteria count at 22 °C were determined. The collected bed samples were shaken for 30 min. in 100 ml of sterile water. Water was then inoculated and to determine the number of bacteria per gram of dry matter of the filter bed, the shaken bed was placed in a dryer it's weight was measured. The number of psychrophilic bacteria was determined after their deep inoculation and growth on enriched agar (HPC method) and the metabolic activity of biomass was measured by the FDA method (Leszczyńska & Oleszkiewicz 1996; Kijowska et al., 2001, Mądrecka et al. 2018). The HPC method is a basic and relatively simple method of determining the number of heterotrophic microorganisms. In practice, when examining the microbial activity of bed-settling bacteria, the most commonly determined factor is the total number of microorganisms incubated at 22°C for 72 hours or saprotrophic psychrophilic bacteria. The precise method of the determination of psychrophilic bacteria in drinking water is described in Polish standard no. PN-EN ISO 6222:2004.

The FDA is a not fluorescent compound, but as it penetrates through the cell membrane and reaches the esterase it is converted to fluorescein. Fluorescein remains inside the cells, which is used to analyze the amount of live cells present in the sample. Flueorescein is rapidly removed from dead cells, making them colorless in the microscopic image (Battin, 1997; Breeuwer & Abee, 2000; Adam & Duncan, 2001; Green et al., 2006).

Samples of the filter bed weighing approximately 2 g were put into a 250 mL volumetric flask filled with sterile water (prepared in advance) and then placed in a shaker for 30 minutes. Afterwards, the liquid formed as a result of shaking was collected from above the filter bed grains. The 3 mL of slurry was pipetted and poured into a cuvette. Just before the measurement, 120 μL of fluorescein diacetate in acetone (FDA) was added. Each sample was stirred and placed in a fluorimeter for 10 minutes.

The assay used the LS 55 Luminescence Spectrometer from Perkin and the FL WinLab program for visualization and interpretation of results. In order to identify microorganisms colonizing the upper layers of biologically active filer (BAF) bed, water and filter bed samples were diagnosed with biochemical diagnostic automated system Vitek 2 Compact (bioMerieux).

3. Results and discussion

Selected parameters of the raw water are presented in Table 1.

Water flowing into the carbon filters were pH equal to 7.3-7.5, dissolved oxygen concentration 10.53-11.43 mg O_2/dm^3, temperature 9.4-13.5°C, total alkalinity 96-278 mg $CaCO_3$ / dm^3 and TOC 3.5-4.1 mg C/dm^3.

Table 1. Quality parameters and concentrations found in the raw water

Parameter	Unit	Range	Average value	Standard deviation
Temperature	°C	7.6-13.0	10.85	0.424
pH	-	7.2-7.5	7.271	0.075
Total alkalinity	mg $CaCO_3/dm^3$	195-245	219	12
TOC	mg C/dm^3	3.9-4.8	4.29	0.283
UV 254	cm^{-1}	9.2-14.0	10.99	0.889

Selected parameters of the treated water are presented in Table 2. Treated water fulfilled the requirements for the quality of water intended for human consumption.

Table 2. Quality parameters and concentrations found in the treated water

Parameter	Unit	Range	Average value	Standard deviation
Temperature	°C	8.5-13.0	11.629	0.778
pH	-	7.2-7.6	7.348	0.087
Total alkalinity	mg $CaCO_3/dm^3$	190-245	4.281	0.141
TOC	mg C/dm^3	3.1-4.8	3.623	0.354
UV 254	cm^{-1}	4.7-7.5	5.920	1.273

Figure 3 shows both the change in the concentration of TOC which is a measure of the organic compounds concentration in water, directly above the filter bed and in filtered water, and the removal efficiency of the TOC in filtration process through a biologically active carbon filter bed. The concentration of TOC in the outflow water from the filters varied over time. In January, the TOC removal efficiency for individual filters was almost the same and was equal to 13% for filter 5 and 14% respectively for filters 6, 7 and 8. Exactly 0.5 mg C/ dm^3 was removed during the filtration process on each filter. The concentration of TOC in water inflow from the filters was equal to 3.6-3.9 mg C/dm^3, and 3.1-3.4 mg C/ dm^3 in outflow water. In February, the removal efficiency varied from 14 to 19%. With the highest efficiency the TOC was removed on filter 5, with the lowest on filter 8. The filtration removed between 0.5-0.7 mg C/dm^3 respectively for filters 8 and 5. The concentration of TOC in water entering filters varied from 3.5 to 3.7 mg C/dm^3 and was equal to 3.0 mg C/dm^3 in the effluent. In March, TOC was removed from treated water with efficiency of 16-21%, respectively for filters 6, 7 and 5, which equals a 0.6-0.8 mg C/dm^3 decrease in TOC concentration. The concentration of TOC in the water entering filters was 3.8-3.9 mg C/dm^3 and 3.1-3.2 mg C/dm^3 in effluent. In May, the TOC was removed with the largest ever registered efficiency. The TOC removal efficiency varied from 23 to 27%, respectively for filters 6, 8 and 7. 0.9-1.1 mg C/dm^3 was removed from water in the filtration process. The TOC concentration in water entering filters was equal to 4.0-4.1 mg C/dm^3 and 3.0-3.1 mg C/dm^3 in the filtered water. The longer the filters have been operating the more effectively the TOC was removed from treated water. During the study, the TOC removal efficiency was variable and ranged from 13 to 27%. These values are equal to respectively a 0.5 mg C/dm^3 decrease for the January analysis for filter 5 and 1.1 mg C/dm^3 for analysis carried out in May for filter No. 7. All filters removed the TOC with comparable efficiency, which was dependent on total filter operating time. There was no relation between the concentration of TOC in the water entering the filters and the operating time of the filters since the last flushing and the removal efficiency of the TOC.

All tested filters worked with similar efficiency despite significant differences in microbial activity and microbiological analyzes. It was probably due to the fractions of organic matter entering the carbon filters. Biodegradable organic carbon, despite the ozonation process, was only a small fraction of organic matter, which was successfully removed by biodegradation even by small numbers of bacteria.

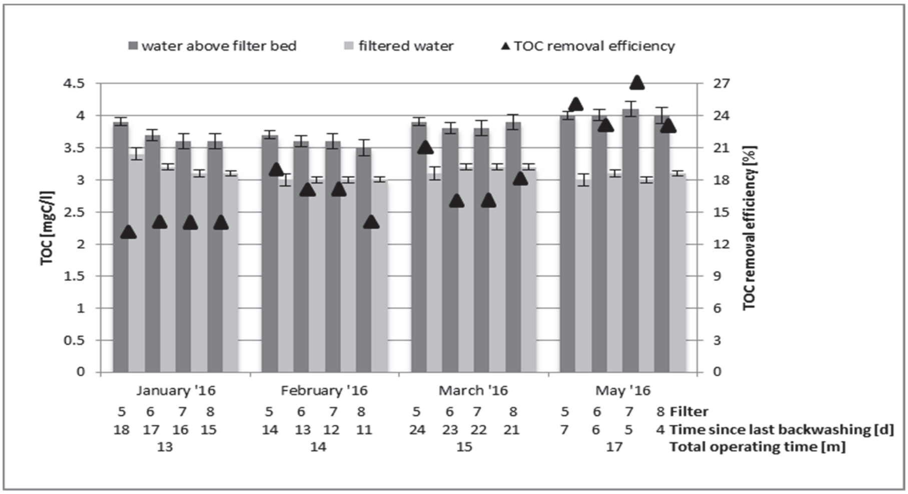

Fig. 3. TOC concentration in water entering the filters and in effluent – BACF exploited on WTP

Table 3 shows the total number of bacteria in the surface layer of the filter beds of filters 5, 6, 7 and 8. In none of the sampling points there were favorable conditions for the development of microorganisms than in any other sampling point. The number of microorganisms per gram dry weight of the filter bed varied from 5760 to 1106072 cfu/gdw. The minimum value was observed in May for point 1 in filter 8, while the maximum was observed in February for point 5 in filter 7. The decrease in total organic carbon concentration during filtration process was neither dependent on the time of filters operation since the last backwashig or on the number of bacteria colonizing the filter beds.

Table 3. Total number of psychrophilic bacteria colonizing the surface layer of filter bed

Filter	Sampling points	Total number of psychrophilic bacteria [cfu/gdw]			
		January	February	March	May
5	1	497500	584200	849300	13900
	2	718100	335800	891900	22100
	3	69300	502100	729200	36800
	4	451300	387800	645800	10300
	5	186400	755200	618900	25100
6	1	3587	1133	5304	214
	2	3888	318	4733	758
	3	4105	649	5283	362
	4	2868	268	7436	589
	5	3074	923	3539	1362
7	1	781	3249	8153	216
	2	1061	2960	4611	104
	3	1578	4375	4631	175
	4	1452	4518	5013	133
	5	444	11061	2398	202
8	1	944	2310	5041	58
	2	991	3694	2451	95
	3	5158	1687	4707	76
	4	1906	1183	2540	99
	5	1867	4540	2636	69

Fig. 4 shows the total number of psychrophilic bacteria in water above the filter bed and in the effluent for filters 5, 6, 7 and 8. It was found that for these filters there is no relation between the operating time since the last backwashing and the total operating time and the number of bacteria present in the water above the filter bed and in the effluent. The number of psychrophilic bacteria in the water above the filter bed in most cases was far greater than in the filtered water. The maximum number of bacteria in the water above the filter bed was equal to 27500 cfu/ml in February for filter 7, while the maximum number of bacteria in the filtered water was 2347 cfu/ml in March for filter 5.

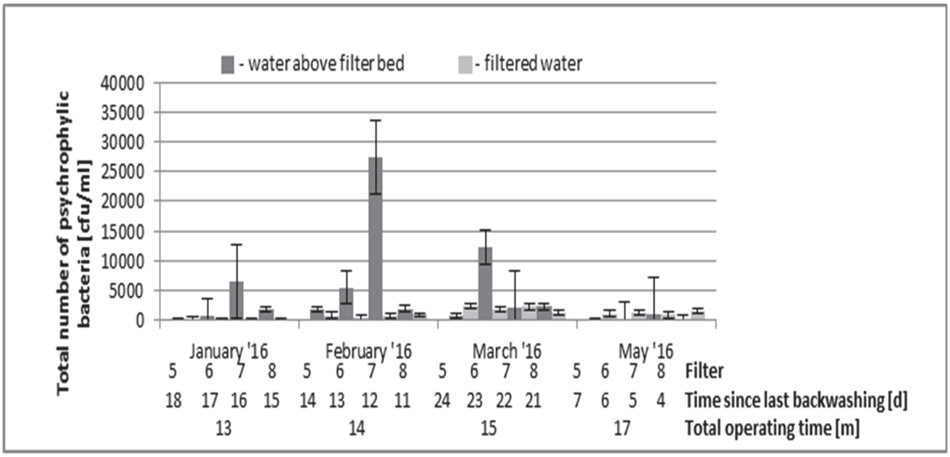

Fig. 4. Total number of psychrophilic bacteria in water above the filter bed and in effluent

Table 4 summarizes the results of performed biochemical diagnostics. It has confirmed the presence of species of bacteria such as *Pseudomonas fluorescens*, *Pseudomonas oleovorans, Acinetobacer lwoffi, Aeromonas salmonicida* and *Sphingomonas paucimobilis*. These are bacteria that are characteristic for biologically active carbon filters. *Pseudomonas fluorescens* are Gram-negative bacteria belonging to the genus *Pseudomonas*. They inhabit aquatic and soil environments. Aerobic conditions and temperatures of 25-30°C are optimum for their development. Having the ability to decompose hydrocarbons these bacteria have a significant impact on the biodegradation process of carbon compounds present in water fed to biologically active carbon filters. *Pseudomonas oleovorans* are aerobic Gram-negative bacteria. The optimum for their development is in the range of 35°C. They live in soil and water environments. These are opportunistic pathogens that can cause meningitis and pneumonia. *Acinetobacter lwoffi* is a Gram-negative rod belonging to the genus *Acinetobacter.* Aerobic conditions are optimal for their development. This bacterium is a typical bacterial flora of the skin and esophagus in about 25% of healthy people. It can be source of infections when people have their immunity system impaired. *Aeromonas salmonicida* is a Gram-negative rod living ubiquitously in the aquatic environment. These are optional anaerobes that do not cause infection in humans. *Sphingomonas paucimobilis* is an aerobic Gram-negative rod found in the soil environment. Rarely, people with impaired immunity can suffer non-life-threatening infections caused by *Sphingomonas paucimobilis.*

Table 4. Identified microorganisms – BAC exploited on WTP

Date	Filter	Sampling points	Identified microorganism	Probability %
January	5	4	*Pseudomonas oleovorans*	95
	5	2	*Acinetobacter lwoffi*	96
	5	3	*Acinetobacter lwoffi*	96
	7	2	*Aeromonas salmonicida*	97
	7	effluent	*Pseudomonas fluorescens*	94
	7	water above filter bed	*Pseudomonas fluorescens*	95
	7	water above filter bed	*Aeromonas salmonicida*	98
	8	water above filter bed	*Pseudomonas fluorescens*	96
February	5	1	*Sphingomonas paucimobilis*	98
	8	1	*Acinetobacter lwoffii*	96
March	8	effluent	*Acinetobacter lwoffii*	96
	8	2	*Pseudomonas fluorescens*	95
	8	4	*Pseudomonas fluorescens*	95
April	5	5	*Pseudomonas fluorescens*	99
May	8	1	*Sphingomonas paucimobilis*	97

Table 5 shows the microbial activity of water after shaking the bed samples from the sampling points 1-5 for the filters 5, 6, 7 and 8. The highest microbial activity was registered for samples collected from filter 6 reaching about 1.0 r.u./s for the sampling point 4. The microbial activity recorded for the samples taken from the filters 5, 7 and 8 was close to each other, and their values reached 0.35121-0.65678, 0.327720-0.567940 r.u./s and 0.363000- 0,738545 r.u./s. The microbial activity for the water used for shaking the filter bed samples was significantly higher than the microbial activity for the water samples from above the filter bed and the filtrate.

Table. 5. Microbial activity of surface layer of filter bed

Sampling points	Microbial activity of surface layer of filter bed [r.u./s]			
	Filter 5	Filter 6	Filter 7	Filter 8
1	0.62959	0.775615	0.443715	0.520615
2	0.60886	0.614075	0.567940	0.738545
3	0.65678	0.588585	0.530925	0.466600
4	0.46200	0.998000	0.327720	0.363130
5	0.35121	0.913275	0.481550	0.363000

Table 6 shows the microbial activity of water above the filter bed and filtered water for filters 5, 6, 7 and 8. The microbial activity measured for water above the filter bed significantly (about twice) exceeded the values measured for the filtered water. The microbial activity of the water above the filter bed was equal to 0.012610-0.14615 r.u./s and the microbial activity of filtered water was equal to 0.005675-0.010195 r.u./s. The microbioal activity of the water above the filter bed and filtered water for all filters was comparable, except for the maximum value reached for filter 5.

Table 6. Average microbial activity of surface layer of filter bed, water above the filter bed and filtered water

Filter	Average microbial activity [r.u./s]					
	Surface layer of filter bed	Standard deviation	Water above the filter bed	Standard deviation	Filtered water	Standard deviation
5	0.54169	0.1305	0.146160	0.120945	0.005680	0.002025
6	0.77791	0.1798	0.012805	0.002015	0.006095	0.002285
7	0.47037	0.0927	0.012610	0.004300	0.008590	0.004300
8	0.49038	0.1545	0.021825	0.003025	0.010195	0.002025

Fig. 5-8 shows the correlation between the average microbiological activity and the total number of psychrophilic bacteria in the surface layers of the filter beds analyzed in May. No linear correlation was found between these results.

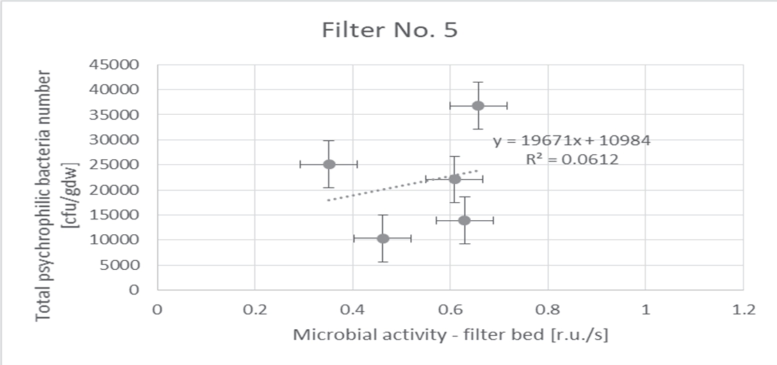

Fig. 5. Correlation between total number of psychrophilic bacteria and microbial activity in the Filter no. 5

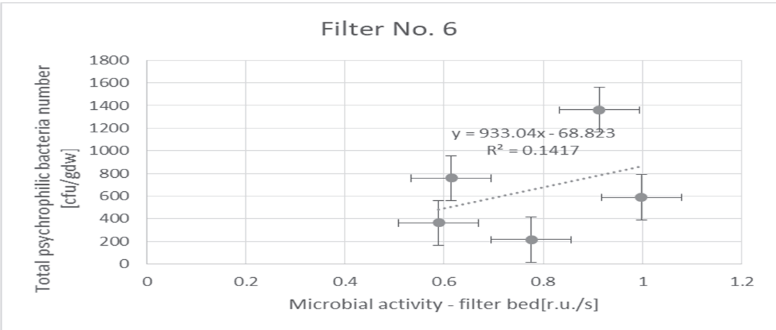

Fig. 6. Correlation between total number of psychrophilic bacteria and microbial activity in the Filter no. 6

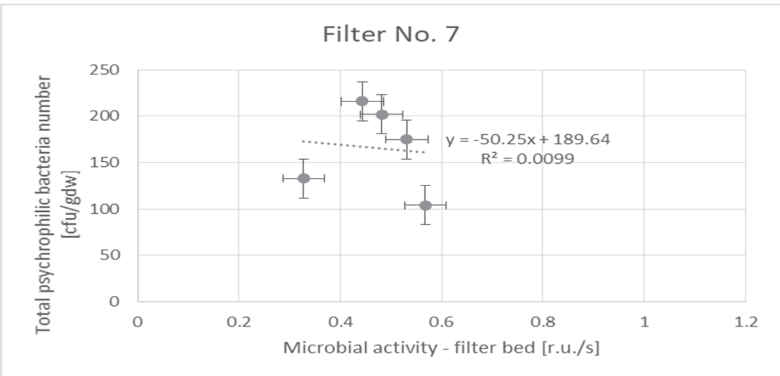

Fig. 7. Correlation between total number of psychrophilic bacteria and microbial activity in the Filter no. 7

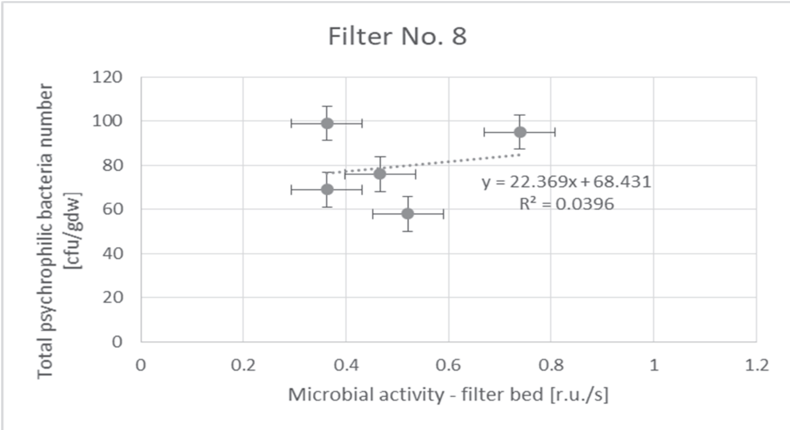

Fig. 8. Correlation between total number of psychrophilic bacteria and microbial activity in the Filter no. 8

4. Conclusion

Carbon filters operated on a full scale Water Treatment Plant during the study were biologically active. It was confirmed by the decrease in the concentration of total organic carbon and the microbial activity.

Activated carbon filtered bed proved to be very effective for the development of microorganisms. As a result of microbiological identification, it has been proven that filter beds were colonized by species of bacteria such as *Pseudomonas fluorescens, Acinetobacter lwoffii, Aeromonas salmonicida.* These are bacteria that often colonize the beds of biologically active carbon filters. What is more strains of the *Enterobacteriaceae* family which may be hazardous to the health of consumers, especially those with impaired immunity have not been bred.

During the study in the filtration process on biologically active carbon filters, 14-27% of the TOC was removed from treated water. The effectiveness of organic matter removal in this process was neither dependent on the number of bacteria colonizing the upper parts of the filter bed nor the time of filter's operating time since the last backwashing.

The conducted tests did not show a linear correlation between the number of psychrophilic bacteria and microbiological activity of the deposits in all of the analyzed filters.

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Abstract

The research was carried out on the full scale Water Treatment Plant with maximal capacity of 150 000 m^3/d. Treated water is characterized by a high content of organic pollutants. In order to eliminate them from water and ensure the biological stability of water in the water supply network, in January 2015 a second stage of water treatment was launched, based on integrated ozonation and filtration through carbon filter beds. Between January and May 2016, samples of water and a filter bed were collected from four carbon filters and then physicochemical and bacteriological analysis were done. The FDA test and biochemical diagnostics were made to prove the microbiological activity of the filter bed. The studies showed a decrease in the content of organic compounds, meassured as TOC and COD ($KMnO_4$), and the biological activity of the analyzed carbon filters. The carbon filter beds were populated by *Pseudomonas fluorescens, Acinetobacter lwoffii, Aeromonas salmonicida* and *Sphingomonas paucimobilis.* In none of the analyzed filters were found strains of the *Enterobacteriaceae* family which may have a potential threat to health of the consumers. The application of carbon filters has reduced the organic matter content in treated water.

Keywords:
biologically active carbon filters, filtration, full scale technical investigation, identification of microorganisms, organic matter, water treatment

Usuwanie związków organicznych z wody w procesie biofiltracji – badania w skali technicznej

Streszczenie

Badania prowadzono w skali technicznej na Stacji Uzdatniania Wody (SUW) o maksymalnej wydajności 150 000 m^3/d. Woda dopływająca do SUW charakteryzuje się zawartością specyficznych zanieczyszczeń organicznych. W celu ich eliminacji z wody oraz zapewnienia biologicznej stabilności wody w sieci wodociągowej, w styczniu 2015 r. uruchomiono drugi stopień oczyszczania wody, oparty o zintegrowane procesy ozonowania i filtracji przez złoże węglowe. Co miesiąc, w okresie od stycznia do maja 2016 r., pobierano próbki wody oraz złoża filtracyjnego z czterech filtrów węglowych. Próbki wody pobierano bezpośrednio znad złoża filtracyjnego oraz na odpływie z filtrów. Próbki złoża filtracyjnego pobierano z jego górnej warstwy, w pięciu punktach każdej komory filtracyjnej. Przeprowadzono analizy fizyczno-chemiczne i bakteriologiczne wody oraz złóż filtracyjnych. W celu wykazania aktywności mikrobiologicznej złóż wykonywano test aktywności esteraz z dwuoctanem fluoresceiny FDA. W próbkach wody i węgla aktywnego w celu zidentyfikowania mikroorganizmów prowadzono diagnostykę biochemiczną z wykorzystaniem zautomatyzowanego systemu Vitek 2 Compact (bioMerieux). Przeprowadzone badania wykazały obniżenie zawartości związków organicznych wyrażonych jako OWO i ChZT ($KMnO_4$) oraz biologiczną aktywność analizowanych filtrów węglowych. Złoża filtrów węglowych zasiedlone były przez *Pseudomonas fluorescens, Acinetobacter lwoffii, Aeromonas salmonicida* oraz *Sphingomonas paucimobilis*. W żadnym z analizowanych filtrów nie wyhodowano natomiast szczepów z rodziny *Enterobacteriaceae* stanowiących potencjalne zagrożenie dla zdrowia konsumentów. Wprowadzenie filtrów węglowych do ciągu technologicznego SUW spowodowało obniżenie zawartości materii organicznej w wodzie uzdatnionej.

Słowa kluczowe:
biologicznie aktywne filtry węglowe, badania w skali technicznej, filtracja, oczyszczanie wody, związki organiczne, identyfikacja mikroorganizmów

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Effect of the Addition of Coal Waste on the Process of Composting and Sorption Capacity of Composts

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1. Introduction

In the European Union countries, biological waste and biodegradable waste constitute from 30 to 40% of municipal solid waste (Kwarciak-Kozłowska & Bańka 2014). The provisions of the EU Landfill Directive (Council Directive 1999/31/EC) oblige Member States to gradually reduce the amount of biodegradable waste deposited in landfills.

Composting is a biological process in which thermophilic and mesophilic microorganisms transform organic matter into gaseous products (CO_2, H_2O, NH_4^+) and a stabilized organic substance, which is a precursor of humus (Bernal et al. 2009, He et al. 2009, de Guardia et al. 2010). Due to the variety of raw materials currently used and the resulting heterogeneity of the compost input, the process flow and conditions require continuous optimization (Himanen & Hänninen 2011).

One of the most important parameters of the efficient composting is the ratio of organic carbon to nitrogen, which determines susceptibility of organic substances to microbiological decomposition. The optimum C/N ratio can be controlled with carbon content by adding components rich in this element.

A very advantageous feature of compost is its high sorption capacity. Soil improvement with organic matter causes an increase in this parameter (Cuske & Karczewska 2016). This is particularly desirable when compost is used on soils contaminated with e.g. heavy metals. The positive effect of the addition of compost on the sorption properties of soils has been demonstrated in numerous studies (Greinert 2009, Bielińska & Mocek 2010, Kyzioł-Komosińska et al. 2011, Ciesielczuk & Rosik-Dulewska 2013). Compost mass is therefore a cheaper alternative to commercial mineral or organic sorbents, whose production is energy-intensive, expensive and requires the use of non-renewable natural resources

(Koh & Dixon 2001). The studies have confirmed the phenomenon of reduction in the migration of heavy metals to soil solution following the addition of stabilized compost to contaminated soils. This concerns in particular the application of compost with other sorbents, e.g. active carbon (Beesley et al. 2010, Karami et al. 2011). The introduction of substances which may increase the sorption capacity (zeolites, diatomites) into the soil reduces the amount of phytoavailable forms of heavy metals in the soil (Williamson et al. 2009, Farrell & Jones 2010).

The two aspects related to the waste composting process presented above, i.e. the possibility of correcting the C/N ratio and improving the sorption properties of composts, were the basis for determination of the scope of the study. The authors assumed that coal sludge generated in the processes of hard coal enrichment, often treated as waste, may be useful in correcting of the C/N ratio and the improvement of the sorption capacity of composts. This sludge is characterized by a carbon content of up to 30% (Sobik-Szołtysek 2006) and high sorption capacity due to a significant share of clay minerals in their composition.

2. Materials and methods

2.1. Analytical methods

Substrates selected for the study, compost mixtures made using these substrates and composts obtained were analyzed according to the following procedures:

- analytical moisture content according to PN-EN 14346:2011,
- pH in distilled water according to PN-Z-15011-3:2001,
- organic matter content according to PN-EN 15169:2011,
- nitrogen content by the Kjeldahl method according to PN-Z-15011-3:2001 and internal procedure for the SpeedDigester K-439 device,
- determination of the total specific surface area by the methylene blue sorption method according to PN-B-04481:1988,
- metal content in the samples after mineralization - ICP-OES SPECTRO ARCOS spectrometer,
- organic matter content as residue on ignition according to PN-EN 15169:2011.

All analyses were performed in three repetitions and the result was presented as an arithmetic mean.

The organic carbon content was calculated using the formula developed by Haug (1993):

$$\%\,C = \frac{(100-\text{ash})}{1{,}8} \tag{1}$$

2.2. Substrates for research

The usefulness and the potential of using different substrates in the composting process is determined primarily by their proper moisture content, optimal C/N ratio and proper structure, forming an environment with good oxygenation. The characteristics of the materials used in the tests are presented in Table 1. All the materials were designated specific symbols, used further in this study. The following determinations were made for the selected substrates: moisture content, organic carbon and nitrogen content, and the C/N ratio (Table 2).

The high moisture content observed for grass and organic fraction of municipal waste was caused by the fact that these components were dosed into the mixtures in the "fresh" form, while the remaining substrates were dosed in the air-dry state. All substrates, except for coal sludge, were characterized by a high content of organic carbon, with the highest values obtained for structure-forming additives such as barley straw and energy willow. The nitrogen content observed for grass higher compared to the literature data, was due to the fact that it was collected in the home garden intensively fertilized with mineral fertilizers rich in nitrogen. High nitrogen content in this substrate resulted in the lowest C/N ratio. The maximum values of this parameter, exceeding 100 (-), were found for barley straw, which was characterized by high carbon content at very low nitrogen content.

Table 1. Materials used in the composting process

Type of materials	Substrate with designation	Material origin and description
Green waste	Grass (T)	Household garden subject to standard treatments. Chopped grass, with natural moisture, taken from the basket of the mechanical mower.
Structure-forming materials	Barley straw (SJ)	Purchased directly from farmers after summer harvesting, air-dry state, fragmented before application
	Energy willow (WE)	A commercial product sold as an alternative fuel, air-dry state, fine texture.
Coal waste	Coal sludge (M)	Filtration presses for water and sludge circulation in hard coal mines, air-dry state, crushed before application.
Municipal waste	Organic fraction of municipal waste (OFOK)	Crushed household material: residues of fruit, vegetables, pasta, rice, coffee and tea grounds, egg shell, without animal products and citrus fruits.

Table 2. Selected physical and chemical properties of the substrates

Parameter	Unit	Component				
		OFOK	T	SJ	WE	M
Moisture content	wt% dry weight	82.0	75.2	4.7	6.4	1.8
C	wt% dry weight	52.4	48.7	54.1	54.2	27.8
$N_{Kjeldahl}$	wt% dry weight	1.6	3.7	0.4	0.8	0.5
C/N	(-)	32.8	13.2	135.3	67.8	55.6

Due to the potential of composts for agricultural use, the content of selected heavy metals in all substrates was analyzed (Table 3). Low content of analyzed metals was found, so there was no risk of exceeding the permissible values for compost specified in the regulations (Ordinance 2008).

Table 3. Content of selected metals in components for composting

Metal	Unit	Component					Permissible content (Ordinance 2008)
		OFOK	T	SJ	WE	M	
Zn	mg/g	0.0164	0.06	0.013	0.083	0.09	-
Pb	mg/g	0.011	0.011	0.0047	0.0037	0.04	0.140
Cd	mg/g	<0.001	0.0006	<0.0005	0.0011	<0.001	0.005
Cr	mg/g	0.088	0.0083	0.0072	0.0023	0.044	0.100
Ni	mg/g	0.0036	0.0039	0.0017	0.0014	0.0168	0.060

2.3. Research stand

The composting process was conducted in cylindrical, isolated bioreactors with a capacity of 5 dm^3 (Fig. 1). The upper cover was equipped with a ventilation opening to drain the gases, while the bottom of the bioreactor is equipped with a moisture removal system in the form of a water-permeable sieve that retains substrate particles. An aeration hose was put on the sieve, connected with a pump (AIRFISH 5W) with a maximum capacity of 4.5 dm^3/min. A temperature sensor configured with a computer program CoolTerm Win, allowing to record and archive temperature measurements every 1 hour, was installed in the bioreactor.

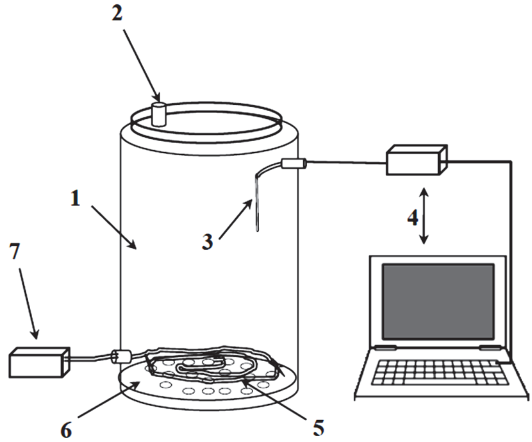

Fig. 1. Research stand: 1 – bioreactor, 2 – gas outlet, 3 – temperature gauge, 4 – temperature recording system, 5 – aeration hose, 6 – perforated spacer, 7 – aeration pump

The composting process was carried out in two research series: series 1, for composts marked as 1, 2 and 3, and series 2, for composts marked as 4, 5 and 6. Since an increase in temperature of only slightly more than 40°C was achieved during the thermophilic phase of the first series, the bioreactors in the second series were additionally insulated to better stabilize the temperature. The thermal insulation was made of 5 cm thick expanded polystyrene, whereas the space between the bioreactor and the walls was filled with expanded polystyrene balls. The bioreactors were then covered with a plastic cover and, additionally, a cover made of expanded polystyrene of the same thickness.

2.4. Sorption tests

The use of composts as sorbents for many different substances described in the literature (Ciesielczuk et al. 2011) is confirmed by the evaluation of their sorption capacity. Since compost is used for the sorption of dyes from aqueous solutions (Jóźwiak et al. 2013), a method of methylene blue (Bhattacharyya & Sharma 2005) was chosen to determine the sorption capacity of the composts. Sorption capacity was calculated from the formula:

$$\mathrm{MBC} = \frac{100\,\mathrm{m}}{2\,m_s}(\mathrm{V_i} + \mathrm{V_{i-1}}) \qquad (2)$$

where:
MBC – sorption capacity of compost compared to methylene blue according to trihydrate substance per 100 g of dry matter of material,

m – mass of methylene blue contained in 1 cm^3 of solution, calculated per trihydrate substance, g,
m_s – mass of compost used for the determination calculated per dry matter at temperature of 105–110ºC, g,
v_i – volume of solution at which sorption capacity was exceeded, cm^3,
V_{i-1} – volume of solution corresponding to the penultimate portion of the methylene blue solution before exceeding the sorption capacity, cm^3.

The specific surface area was calculated according to the formula:

$$S_t = k_1 \cdot MBC \tag{3}$$

where:
k_1 – coefficient with the value adopted as 20.94 m^2/g,
MBC – sorption capacity of compost compared to methylene blue according to trihydrate substance per 100 g of dry matter of material.

In order to confirm sorption capacity of the obtained composts, zinc sorption from aqueous solutions was carried out by batch method (Roy et al. 1991) in a constant liquid-solid contact ratio of 1:20. A base solution of 10 g/L Zn^{2+} was obtained by dissolution of the calculated stoichiometric reaction of $ZnCl_2$ mass (Chempur reagent, analytical grade) in distilled water. A solution with initial concentration of Zn^2+ 100 mg/L and compost dried to solid mass at the temperature of about 60°C, crushed and passed through a sieve with a mesh diameter of 0.1 mm, was used. The mixtures were shaken for 24 hours and then filtered. The content of Zn^{2+} ions in the obtained eluate was determined by inductively coupled plasma atomic emission spectroscopy (ICP).

Sorption efficiency (S) was calculated from the formula:

$$S = \frac{(C_0 - C_k)}{C_0} \times 100, \% \tag{4}$$

where:
C_0 – initial concentration of zinc in the solution, mg/L,
C_k – equilibrium concentration of zinc in solution, mg/L.

2.5. The course of research

The composition of mixtures subjected to the composting process was selected based on the results of analyses of individual substrates (Table 2). The parameter determining the share of individual initial substrates (OFOK, T, WE, SJ) was C/N ratio. Mixtures with the same proportion of basic substrates were modified by adding coal sludge (M) in doses of 10 and 25wt%. The symbols and the composition of individual mixtures are presented in Table 4.

Table 4. Percentage of basic substrates in the tested compost mixtures

Mixture number	Composition of a compost mixtures *
1	T_{40}+SJ_{20}+$OFOK_{40}$
2	T_{40}+WE_{20}+$OFOK_{40}$
3	T_{50}+SJ_{15}+$OFOK_{10}$+M_{25}
4	T_{60}+SJ_{10}+$OFOK_{20}$+M_{10}
5	T_{50}+WE_{15}+$OFOK_{10}$+M_{25}
6	T_{60}+WE_{10}+$OFOK_{20}$+M_{10}

* the subscripts denote wt% of the basic component

The prepared compost mixtures were subjected to the testing procedure using the following stages:

- performing determinations (moisture, content of organic matter, organic carbon and nitrogen) for prepared compost mixtures - initial state,
- composting in bioreactors for a period of 4 weeks (stage 1),
- compost collection after 4 weeks and performing analysis (moisture, organic matter, organic carbon and nitrogen content),
- compost maturation in natural conditions for the next 4 weeks (Stage 2),
- sampling and analysis of compost (moisture content, organic matter, organic carbon and nitrogen content) after 8 weeks of the experiment.

3. Results and discussion

3.1. Analysis of the initial properties of compost mixtures

Samples were obtained from the compost mixtures prepared for the experiments, for which the analyses and calculations presented in Table 5 were performed.

The values of optimal moisture content for compost mixtures in the literature range from 45 to 70% (Richard et al. 2002, Jędrczak 2007, Ozimek & Kopec 2012). All analyzed mixtures met this condition, with the highest values of this parameter obtained for mixtures 1, 2, 4 and 6. Numbering and composition of compost mixes in accordance with Table 4. This was a result of high moisture content of two basic substrates, i.e. grass and organic fraction of municipal waste, whose total share in these mixtures amounted to 80% by weight. The application of large contents of these substrates resulted from the analysis of literature reports in which the dependence of obtaining high temperatures in the thermophilic phase on their content in the compost was indicated (Bień et al. 2011).

Table 5. Initial conditions for compost mixtures

Mixture number	Moisture content	Organic matter content	C	N Kjeldahl	C/N
	% by weight	% by weight	% by weight	% by weight	(-)
1	64.9	92.8	51.7	1.74	29.7
2	65.1	91.4	50.8	1.89	26.9
3	49.1	75.8	42.1	1.49	28.3
4	62.3	78.5	43.6	1.63	26.7
5	50.5	75.3	41.8	1.58	26.4
6	63.5	82.5	45.7	1.79	25.5

The C/N ratio, which according to Jędrczak (2007) should be in the range of 25-35, is given as the basic parameter characterizing the optimal composition of the compost mixture. Other authors (Mustin 1987, Dach 2010) demonstrated that the ratio should range from 20 to 30. Comparison of the obtained results with the literature data reveals that all the tested mixtures reached the recommended C/N ratios. The use of municipal organic waste fraction (OFOK) in compost improves the C/N ratio due to the high content of organic carbon (Siebielska and Janowska 2011).

A higher content of organic matter and organic carbon can be observed in the mixtures without the use of coal sludge (mixtures 1-2) compared to mixtures with this addition. This is due to the high content of inorganic carbon in coal sludge.

The nitrogen content was determined primarily by the grass content, because this substrate was characterized by the highest content of this element (3.7% by weight).

3.2. Temperature changes during composting

Figures 2 and 3 show the temperatures measured during composting in bioreactors (first 4 weeks). Mixtures 1-3 (the first series of experiments) were composted without thermal insulation, whereas mixtures 4-6 – with thermal insulation (the second series of experiments).

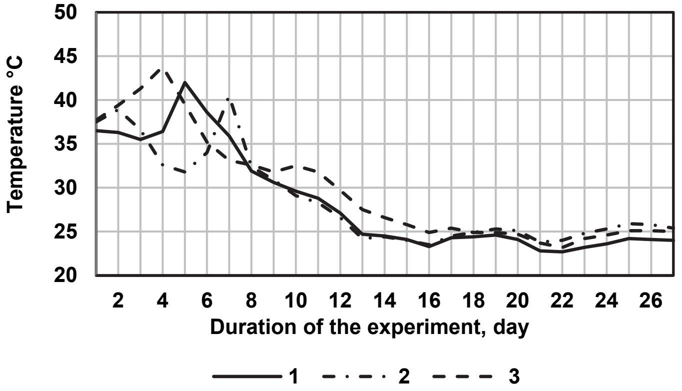

Fig. 2. Mean daily temperature values for mixtures 1-3 (the first series of experiments)

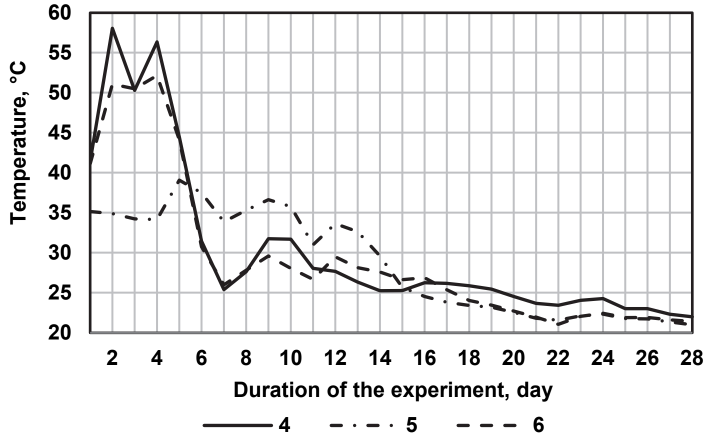

Fig. 3. Mean daily temperatures for mixtures 4-6 (the second series of experiments)

According to literature (Richard 1992), composting is most effective in the temperature range 45-55°C, while an increase in temperature of above 60°C causes the death of microorganisms, which results in a decrease in the rate of decomposition of organic matter. This can cause odors to be emitted into the environment and reduce the quality of the compost. A further increase in temperature to 75°C causes denaturation of protein and consequently the complete stopping the biological processes during composting. At temperatures below 20°C, microorganisms do not proliferate, which also slows down the rate of transitions. Succession of mesophilic and thermophilic microorganisms in the composted material, related to temperature changes, is an indicator of the correct course of the composting process (Ishii et al. 2000).

In the first series of studies, temperatures assumed to be optimal were not obtained. However, no temperature drop below the critical level (20°C) was observed. The highest temperature was reached by a mixture 3 containing a 25% admixture of coal sludge. Starting from the 13th day of the experiment, the temperature stabilized at a similar level. According to Sidełko et al. (2014), the temperature drop may be related to a reduction in microbiological activity due to the effect of a limiting factor, i.e. oxygen content in the compost pores, or to the depletion of organic compounds, which represent an easily accessible source of carbon. The use of additional insulation in the second series had a positive effect on mixtures 4 and 6. The temperatures observed on the first 5 days of the process reached a satisfactory level. The exception was mixture 5, for which the maximum temperature of 39.1°C was reached only on day 5. This mixture was characterized by the lowest initial content of moisture, organic matter and organic carbon. Insufficient water content in the compost can inhibit biological processes (Liang et al. 2003) because water is a transport medium for nutrients necessary for the proper course of active metabolic processes of microorganisms (McCartney & Tingley 1998). After 9 days, the temperature of composts decreased gradually and evenly. The obtained results confirmed that ensuring good thermal insulation allows for keeping the required temperature regime needed for both the course of the process and for the hygienization of compost. The effect of the amount of coal sludge added and the type of applied structure-forming material (SJ and WE) on the maximum temperatures was observed. If the same amount of coal sludge (25%) was used, higher temperatures were obtained for mixtures with barley straw, for which the C/N ratio is twice as high as for the WE mixture.

3.3. Analysis of the physicochemical properties of composts

3.3.1. Changes in organic matter content

The organic matter content decreases during the composting process. Research conducted by Sidełko (2009) showed that the content of organic matter in the compost decreased gradually, regardless of the duration of the composting cycle. It was found that the organic matter content decreased by 13-15%. Figure 4 shows changes in the organic matter content of compost during the experiment.

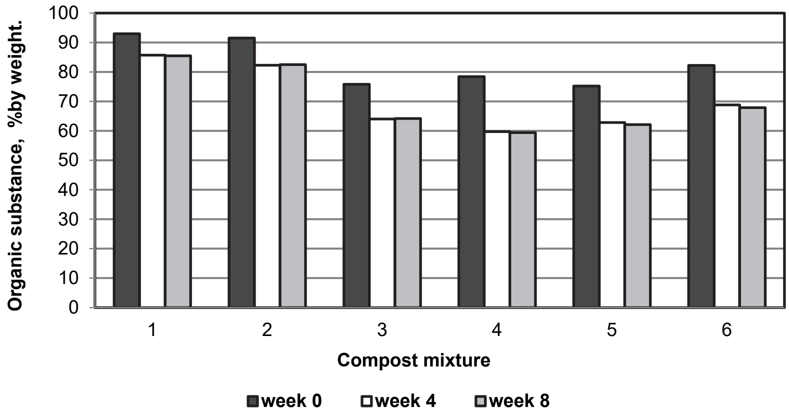

Fig. 4. Changes in organic matter content over 8 weeks of the experiment

A decrease in organic matter content of 7.85-23.85% was observed in all composts after 4 weeks of composting, with the smallest decrease in composts obtained without the addition of coal sludge but with the highest OFOK content (1 and 2). Furthermore, the greatest decrease in organic matter (by 20.1% on average) was observed in the mixtures with 10% coal sludge and 60% grass (composts 4 and 6). Changes in organic matter content after 8 weeks were very slight compared to those after 4 weeks. This indicates that the process of mineralization of organic compounds was inhibited. The downward tendencies in the content of organic matter in compost recorded during the research is consistent with the literature reports in this field.

3.3.2. C/N ratio changes

The C/N ratio usually decreases during composting if the initial C/N ratio is > 25. Mature compost should be characterized by a C/N ratio of < 20, which is indicative of an adequate degree of organic matter conversion. A higher nitrogen content in the compost guarantees obtaining better parameters required for organic fertilizers. Changes in the C/N ratio during the tests are presented in Figure 5.

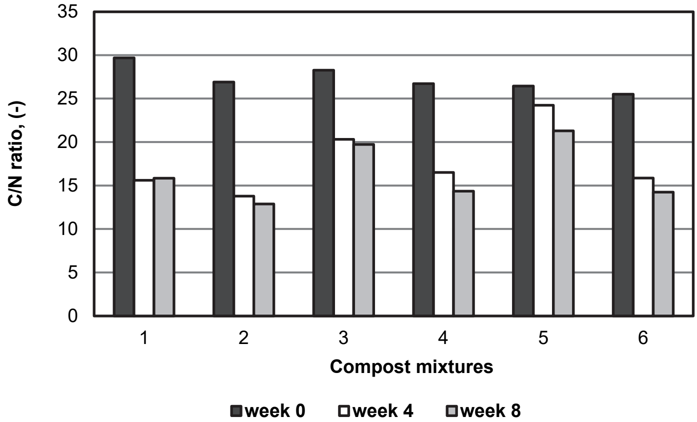

Fig. 5. Changes in the C/N ratio during 8 weeks of the experiment

After 4 weeks of the experiment, a significant decrease in C/N values was observed in all tested compost blends. During the next 4 weeks, the dynamics of changes in C/N values was low; after 8 weeks, almost all the mixtures, except for mixture 5, reached the value of C/N ratio below 20, which was characteristic of mature composts.

The highest declines after week 4 (Fig. 6) were observed for mixtures without coal sludge (mixtures 1 and 2) and amounted to 47.5 and 48.7%, respectively.

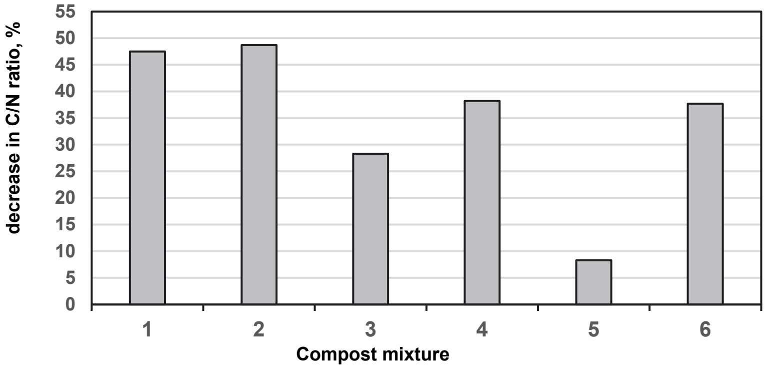

Fig. 6. Decrease in C/N ratio after 4th week of composting (stage 1) with respect to initial value

For mixtures with coal sludge, a decrease in C/N value was observed in the range from 28.3 to 38.2%. The exception was mixture 5, for which this decrease was only 8.3%. This mixture was characterized by the lowest maximum temperature reached in the thermophilic phase, resulting in lower activity of microorganisms responsible for changes in carbon content. An effect of the amount of coal sludge added on the amount of C/N decrease can be observed, with the lowest values observed for 25% content of this component in the mixture. Therefore, the change in the C/N ratio depends mainly on the coal sludge content, since the content of nitrogen in these mixtures remained at a similar level.

3.3.3. Evaluation of sorption capacity of compost

Compost from municipal and green waste has been commonly used to remediate soils contaminated with heavy metals (Bolan et al. 2014). The transformation of organic matter during the composting process changes the speciation of heavy metals (He et al. 2009), whereas the degree of leaching and bioavailability to plants depends on the degree of maturity of the compost applied to the contaminated soil (Weber et al. 2007). Figure 7 shows the size of the compost specific surface area and the Zn^{2+} ion removal efficiency obtained for the compost. The specific surface area was determined by means of the methylene blue sorption method, whereas the efficiency of zinc ion sorption was evaluated using the batch sorption method.

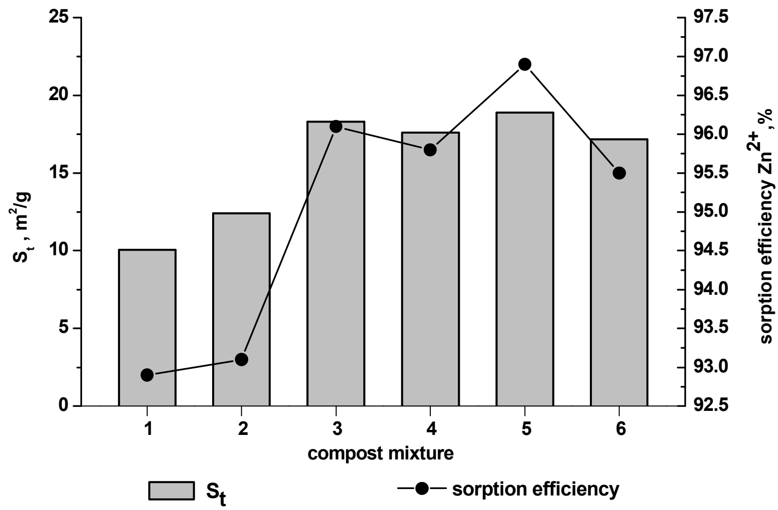

Fig. 7. Specific surface area and efficiency of zinc ion sorption for the composts obtained

In all composts with addition of coal sludge (3-6), the specific surface area has increased compared to composts without this addition (1 and 2). This is due to the presence of clay minerals in this component, which have a strongly developed specific surface area. The largest surface on which the sorption process occurs was found for composts 5 and 3, containing 25% of coal sludge. The values of this parameter were 18.9 and 18.3 m^2/g, respectively. The specific surface area of composts with 10% of coal sludge was slightly lower, at the level of over 17 m^2/g. These values are higher than the values presented in literature reports in which the specific surface area of composts was determined as 14.54 m^2/g (Kyzioł-Komosińska et al. 2011).

The application of the batch method for the assessment of the sorption capacity of composts confirmed the relationship between the specific surface area of the material and its sorption properties. At the same initial zinc concentration (100 mg/dm^3), mixtures 5 and 3 also had the highest sorption efficiency. The percentage of sorption for them was 96.9 and 96.1%, respectively. The remaining two mixtures with 10% of coal sludge (compost 4 and 6) were characterized by similar high efficiency of Zn ion removal at the level of 95.5-95.8%. Therefore, it can be stated that the addition of coal sludge to the compost improves its sorption properties. However, the dose size in the range studied does not have a significant effect on the course of the sorption process.

4. Conclusion

Analysis of the results obtained during the experiment leads to the following conclusions:

- the use of thermal insulation of bioreactors stabilized and improves thermal conditions of the composting process,
- the effect of the amount of added coal sludge and the type of applied structure-forming material (SJ and WE) on the maximum temperatures was observed; the highest temperatures were obtained for mixtures with coal sludge and SJ admixture, which has twice as high C/N ratio as WE,
- after 4 weeks of composting, a decrease in organic matter content and C/N values was observed in all composts,
- the effect of the amount of coal sludge addition on the decrease of the C/N ratio value was observed, which was the lowest for 25% content of this component in the compost mixture; therefore, too high content of coal sludge in the compost mixture adversely affects the composting process and does not allow to reach the expected value of the C/N ratio for the mature compost,
- all composts prepared with the addition of coal sludge increased their sorption surface area and, consequently, their sorption capacity compared to composts

prepared without this addition; this was due to the presence of clay minerals with a strongly developed specific surface area in this component,

- a high capability of removing zinc ions (sorption above 92.9%) regardless of the type and proportion of individual substrates was found for all composts, However, the highest efficiency (over 96%) was observed in compost with 25% content of coal sludge.

In conclusion, the obtained results confirmed the beneficial effect of 10% of coal sludge addition on the course of the composting process, improvement of the sorption properties of composts, and the quality of the obtained final products. Research on the effect of the addition of coal waste on the course of the composting process and sorption capacity of composts needs to be continued, especially in terms of selection of an optimal dose of coal sludge, and the analysis of the effect of such composts on the phenomena occurring in soils due to human impacts.

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Abstract

EU directives on the landfill of waste oblige member states to gradually reduce the deposit of biodegradable waste in landfills. In particular, the entire mass of green waste should be transformed into compost, representing a valuable material. Scientific publications contain numerous reports concerning co-composting of green waste with other types of waste materials, including mineral ones. Appropriate choice of input materials may have a positive effect on the properties of the final product. In particular, improving the sorption capacity of compost in terms of the possibility of using it to improve the properties of the soil seems to be a very important issue.

The aim of the study was to determine the effect of the addition of waste coal sludge on changes in the sorption capacity of the obtained composts.

The potential of using different substrates in the composting process is determined primarily by their proper moisture content, optimal C/N ratio and proper structure, forming an environment with good oxygenation. After theoretical analysis and practical testing, several substrate combinations were selected for the study. The process was conducted using only basic materials (grass, organic fraction of municipal waste, structure-forming materials), and coal sludge in the amount of 10 and 25% by weight.

Since composting is a biological process, the course and conditions of the process need to be optimized and controlled. The research was conducted in two series: series 1, at room temperature of bioreactors, and series 2, with additional thermal insulation of bioreactors. The sorption capacity of the obtained composts was determined with reference to methylene blue and zinc sorption from aqueous solutions (the batch method) at a constant liquid-solid contact ratio of 1:20.

The most favorable process parameters and satisfactory quality of the obtained compost were observed in mixtures with a lower proportion of coal sludge composted in bioreactors with additional insulation (series 2). In all composts produced with the addition of coal sludge, higher values of the specific surface area (S_t) with reference to methylene blue were obtained compared to samples without added sludge. These composts also showed a high capability to remove zinc ions (above 92.9%), regardless of the type and proportion of individual substrates.

The obtained results confirmed the beneficial effect of 10% of coal sludge addition on the efficiency of the composting process, improvement of the sorption properties of composts, and the quality of the obtained final products.

Keywords:

composting, coal sludge, sorption capacity

Wpływ dodatku odpadów węglowych na przebieg procesu kompostowania i pojemność sorpcyjną kompostów

Streszczenie

Dyrektywy Unii Europejskiej w sprawie składowania odpadów zobowiązują państwa członkowskie do stopniowego ograniczenia deponowania odpadów biodegradowalnych na składowiskach. Zwłaszcza cała masa odpadów zielonych powinna ulegać przetworzeniu na cenny materiał – kompost. W publikacjach naukowych pojawiają się liczne doniesienia dotyczące współkompostowania odpadów zielonych z innymi materiałami odpadowymi, w tym mineralnymi. Odpowiedni dobór materiałów wsadowych może korzystnie wpływać na właściwości uzyskiwanego produktu. Zwłaszcza podwyższenie pojemności sorpcyjnej kompostu w aspekcie możliwości wykorzystania go do poprawy właściwości podłoża glebowego wydaje się być zagadnieniem bardzo istotnym.

Celem podjętych badań było określenie wpływu dodatku odpadowych mułów węglowych na zmiany pojemności sorpcyjnej wytworzonych kompostów.

O możliwości wykorzystania w procesie kompostowania różnych substratów decyduje przede wszystkim ich odpowiednia wilgotność, optymalny stosunek C/N oraz właściwa struktura, tworząca środowisko o dobrym natlenieniu. Po analizie teoretycznej i próbach praktycznych do badań wybrano kilka kombinacji substratów. Proces prowadzono z wykorzystaniem wyłącznie materiałów podstawowych (trawa, organiczna frakcja odpadów komunalnych – OFOK, materiały strukturotwórcze), jak i z dodatkiem mułów węglowych w ilości 10 i 25% wag. Z uwagi na to, że kompostowanie jest procesem biologicznym przebieg i warunki prowadzenia procesu wymagają optymalizacji i kontroli. Badania prowadzono w dwóch seriach: seria I – pokojowa temperatura otoczenia bioreaktorów, seria II – dodatkowa izolacja termiczna bioreaktorów. Pojemność sorpcyjną uzyskanych kompostów określono w odniesieniu do błękitu metylenowego oraz sorpcji cynku z roztworów wodnych (metoda batch) w stałej proporcji kontaktu ciecz - ciało stałe, wynoszącej 1:20.

Najkorzystniejsze parametry procesowe oraz satysfakcjonującą jakość uzyskanego kompostu zaobserwowano w mieszankach z mniejszym udziałem mułów węglowych, kompostowanych w bioreaktorach z dodatkowym ociepleniem (seria II). We wszystkich kompostach wytworzonych z dodatkiem mułów węglowych uzyskano wyższe wartości powierzchni właściwej (S_t) w odniesieniu do błękitu metylenowego w porównaniu do próbek bez dodatku mułu. Również właśnie te komposty wykazały dużą zdolność do usuwania jonów cynku (powyżej 92,9%), niezależnie od rodzaju i udziału poszczególnych substratów. Uzyskane rezultaty badań potwierdziły korzystny wpływ 10% dodatku odpadowego mułu węglowego zarówno na przebieg procesu kompostowania, poprawę właściwości sorpcyjnych kompostów, jak i jakość uzyskanych produktów końcowych.

Słowa kluczowe:
kompostowanie, muły węglowe, pojemność sorpcyjna

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Diversity of Vascular Flora in *Salix viminalis* L. Crops Depending on the Harvest Cycle

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1. Introduction

The strategic objective of Polish state policy is to increase the use of renewable energy resources, with a target of 15% in gross final energy consumption 2020 (Strategy for renewable energy development 2000). One of the activities which contribute to the increase in renewable energy sources is the cultivation of energy crops, including fast-growing trees such as poplar (*Populus* sp.) and willow (*Salix* sp.). Plantations of poplar (short rotation coppices) are mainly established in southern European countries, while willow predominates in northern and central Europe (Reddersen 2001, Rowe et al. 2011, AEBIOM 2017). In Poland, the main energy crop is *Salix viminalis* L. and its numerous varieties and hybrids (Antolak et al. 2014, Stolarski 2015). In the 21st century, willow energy plantations are becoming more and more common on the agricultural land of our country, mainly in the eastern and northern regions. In 2014, they occupied a total area of 7728 ha, of which about 230 ha were in the Łódź voivodeship (Grzybek 2015, estimated by authors).

Due to the easy adaptation of *Salix viminalis* L. to various habitat conditions, willow energy plantations have been established in various sites, i.e. on arable and fallow land or permanent grassland. They are situated among arable fields, on the borders with small rivers and meadows, and they are today one of the most valuable elements of the agricultural landscape (Dudkiewicz & Bolibok 2011, Antolak et al. 2014). The useful life of willow energy crops is estimated to be about 25 years, which makes them a valuable habitat for many species of fauna (mainly birds, insects and soil fauna) and flora (Fry & Slater 2011, Chauvat et al. 2014). It should be also emphasized that the *Salix viminalis* L. plantations compensate in large part the loss of trees and shrubs in the agricultural landscape, taking over their ecological functions.

Most of the studies carried out in Poland and other European countries concern the yield of willow and its energy value (Walle et al. 2007, Szczukowski et al. 2011, Tworkowski et al. 2011, Dimitriou & Mola-Yudego 2017). There are only a few papers discussing the vegetation accompanying the willow (Baum et al. 2012, Birmele et al. 2015). In the literature, only the problem of weed control in the first years of cultivation has been widely discussed (Miziniak 2011, Larsen et al. 2014), while the assessment of floristic diversity in these agro-ecosystems and their importance has been presented only in a few papers (Feledyn-Szewczyk 2013, Birmele et al. 2015). Moreover, they focus mainly on young plantations i.e. 1-3 years old (occasionally 4-5) and harvested usually every 2-3 years (Rola et al. 2007, Wojciechowski et al. 2009). The results of Korniak (2007) and Wojciechowski et al. (2009) showed that, in these years, many groups of plants accompanying the willow are short-lived species. Less short-lived species are found in 3-year-old plantations than in those that are 1 year old (Wojciechowski et al. 2009). Many of these species belong to the *Stellarietea mediae* class (Wnuk & Ziaja 2007, Kutyna et al. 2009). However, there are no studies on the vegetation accompanying the willow in older plantations over 5 years old, or in plantations which are harvested very rarely and irregularly or even not harvested at all, mainly for economic reasons. Such plantations are now more and more common; therefore it is important to know their biodiversity, including floristic diversity.

The research hypothesis assumes that the floristic diversity depends on the age of the plantation and the cycle of willow harvesting. The aim of the study was to assess the vascular flora of plantations of *Salix viminalis* L. which were established on permanent grassland in central Poland, and its multifaceted analysis. The dynamics of changes in the flora developed in older willow crops (over 5 years) on two types of plantations (harvested every 2 years and unharvested) fell within the scope of the study.

2. Material and methods

The study area was located in Łódź voivodeship, central Poland. The studies were carried out on 3 *Salix viminalis* L. plantations, in 2 locations: Wojciechowice Duże in Kutno district (2 plantations) and Retki in Łowicz district (1 plantation) (Fig. 1). According to the physicogeographical classification of Poland, the area is located in the Kutno Plain macroregion and in the Central Masovian Lowlands macroregion (Kondracki 2013, www.geoportal.lodzkie.pl).

Fig. 1. Location of the study area in Łódź voivodeship: 1 – Wojciechowice Duże, 2 – Retki

2.1. Soil conditions and plantation characteristics

The study was carried out in the years 2011–2014 and in 2018, on *Salix viminalis* L. plantations which were previously perennial grasslands. In both locations the plantations were bordered by the small lowland rivers Słudwia and Ochnia, and partly by perennial grasslands. The *Salix viminalis* L. plantations were established on moderately fertile soils which are usually used for perennial grassland. The all plantations were located on soils classified into medium grassland complex (2z). These soils were periodically too dry or to wet. They were light sandy soils with high total porosity and a large water capacity. The content of humus of "muck" type was 1-2%. The soils belonged mainly to III meadow soil-valuation class. The information about the soils was based on agricultural maps on a scale of 1:5000 obtained from the Voivodeship Geodesy Office in Łódź (Solna St. 14, 91-423 Łódź, Poland), and on the Łódź Voivodeship Geoportal (www.geoportal.lodzkie.pl). The studied willow energy plantations were established in the years 2004–2006 (density – 35.000 sprouts per ha), so in the first year of the study (2011) they were 5-7 years old. The studied willow energy crops differed in the cycle of the willow harvest, i.e. one group of plantations was harvested usually every 2 years (only in two cases the plantations were harvested after 3 years), and the other was not harvested throughout the entire research period (Table 1).

Table 1. Characteristics of energy willow plantations

Location	Year of establishment	Harvest cycle	Plantation area
Wojciechowice Duże	2004	every 2 years*	0.45 ha
Wojciechowice Duże	2005	every 2 years*	0.40 ha
Retki	2006	not harvested	1.71 ha

*in two cases the plantations were harvested after 3 years

2.2. Weather conditions

The weather conditions during the study period were determined based on the dates recorded at the Meteorological Station of the Institute of Soil Science and Plant Cultivation, located in Bratoszewice, near Łódź. Long-term data were recorded for Łódź. The sum of precipitation in the vegetation period was similar in the years 2011, 2012, 2014 and 2018 (400.0-421.7 mm). Mean air temperatures between April and October in 2011-2014 were similar to each other and similar to the long-term mean. In 2018 the temperature was about 2,9°C higher than the long-term mean. Detailed data regarding average monthly air temperatures and sum of monthly precipitation are shown in table 2.

2.3. Methods

The vegetation accompanying willow (*Salix viminalis* L.) energy crops was identified based on an analysis of 24 phytosociological relevés i.e. four relevés carried out in two types of plantations (harvested and not harvested) in each of the three study periods (2011-2012, 2014, 2018). Each of them represented an area of 100 m^2, roughly square-shaped, and was made using the Braun-Blanquet (1964) method. Subsequently, the number and share of each species was determined. The share of each plant species was determined based on constancy class (S) and cover coefficient (D) calculated according to Pawłowski (1972). The Latin names of vascular plants were given after Mirek et al. (2002), and the phytosociological classifications were after Matuszkiewicz (2012). For each species, the following parameters were determined: family, geographical and historical groups, apophyte origin, biological stability, life-form, and status as an invasive, endangered, near-endangered, or protected species. If the origin of an apophyte had not been established, it was listed as "other". The geographical and historical groups, apophyte origins, biological stability and life-form were identified based mainly on the following sources: Anioł- Kwiatkowska (1974), Korniak (1992), Mirek et al. (2002), Rutkowski (2008), Sowa & Warcholińska (1981), Szafer et al. (1969), Zając & Zając (1975,1992), Zając (1979). Invasive species status was determined based on Tokarska-Guzik et al. (2012). Endangered species were identified based on the "The Red Book of Plants of Łódzkie Voievodeship"

(Olaczek 2012), and near-endangered species were identified based on the "Polish Red List of Pteridophytes and Flowering Plants" (ed. Kaźmierczakowa et al. 2016). Protected plant species were identified based on the Polish Regulation of the Minister for Environment of October 9, 2014, on Plant Species Protection. Herbs were identified based mainly on Bańkowski & Serwatka (1977) and Mowszowicz (1985).

Table 2. Weather conditions in the growing seasons in the years 2011-2014 and 2018 (Meteorological station in Bratoszewice)

Year / Month	Average monthly air temperature (°C)				
	2011	2012	2014	2018	1971-2000
IV	10.5	9.2	10.2	13.2	7.7
V	13.7	14.8	13.3	16.5	13.4
VI	17.9	16.5	15.7	18.3	16.1
VII	17.7	19.9	20.6	20.2	17.7
VIII	18.6	18.7	17.6	20.5	17.6
IX	15.0	14.3	14.6	15.3	13.0
X	8.9	8.2	9.9	9.9	8.2
IV-X	14.6	14.5	14.5	16.2	13.3
Sums of monthly precipitation (mm)					
Month	2011	2012	2014	2018	1971-2000
IV	22.3	54.2	43.3	34.7	36.0
V	46.1	21.4	106.3	44.2	51.0
VI	58.8	70.9	61.2	24.7	68.0
VII	165.2	117.6	50.4	146.6	88.0
VIII	92.4	41.1	84.9	83.9	61.0
IX	6.5	58.1	31.9	29.4	51.0
X	23.1	36.7	24.4	58.2	40.0
IV-X	414.4	400.0	402.4	421.7	395.0

This paper presents the characteristics of vascular flora accompanying willow (*Salix viminalis* L.) energy crops and an analysis of this flora in two types of plantations: those harvested every 2 years and those not harvested. The analysis of vascular flora was conducted in the years 2011-2012, 2014 and 2018 (i.e. 6-8, 9-10, 13-14 years after planting the willow in the plantations which were cut, and 5-6, 8, 12 years after planting the willow in the plantation which was not cut during the research period).

2.4. Statistical analysis

The canonical correspondence analysis (CCA) was performed to describe the species cover in the phytosociological relevés. The explanatory variable (during the CCA analysis) for the phytosociological relevés was the affiliation to one of the 6 combinations of location -by- year of the study (categorical variable, presented in the chart as the ellipses of standard deviations). Thus the CCA chart presents floristic changes (occurrence of individual plant species) in two studied locations over the years.

The principal component analysis (PCA) was performed to describe the changes in the total coverage of species groups from a given family. The first step was to calculate the total coverage of species from a given family in each phytosociological relevé separately. Next the data was centered for the given family across a collection of phytosociological relevés. Such prepared data was analyzed by the PCA. This way the corresponding graph presents changes in the occurrence of main families of species in two studied locations over the years.

The PCA was also performed to describe the changes in the total coverage of species related to the phytosociological classes. The total coverage of species of each class was centered across relevés and such prepared data was analyzed. This way the PCA biplot presents the phytosociological trend in the two locations studied over the years.

The CCA analysis calculations were made in the R software (R Core Team, 2017) using the "cca" function contained in the "vegan" package. The PCA analyses and the biplots were done according Sienkiewicz-Paderewska & Paderewski (2015) by the use of svd function. Biodiversity coefficients were calculated using the "vegan" package by the "diversity" function for H' and "Cspecnumber" for species richness index. The Shannon-Wiener diversity index was also measured for each plantation in each period of study.

3. Results

62 vascular plant species were found accompanying willow (*Salix viminalis* L.) energy crops L. crops which were established on permanent grasslands (Table 3). These species belonged to 22 botanical families (Table 4). The most numerous family was *Poaceae*, of which 15 species were found (24.2%). Other numerous families were: *Asteraceae, Rosaceae, Lamiaceae,* which made up about 30% of all identified species. A large number of families (16) were represented only by 1-2 species.

Table 3. Species occurring in cut and uncut plantations in the all periods of the study

No	Species	Harvested plantations			Unharvested plantations		
		2011-2012	2014	2018	2011-2012	2014	2018
1	*Achillea millefolium* L.s.str.		x				
2	*Agrostis canina* L.	x	x	x			
3	*Agrostis capillaris* L.	x	x				
4	*Agrostis gigantea* Roth	x	x	x			
5	*Alopecurus pratensis* L.	x					
6	*Anthriscus sylvestris* (L.) Hoffm.				x		x
7	*Arctium minus (Hill) Bernh.*				x		
8	*Arrhenatherum elatius* (L.) P.Beauv. Ex J. Presl & C. Presl				x		
9	*Artemisia vulgaris* L.				x		
10	*Bromus inermis* Leyss.				x		
11	*Carex hirta* L.	x		x	x		
12	*Carex ovalis* Gooden.	x					
13	*Chelidonium majus* L.				x		x
14	*Cirsium arvense* (L.) Scop.	x	x	x	x		
15	*Convolvulus arvensis* L.	x	x	x	x	x	x
16	*Crataegus monogyna* Jacq.	x		x			x
17	*Dactylis glomerata* L.			x			
18	*Deschampsia caespitosa* (L.) P. Beauv.	x	x	x	x	x	x
19	*Elymus repens* (L.) Gould	x	x	x	x		
20	*Equisetum arvense* L.	x		x			
21	*Equisetum palustre* L.	x					

Table 3. cont.

No	Species	Harvested plantations			Unharvested plantations		
		2011-2012	2014	2018	2011-2012	2014	2018
22	*Erigeron annuus* (L.) Pers.				x		
23	*Festuca rubra* L.	x	x	x			
24	*Filipendula ulmaria* (L.) Maxim.	x			x		
25	*Galeopsis bifida* Boenn.	x					
26	*Galeopsis ladanum* L.	x					
27	*Galeopsis tetrahit* L.	x	x	x			
28	*Galium aparine* L.	x	x		x	x	
29	*Galium mollugo* L.	x	x				
30	*Geum urbanum* L.	x	x	x	x		x
31	*Glechoma hederacea* L.	x	x		x	x	x
32	*Holcus lanatus* L.				x		x
33	*Hypericum perforatum* L.		x				
34	*Iris pseudacorus* L.				x		
35	*Juncus effusus* L.	x					
36	*Lactuca serriola* L.		x				
37	*Lychnis flos-cuculi* L.				x		
38	*Lysimachia nummularia* L.		x		x	x	x
39	*Melandrium album (Mill.) Garcke*			x	x		
40	*Phalaris arundinacea* L.	x	x			x	
41	*Phleum pratense* L.	x	x	x			
42	*Plantago lanceolata* L.		x				
43	*Plantago major* L.				x		
44	*Poa pratensis* L.	x	x		x	x	
45	*Poa trivialis* L.	x			x		
46	*Polygonum hydropiper* L.	x	x				
47	*Polygonum persicaria* L.	x		x			
48	*Potentilla anserina* L.	x				x	

Table 3. cont.

No	Species	Harvested plantations			Unharvested plantations		
		2011-2012	2014	2018	2011-2012	2014	2018
49	*Potentilla reptans* L.	x	x	x	x	x	x
50	*Quercus robur* L.			x		x	
51	*Ranunculus repens* L.				x		
52	*Rosa canina* L.		x	x			
53	*Rubus caesius* L.				x	x	x
54	*Rumex acetosella* L.	x	x	x			
55	*Sambucus nigra* L.			x	x		x
56	*Stachys palustris* L.	x			x		
57	*Stellaria graminea* L.		x			x	
58	*Stellaria media* (L.) Vill.			x	x		
59	*Taraxacum officinale* F.H. Wigg.					x	
60	*Torilis japonica* (Hoult.) DC.		x				
61	*Urtica dioica* L.	x	x	x	x	x	x
62	*Veronica chamaedrys* L.		x	x			

Table 4. Botanical systematics of species accompanying the *Salix viminalis* L. crops

No	Name of family	Number of species
1	Poaceae	15
2	Asteraceae	7
3	Rosaceae	7
4	Lamiaceae	5
5	Caryophyllaceae	4
6	Polygonaceae	3
7	Cyperaceae	2
8	Apiaceae	2
9	Equisetaceae	2
10	Plantaginaceae	2

Table 4. cont.

No	Name of family	Number of species
11	Rubiaceae	2
12	Convolvulaceae	1
13	Caprifoliaceae	1
14	Fagaceae	1
15	Iridaceae	1
16	Papaveraceae	1
17	Primulaceae	1
18	Ranunculaceae	1
19	Urticaceae	1
20	Juncaceae	1
21	Hypericaceae	1
22	Scrophulariaceae	1
Total	22	62

The willow energy plantations differed in the species richness and species composition of the accompanying vegetation. The plantations which were harvested every 2 years were characterized by greater species richness (48 species) compared to the plantation which was not harvested (37 species). This resulted mainly from better light conditions for the plants.

Consider the two type of plantations: harvested and unharvested together we can say that dominated meadow species (31% in harvested plantations and 24 in unharvested) and woodland-shrub species (25% in harvested plantations and 30% in unharvested). The shares of species from segetal and ruderal habitats were 27% in harvested plantations and 24% in unharvested, and from other habitats – 17%-22% subsequently in harvested and unharvested plantations.

The dynamics of the flora species in the studied willow energy crops differed depending on the cycle of willow harvest (Fig. 2). The 5-7 years old plantations differed in plant composition. The most willing species in cut plantations were: *Equisetum palustre* L., *Galeopsis bifida* Boenn., *Polygonum persicaria* L., *Carex ovalis* Gooden., *Galeopsis ladanum* L., *Equisetum arvense* L., *Juncus effuses* L., *Potentilla anserina* L., *Alopecurus pratensis* L., *Galium mollugo* L. and *Poa trivialis* L. whereas in uncut plantation *Melandrium album* (Mill.) Garcke, *Lychnis flos-cuculi* L., *Erigeron annuus* (L.) Pers., *Plantago major* L., *Iris pseudacorus* L., *Artemisia vulgaris* L., *Arctium minus* (Hill) Bernh., *Bromus inermis* Leyss., *Ranunculus repens* L. and *Arrhenatheretum elatius* (L.) P. Beauv. Ex J. Presl & C. Presl occurred more often in the same time. After 2 years the species compositions in cut plantations approached to uncut plantation and they were close to each other. The most common species for both plantations in 2014 were: *Galium aparine* L. and *Poa pratensis* L. In uncut plantation there were also the same species as before (*Quercus robur* L., *Stellaria graminea* L., *Taraxacum officinale* F.H. Wigg.). In the cut plantations there were many species occurred 2 years before (*Deschampsia caespitosa* (L.) P. Beauv., *Agrostis canina* L., *Cirsium arvense* (L.) Scop., *Rumex acetosella* L., *Phalaris arunidnacea* L., *Phleum pretense* L., *Polygonum hydropiper* L., *Festuca rubra* L., *Filipendula ulmaria* (L.) Maxim., *Agrostis capillaris* L., *Hypericum perforatum* L., *Plantago lanceolata* L., *Achillea millefolium*, *Lactuca serriola* L., *Veronica chamaedrys* L., *Torilis japonica* (Houtt.) DC., *Stachys palustris* L., *Galeopsis tetrahit* L.). After next 4 years in uncut plantation the most occurred species were: *Rubus caesius* L., *Chelidonium majus* L., *Lysimachia nummularia* L. and *Crataegus monogyna* Jacq. In the same time the species composition in cut plantation were more stable. The succession trend was similar (to the upper-left part of the Figure 2) but the plant compositions were similar to those seen four years earlier. The species especially connected with such conditions were: *Urtica dioica* L., *Dactylis glomerata* L., *Agrostis gigantea* Roth, *Anthriscus sylvestris* (L.) Hoffm., *Geum urbanum* L. (Fig. 2).

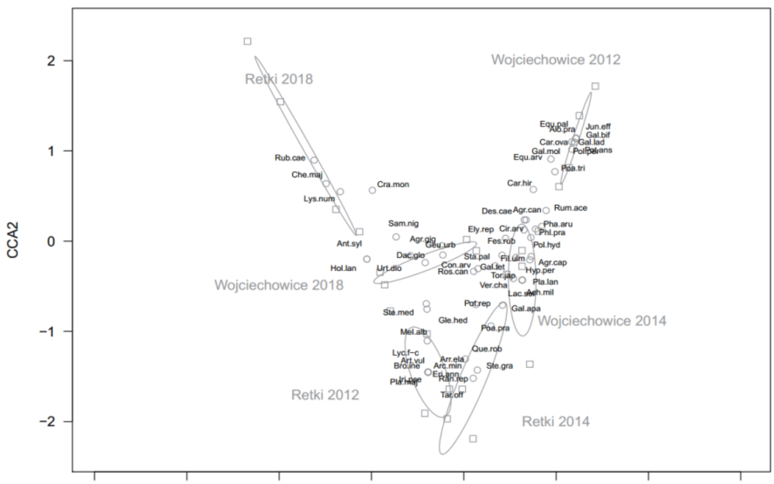

Fig. 2. The canonical correspondence analysis plot for species cover in phytosociological relevés belonging to six groups defined by location and study time (categorical explanatory variable). Squares – phytosociological relevés; Ellipses – ellipses of standard deviations for phytosociological relevés grouped by location and time; circles – species. Wojciechowice Duże – harvested plantations; Retki – unharvested plantation

The dynamics of the number of flora species in the studied willow energy crops differed depending on the cycle of willow harvest. The number of plant species in both types of plantations (harvested every 2 years and uncut) decreased over time (Fig. 3). But this process occurred faster in the uncut plantation. A clear reduction in the number of species in the uncut plantation was recorded in 2014 (8 years after planting the willow crop and 4 years after the last harvest). As a result, in 2018 (i.e. after 7 years of research) the number of species in the uncut plantations was more than 50% lower, while in the plantations which were harvested this number was about 1/3 less (Fig. 3).

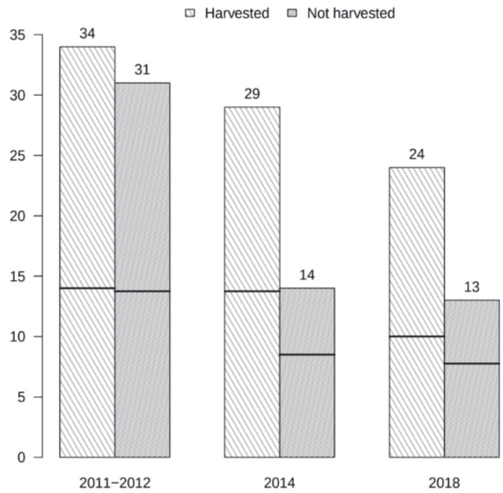

Fig. 3. Number of species in two types of *Salix vimin*alis L. plantations: harvested and not harvested in three periods of study; the horizontal lines mean the average number of species in one phytosociological relevé

Analysis of the proportion of different geographical and historical plant groups showed that in two types of plantations, native (apophyte) species definitely dominated (Table 5 and 6). The share of apophytes in the harvested plantations was about 97% in 2011-2012 and 2014 and 100% in 2018 year. While in the unharvested plantations the share of apophytes was 100% already in 2014. Among apophytes in harvested plantations, the most numerous groups of plants were meadow species (39.3-51.6%) and woodland/shrub species (27.3-39.3%). In the uncut plantation, a slightly larger proportion of woodland/shrub apophytes (forest origin) was found – 42.9-69% (Table 5 and 6). Among apophytes, the groups with the smallest share were photophilous sandyside species and other (3.0-4.1%) in the harvested plantations and xerothermic grassland and waterside and wetside species (6.7-8%) in the uncut plantation (Table 5).

Table 5. Characteristics of flora of *Salix viminalis* L. in uncut plantations in the years 2011-2012, 2014 and 2018

Category	2011-2012		2014		2018	
	No.	%	No.	%	No.	%
Total number of species	31	100	14	100	13	100
Geographical and historical groups						
Antropophytes	1	3.2	0	0.0	0	0.0
Apophytes	30	96.8	14	100	13	100
Apophytes origin						
Meadow species	12	40.0	6	42.9	3	23
Woodland and shrub species	15	50.0	6	42.9	9	69
Xerothermic grasslands	2	6.7	1	7.1	1	8
Waterside and wetside	1	3.3	1	7.1	0	0.0
Biological stability						
Perennial species	25	80.6	13	92.9	13	100
Short-lived species	4	12.9	1	7.1	0	0
Short-lived species-perennial species	2	6.5	0.0	0.0	0.0	0.0
Life-form						
Hemicryptophyte	18	58.0	8	57.4	8	61.5
Therophyte	3	9.7	1	7.1	0	0.0
Geophyte	5	16.1	1	7.1	1	7.7
Herbaceous chamaephyte	2	6.5	1	7.1	1	7.7
Nanophanerophyte	2	6.5	1	7.1	3	23.1
Megaphanerophyte	0	0.0	1	7.1	0	0.0
Hydrophyte,Helophyte	1	3.2	1	7.1	0	0.0
Phytosociological classes						
Agropyretea intermedio-repentis	2	6.5	1	7.1	1	7.7
Artemisietea vulgaris	11	35.6	4	28.6	6	46.1
Epilobietea angustifolii	1	3.2	0	0.0	1	7.7
Festuco-Brometea	1	3.2	0	0.0	0	0.0
Molinio-Arrhenatheretea	13	41.9	6	42.9	4	30.8
Phragmitetea	1	3.2	1	7.1	0	0.0
Rhamno-Prunetea	0	0.0	0	0.0	1	7.7
Stellarietea mediae	1	3.2	0	0.0	0	0.0
Sporadic species	1	3.2	2	14.3	0	0.0

Table 6. Characteristics of flora of *Salix viminalis* L. in cut plantations in the years 2011-2012, 2014 and 2018

Category	2011-2012		2014		2018	
	No.	%	No.	%	No.	%
Total number of species	34	100	29	100	24	100
Geographical and historical groups						
Antropophytes	1	3.0	1	3.4	0	0.0
Apophytes	33	97.0	28	96.6	24	100
Meadow species	17	51.6	11	39.3	10	41.9
Woodland and shrub species	9	27.3	11	39.3	9	37.5
Xerothermic grasslands	1	3.0	1	3.6	1	4.1
Sandyside	1	3.0	1	3.6	1	4.1
Waterside and wetside	4	12.1	3	10.6	2	8.3
Other	1	3.0	1	3.6	1	4.1
Biological stability						
Perennial species	28	82.4	24	82.8	20	83.3
Short-lived species	6	17.6	5	17.2	4	16.7
Life-form						
Hemicryptophyte	18	53.0	17	58.7	10	41.7
Therophyte	6	17.7	4	13.8	4	16.7
Geophyte	8	23.5	4	13.8	5	20.9
Herbaceous chamaephyte	0	0.0	2	6.9	1	4.1
Nanophanerophyte	1	2.9	1	3.4	3	12.5
Megaphanerophyte	0	0.0	0	0.0	1	4.1
Hydrophyte,Helophyte	1	2.9	1	3,4	0.0	0.0
Phytosociological classes						
Agropyretea intermedio-repentis	3	8.9	2	6.9	3	12.5
Artemisietea vulgaris	5	14.7	6	20.7	4	16.7
Bidentetea tripartiti	1	2.9	1	3.4	0	0.0
Epilobietea angustifolii	0	0.0	0	0.0	1	4.1
Molinio-Arrhenatheretea	15	44.2	10	34.5	7	29.3
Phragmitetea	1	2.9	1	3.4	0	0.0
Rhamno-Prunetea	1	2.9	0	0.0	1	4.1
Scheuchzerio-Caricetea nigrae	1	2.9	1	3.4	1	4.1
Stellarietea mediae	2	5.9	3	10.3	3	12.5
Thlaspietea rotundifolii	1	2.9	0	0.0	0	0.0
Trifolio-Geranietea	1	2.9	1	3.4	0	0.0
Sporadic species	3	8.9	4	13.8	4	16.7

Changes in the geographical and historical groups over the seven years of the study indicate a slight increase in the share of apophytes and the decrease of anthropophytes (Table 5 and 6). These changes were found earlier in the vegetation of the uncut plantation than in the harvested plantation. The long period of willow cultivation and the lack of systematic harvesting created appropriate light conditions for development of woodland/shrub apophytes, rather than meadow apophytes, which increased their share by 10 pts.% in both types of plantations (Table 5 and 6).

An analysis of changes in vegetation accompanying the willow crops throughout the 7 years of the study showed an increase in the share of perennial species and a decrease in the share of short-lived species only in the unharvested plantation (Table 5 and 6). In this plantation, the presence of short-lived species was not found at all in the third research period, i.e. 12 years after planting the willow crops and 8 years after its last harvest. However, on the harvested (every 2 years) plantations, the share of perennial and short-lived species throughout the study period remained almost the same.

In both types of plantations, most species were hemicryptophytes (the life form of Raunkiaer): 58.0-61.5% in the uncut plantation and 41.7-58.7% in the harvested plantations (Table 5 and 6). The proportions of therophytes and geophytes were higher in the cut plantations than in uncut plantation (Table 5 and 6). An increase in the number of nanophanerophytes was found in the third period of the study in both types of plantations, as well as a decrease in the number of hemicryptophytes in harvested plantations. Over the years the disappearance of the therophytes and geophytes in the uncut plantation were noted and in 2018, therophytes were not observed. There were only very small changes in the share of species with other life-forms.

The vast majority (in each type of plantations about 70%) of species achieved low degrees of phytosociological constancy, i.e. I and II classes. The higher constancy classes (III, IV, V) were reached about 30% of species which are given in Table 7. The species which achieved higher classes of phytosociological constancy (III, IV, V) were mainly native, perennial, meadow and woodland/shrub species e.g. *Deschampsia caespitosa* (L.) P. Beauv. (S = V) and *Geum urbanum* L. (S = III), and segetal-ruderal species (30%) e.g. *Convolvulus arvensis* L. (S = III).

Over several years of willow cultivation, the species composition and cover with the accompanying vegetation changed. The lack of systematic harvest of the willow plants contributed to considerable development of the trees. An abundance of some species systematically increased for example ruderal plants as *Urtica dioica* L., in cut plantations. Its cover coefficients were 130 in 2011-2012, 1002 in 2014 and 3062 in 2018 year. In the harvested plantations, the abundance of woody and shrub species remained at a similar level throughout the whole research period for example: *Crataegus monogyna* Jacq. abundance was: in 2011-2012 (+) and in 2018 (1), *Rosa canina* L. in 2014 (+) and in 2018 (+).

Among the species accompanying willow energy crops, a large percentage is represented by herbs. In harvested plantations their share ranged from about 50% in 2011-2012 to about 66% in subsequent years (2014 and 2018, Table 3). In unharvested plantation the share of herbs in each period of the study was slightly higher than in harvested plantations and ranged from 54% to 69%. However the melliferous species long flowering, with colorful and fragrant flowers in willow crops were recorded sporadically, only in harvested plantations and only in the first and second study periods (5% in 2011-2012 and 3% in 2014, Table 3).

Table 7. Species with the highest constancy (III-V) in harvested and unharvested plantations in all period of the time

No	Species	Constancy classes	Cover coefficient	Constancy classes	Cover coefficient
		harvested		unharvested	
1	*Deschampsia caespitosa*	V	2396	V	502
2	*Urtica dioica*	V	1398	V	1250
3	*Cirsium arvense*	IV	377	-	-
4	*Rumex acetosella*	IV	334	-	-
5	*Convolvulus arvensis*	III	126	V	48
6	*Geum urbanum*	III	459	III	208
7	*Galium aparine*	III	313	III	250
8	*Festuca rubra*	III	250	-	-
9	*Agrostis canina*	III	208	-	-
10	*Glechoma hederacea*	III	167	V	791
11	*Potentilla reptans*	III	167	IV	250
12	*Phleum pratense*	III	126	-	-
13	*Rubus caesius*	-	-	III	1104
14	*Poa pratensis*	II	459	III	520
15	*Lysimachia nummularia*	I	41	III	604

Among the few anthropophytes in the willow plantations, only two invasive non-native species (neophytes) were recorded: *Erigeron annuus* (L.) Pers. and *Quercus robur L.* They occurred sporadically (in 3 relevés) and in the lowest abundance (+, 1) (Table 3). However, in the studied willow plantations, no endangered and near-endangered species, for either Poland or the Łódź region, were found.

The PCA biplot, based on total abundance of species belonging to each family, concerned on the changes in the occurrence of *Poaceae, Rosaceae and Urticaceae* families (Fig. 4). Generally, the *Poaceae* family more often occurred in 2012 and gave the place for the *Rosaceae* family (especially in uncut plantation) or *Urticaceae* family (especially in cut plantations, Fig. 4) in 2018.

It was found that the average cover coefficient of vegetation accompanying the *Salix viminalis* L. crops was higher in harvested (80%) than in unharvested plantations (68%). The average cover coefficient of the crop plant (*Salix viminalis* L.) was completely different: higher in unharvested (77%) than in harvested plantations (66%).

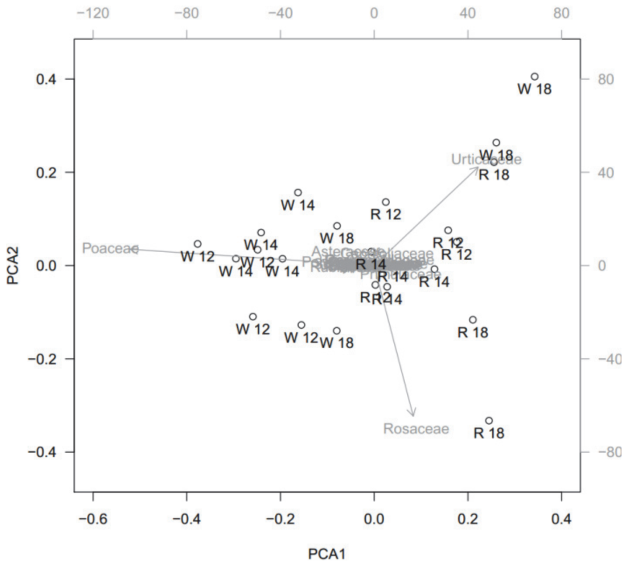

Fig. 4. The principal component (PC) analysis biplot for the total coverage of species belonging to botanical families. The PCA1 has retained 54% of the variability and PCA2 24%; W – harvested plantations, R – unharvested plantation; 12 – phytosociological releves made in the 2011 or 2012 years; 14 – phytosociological releves made in the 2014 year; 18 – phytosociological releves coming from 2018 year

The number of phytosociological classes and the number of species belonging to individual classes were more varied in cut plantations. Generally, the class *Molinio-Arrhenatheretea* with more total cover in 2012 was swapped in 2018 into *Artemisieta vulgaris* class (Fig. 5). The vegetation in harvested plantations represented more phytosociological classes than in the uncut plantations. The largest share of vegetation in harvested plantations was made up of species from the following classes: *Molinio-Arrhenatheretea, Artemisieta vulgaris*, *Agropyretea intermedio-repentis* and *Stellarietea mediae* (in total over 70%). But in unharvested plantations, most species belonged to the *Molinio-Arrhenatheretea* and *Artemisieta vulgaris* classes (in total over 70%) (Table 5 and 6).

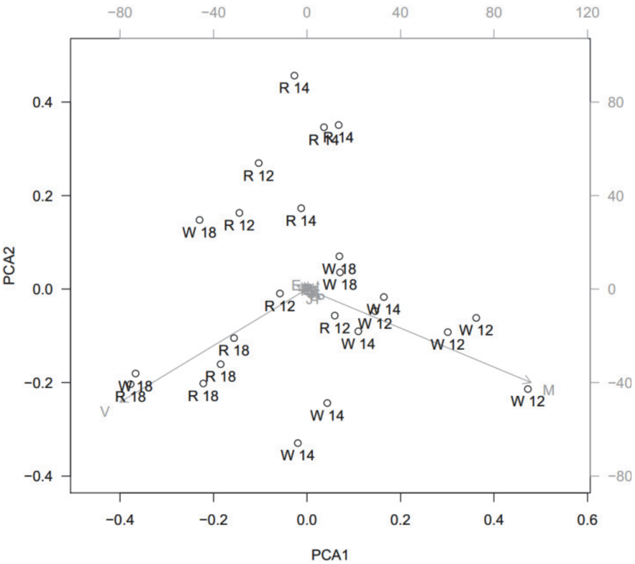

Fig. 5. The principal component (PC) analysis biplot for the total coverage of species groups associated with phytosociological classes. The PCA1 has retained 75% of the variability and PCA2 19%; W- harvested plantations, R – unharvested plantation; 12 – phytosociological relevés made in the 2011 or 2012 years; 14 – phytosociological relevés made in the 2014 year; 18 – phytosociological relevés coming from 2018 year; V – class *Artemisietea* vulgaris; M – class *Molinio-Arrhenatheretea*

The analysis of changes in the share of phytosociological classes showed that in cut plantations, the share of species belonging to the *Molinio-Arrhenatheretea* class decreased (from 44.2% in 2011-2012 to 29.3% in 2018) and species belonging to the *Stellarietea mediae* class (characteristic for arable land) increased (from 5.9% in 2011-2012 to 12.5% in 2018). This was related to the availability of light after subsequent willow harvests. Whereas in the uncut plantation the share of ruderal species from the *Artemisieta vulgaris* class increased slowly (from 35.6% in 2011-2012 to 46.1% in 2018), the share of meadow species of the *Molinio-Arrhenatheretea* class decreased from 41.9% to 30.8% in the last year (Table 5 and 6).

A biodiversity analysis in the plant communities accompanying willow crops, using the Shannon-Wiener diversity index (H), showed differentiation depending on the age of *Salix viminalis* L. (Table 8). The floristic diversity decreased in uncut plantation with the age of willow – H from 2.5 to 1.6. In cut plantations floristic diversity was a bit higher; H in the first period of study was 2.2, in the second – 2.5 and in the year 2018 was 1.8.

Table 8. Values of Shannon-Wiener index (H') for each period of study in harvested and unharvested *Salix viminalis* L. plantations

Plantation	2011-2012	2014	2018
harvested	2.2	2.5	1.8
not harvested	2.5	2.2	1.6

4. Discussion

The species of flora occurring among older willow (*Salix viminalis* L.) energy crops (aged 5-7 years to 12-14 years) established on permanent grassland belong mainly to meadow-pasture communities. This indicates that the vegetation accompanying the willow energy crops, despite the passage of time, had not completely lost all features of the previous habitat communities. A decline in the number of species observed over a seven–year period indicates that the vegetation accompanying older willow energy crops is relatively poor in terms of species richness. A similar change in floristic diversity in younger plantations was observed by Korniak et al. (2009) and Wojciechowski et al. (2009). These authors reported 13.3% and 21.2% fewer species respectively in 3-year-old plantations compared to those which were 1-2 years old.

The results of our study show that, regardless of the age of willow plantation, native species (apophytes) predominate in the flora accompanying the willow crop. A high proportion of this group of plants (82-89%) was found in 2-4-year-old willow plantations by, among others, Jezierska-Domaradzka & Domaradzki (2009) and Korniak et al. (2009). The low proportion of species of foreign origin (anthropophytes), which was about 3% in our studies, is probably the result of the technology of willow cultivation. This technology is not conducive to the development of anthropophytes, which was previously noticed by Anioł-Kwiatkowska et al. (2009). The high share of meadow and woodland apophytes in the flora of the studied *Salix viminalis* L. plantations is the result of the lack of willow harvesting and the age of the plantations in question. As is well known, a lack of harvesting enables slow secondary succession towards a forest ecosystem. In the last year of the study (2018), the share of woodland and shrub apophytes was more than 30 pts.% higher in the uncut plantation than in the harvested ones. In both types of plantations dominated perennial species over short-lived species (82.4-83.3% in harvested plantations and 80.6-100% in unharvested plantations). This was related to the age of the *Salix viminalis* L. crops, which were 5-7 years in the first year of the study.

Analysis of the dynamics of changes in the participation of groups (according to geographical-historical classification of species) showed that the share of apophytes increases and the share of anthropophytes decreases with the age of willow plantations. A systematic increase in the share of perennial and woodland species was also noted. The increase in perennial species correlated with the age of willow recorded in our studies was also noted by Kościk & Ziemińska-Smyk (2009). Similar values for the proportion of perennial species was also observed by Jezierska-Domaradzka & Domaradzki (2009) and Korniak et al. (2009) in younger willow energy crops (2-4 years old), as well as by Sekutowski et al. (2014) in canary grass (*Phalaris arundinacea*) crops (1-4 years old). Studies presented in the literature usually concern the initial period of cultivation of *Salix viminalis* L., i.e. years 1-3, in which vegetation shows greater changes than in older plantations (9-10 years old). However, there are no studies on the dynamics of flora changes in older *Salix viminalis* L. crops (from 5-7 years to 12-14 years old) in either domestic or foreign literature. It should also be emphasized that in the available literature no reference was found to the dynamics of flora changes in unharvested plantations. The discussion of our results is also made more difficult by the fact that many authors do not mention the age of the studied willow energy crops, which is essential for vegetation dynamics analysis.

The long willow cultivation period creates favorable conditions for the development of hemicryptophytes, plants whose buds are protected against frost by the layer of leaves and soil. A high proportion (38-60%) of this group of plants in younger willow energy plantations (1-3 years old) was recorded by Wojciechowski et al. (2009).

Analysis of the flora of willow energy crops showed that most species achieved low constancy classes. It was proved that despite the age of the willow (12-14 years), the proportions of the constancy classes are similar to that of the 3-year-old plantations, in which Korniak et al. (2009) found that 89% of species had either I or II phytosociological constancy classes. The small share of species with higher phytosociological constancy classes indicates the transience and instability of plant communities found in willow plantations.

The average cover coefficient of vegetation accompanying energy willow crops was higher in harvested plantations. This was related to the amount of light available to the plants. It is difficult to compare these results with other studies due to the lack of research on harvested and unharvested plantations.

Analysis of the studied flora in terms of belonging to phytosociological classes showed that the willow communities of older (12-14 years old) plantations consist mainly of two classes: *Molinio-Arrhenatheretea* and *Artemisieta vulgaris.* The earlier statement of Jezierska-Domaradzka & Domaradzki (2009) with regard to 2-4- and 5-7-year-old plantations indicated also a considerable share of species from *Stellarietea mediae* class. In our studies, species from this class were present only in cut older (12-14 years old) plantations. While in unharvested plantations species from *Stellarietea mediae* class had a small share (3.2%) only in 5-7-year-old plantations.

Among the species accompanying willow energy crops, a large percentage is represented by herbs. These plants are important for human and animal health (Bańkowski & Serwatka 1977). However the melliferous species long flowering, with colorful and fragrant flowers in willow crops were recorded sporadically. Among the few anthropophytes in the willow plantations, only two invasive non-native species (neophytes) were recorded: *Erigeron annuus* (L.) Pers. and *Quercus robur* L. They occurred sporadically. In the studied willow plantations, no endangered and near-endangered species, for either Poland or the Łódź region, were found. An analysis of published national papers showed that the problem of invasive, endangered and near-endangered species in *Salix viminalis* L. crops has not been discussed. In foreign literature, authors have proved the presence of several invasive species occurring amongst energy crops, recognizing their presence as harmful (Fehér et al. 2013, Pučka et al. 2016). The presented results of our own research may be a contribution to this issue in the study of energy crop flora in the future.

Results of our study confirmed the research hypothesis. The floristic diversity depended on the age of the plantation and the cycle of willow harvesting. The highest value of the Shannon-Wiener diversity index in uncut plantations was in the first year of the study. In cut plantations the highest value of this diversity index was in the 2014 year which was probably the result of the willow harvesting. Diversity index reported by Marks et al. (2014) in 4 years old willow plantations had a similar values (1,96 -2,10). Feledyn-Szewczyk (2013) studying various energy crops (miscanthus, reed canary grass, big bluestem, switchgrass, false acacia, prairie cordgrass, virginia mallow, Jerusalem artichoke, poplar, willow), presented overall values H 1.8–2.7 (including 4-5 years old willow, harvested every year or every 3 years). Whereas Wróbel et al. (2011) reported that the flora accompanying 4-5 years old energy willow crop characterized by relatively high floristic diversity (H 2.72-3.5). But this plantation was established on wet grassland, on pure silts, over-dried and fertilized with sewage-sludge.

To summarize, it should be stated that the presented analysis of vegetation accompanying willow in harvested plantations (every 2 years) to a large extent coincides with changes in younger plantations (mainly 4 years old) reported by other authors, in different regions of Poland, and reflects general trends in the transformation of flora in willow plantations.

5. Conclusion

1. The species composition of the *Salix viminalis* L. plantations, established on perennial grassland, is related to the previous use of the land (i.e. meadow communities).

2. Analysis of changes in flora in both types of plantations (i.e. harvested and unharvested) showed a downward trend in the number of species and anthropophytes. This was more evident in the unharvested plantations.
3. In older plantations of the *Salix viminalis* L., native and perennial species are dominant. Changes in the floristic composition of *Salix viminalis* L. plantations over the seven years studied (2011-2018) were mainly due to the age of the willow plantations and the degree of soil shading by the willow plants. These changes in the unharvested plantations led to the formation of forest communities.

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Abstract

The aim of the study was to assess the vascular flora of plantations of *Salix viminalis* L. which were established on permanent grassland in central Poland, and its multifaceted analysis. The dynamics of changes in the flora developed in older willow crops (over 5 years) on two types of plantations (harvested every 2 years, and unharvested) fell within the scope of the study.

The study was carried out in the years 2011-2014 and in 2018, on three *Salix viminalis* L. plantations in two locations of the Łódź region. The plantations were established in the years 2004-2006, so in the first year of the study they were 5-7 years old. Plantations differed in the cycle of the willow harvest, one group was harvested every 2 years, and the other was not harvested throughout the entire research period. The vegetation accompanying willow energy crops was identified based on an analysis of 24 phytosociological relevés which were made using Braun-Blanquet method. For each species, the following parameters were determined: family, geographical and historical groups, apophyte origin, biological stability, life-form, and status as an invasive, endangered, near-endangered, or protected species. The CCA and PCA analysis were done and Shannon-Wiener diversity index was calculated.

The species composition of the *Salix viminalis* L. plantations was related to the previous use of the land i.e. to meadow communities. In total, 62 vascular plant species were found in willow energy crops, which belonged to 22 botanical families. The most numerous families were: *Poaceae*, *Asteraceae, Rosaceae* and *Lamiaceae*. In harvested plantations were found more species than in not harvested. The number of plant species in both types of plantations decreased over time but faster in the uncut plantation. In two types of plantations, native (apophyte) species, perennial species and hemicryptophytes dominated. The long period of willow cultivation and the lack of systematic harvesting created appropriate light conditions for development of woodland/shrub apophytes, rather than meadow apophytes, which increased their share in both types of plantations. The vast majority (about 70%) of species achieved only I or II degrees of phytosociological constancy.

The analysis of changes in the share of phytosociological classes showed that in cut plantations, the share of species belonging to the *Molinio-Arrhenatheretea* class decreased and the share of species belonging to the *Stellarietea mediae* class increased. While in the uncut plantation the share of ruderal species from the *Artemisieta vulgaris* class increased slowly and the share of meadow species of the *Molinio-Arrhenatheretea* class decreased. Shannon-Wiener diversity index in uncut plantation decreased with the age of *Salix viminalis* L. from 2.5 to 1.6. In cut plantations floristic diversity was a bit higher.

Keywords:
Salix viminalis L. crops, vascular flora, dynamic of flora, age of plantation, biodiversity

Różnorodność flory upraw *Salix viminalis* L. w zależności od cyklu zbioru wierzby

Streszczenie

Celem pracy było określenie składu gatunkowego roślin naczyniowych na plantacjach *Salix viminalis* L. założonych na trwałych użytkach zielonych w środkowej Polsce oraz szeroka jego analiza. Ponadto celem badań było poznanie dynamiki zmian flory starszych upraw wierzby (ponad 5 letnich) na dwóch rodzajach plantacji: ciętych co 2 lata i nieciętych.

Badania przeprowadzono w latach 2011-2014 i 2018 na trzech plantacjach *Salix viminalis* L. w dwóch miejscowościach województwa łódzkiego. Plantacje założone były w latach 2004-2006, a więc w pierwszym roku badań były to plantacje 5-7 letnie. Plantacje różniły się cyklem zbioru wierzby, tj. jedna grupa cięta była co 2 lata, a druga przez cały okres badań nie była cięta. Roślinność towarzyszącą uprawom wierzby energetycznej oceniono na podstawie analizy 24 zdjęć fitosocjologicznych wykonanych według metody Brauna-Blanqueta. Florę naczyniową scharakteryzowano pod względem: przynależności do rodziny botanicznej i grupy geograficzno-historycznej. W odniesieniu do apofitów podano ich pochodzenie, trwałość biologiczną oraz formę życiową. Ponadto określono status rośliny inwazyjnej, zagrożonej, bliskiej zagrożeniu i chronionej. Obliczono wskaźnik różnorodności biologicznej Shannona-Wienera oraz wykonano analizę PCA i CCA.

Skład gatunkowy flory upraw *Salix viminalis* L. nawiązywał do wcześniejszego sposobu użytkowania terenu tj. do zbiorowisk łąkowych. Flora naczyniowa plantacji wierzby energetycznej liczyła 62 gatunki, które należały do 22 rodzin botanicznych. Najliczniej reprezentowanymi rodzinami były: *Poaceae, Asteraceae, Rosaceae* i *Lamiaceae.* Plantacje cięte co 2 lata charakteryzowały się większym bogactwem gatunkowym w porównaniu do plantacji nie ciętej. Liczba gatunków na obu typach plantacji zmniejszała się wraz z wiekiem plantacji, lecz proces ten szybciej postępował w uprawie nie ciętej. Na obu typach plantacji dominowały apofity, gatunki wieloletnie oraz hemikryptofity.

Długoletni okres uprawy wierzby oraz brak systematycznego jej cięcia stwarzał warunki do rozwoju apofitów leśno-zaroślowych, które zwiększyły swój udział kosztem apofitów łąkowych na obu typach plantacji. Zdecydowana większość (ok. 70%) gatunków osiągnęła niskie stopnie stałości fitosocjologicznej tj. I i II.

Analiza przemian udziału klas botanicznych wykazała, że na plantacjach regularnie ciętych zmniejszył się udział gatunków klasy *Molinio-Arrhenatheretea* a zwiększył udział gatunków klasy *Stellarietea mediae.* Na plantacji nie ciętej następowało natomiast powolne zwiększanie się udziału gatunków ruderalnych klasy *Artemisietea vulgaris* a zmniejszanie udziału gatunków łąkowych z klasy *Molinio-Arrhenatheretea.* Wartości wskaźnika Shannona-Wienera zmniejszyły się wraz z wiekiem uprawy; na plantacji nie ciętej z 2.5 do 1.6. Na plantacji ciętej wskaźniki różnorodności były nieco wyższe.

Słowa kluczowe:
Salix viminalis L., flora naczyniowa, dynamika flory, wiek plantacji, bioróżnorodność

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Quality Analysis of Waters from Selected Small Watercourses within the River Basins of Odra River and Wisła River

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1. Introduction

Eutrophication of inland waters, in connection with increase in phosphorus (P) and nitrogen (N) content is a global issue, especially in agricultural areas. Excessive increase in the content of mineral components in rivers is the result of such substances being carried from the areas of intensive agriculture (Withers et al. 2008). Increase in nitrogen and phosphorus content causes fluctuations in water quality, and the excess of nutrients promotes the growth of phytoplankton (water blooming) and macrophytes, resulting in loss of habitats and beneficial species of plants and animals (Smith 2003). In 19th ct. Europe this process was considered as a significant environmental protection issue and it continues to be a long-term challenge to sustainable management of aquatic ecosystems (Leaf, 2017). This resulted in undertaking a number of water quality tests for major rivers and their major tributaries, including their content of anthropogenic mineral ingredients – mostly of farming origin (Domagała & Kondratowicz 2006, Dupas et al. 2015) and investigating the possibility of reducing such content (Keck & Lepori 2012). It needs to be stressed that small tributaries - watercourse of third and higher orders, lay a material role in shaping the quality of water in large rivers (Alexander et al. 2007). Small watercourses located within agricultural areas play an important role in water retention; they are used in economy and improve the landscape value. They also form a refugium for multiple species of aquatic plants and animals, and affect the biodiversity of land (Williams et al. 2003). In addition, it is commonly known that small watercourses play critical role in biogeochemical connectivity of aquatic and terrestrial ecosystems and are a vital part of the macrocomponent supply line to a receptacle – a higher-order river (Withers & Jarvie 2008). Usually they bring in disproportionally higher quantity of biogenic substances than contained in the receptacle, and despite being thinned they still constitute a serious source of charge causing degradation of water quality (Biggs et al. 2017, Kelly-Quinn et al. 2017). In spite of that, as compared with larger rivers, European countries do not have systems in place for strategic monitoring of physical and chemical properties of small watercourses (Biggs et al. 2017, Lassaletta et al. 2010). Also in Poland, except for a few studies (Liberacki & Szafrański 2008, Sojka et al. 2016), no comprehensive evaluation of the volume of charge carried by small rivers to higher-order rivers, including its potential impact.

The purpose of this study is to assess the ecological status of small watercources of lowlands tributaries of Odra and Wisła rivers on the basis of selected concentrations of physicochemical parameters (nitrogen and phosphorus compounds).

2. Study area

Studies were conducted on 10 small watercourses within the Odra river basin and Wisła river basin (Fig. 1). In the north-western section of Odra river basin, the following rivers were selected for the study: Płonia, Myśla, Tywa, Rurzyca and Wardynka, and in Central Poland the area of Wisła river basin was represented by Kanał Habdziński, Zielona, Czarna-Cedron, Kraska and Molnica. Three measuring stations were established on each river, mostly on agricultural land.

The characteristics of the adjacent areas were based on calculations in the QGIS program using data of Corine Land Cover.

In the catchments of all 10 examined rivers, land cover was mainly agricultural. This particularly concerned rivers in the central part of Poland (B), where the catchment areas of the Molnica and Kraska rivers were dominated by agricultural land (Kraska 88.3% and Molnica 84.2%). The catchment areas of the Habdziński Canal were also dominated by agricultural areas (79.1%), but anthropogenic areas (16.8%) also had a significant share. The catchment areas of the Zielona and Czarna Cedron rivers, apart from agricultural areas (72.6% and 60.9%, respectively) also consisted of forests and semi-natural ecosystems (20.8% and 30.8%). Areas in western Poland (A) were also dominated by agricultural areas (in the catchments of all rivers in this region, it constituted over 50% of the area coverage).

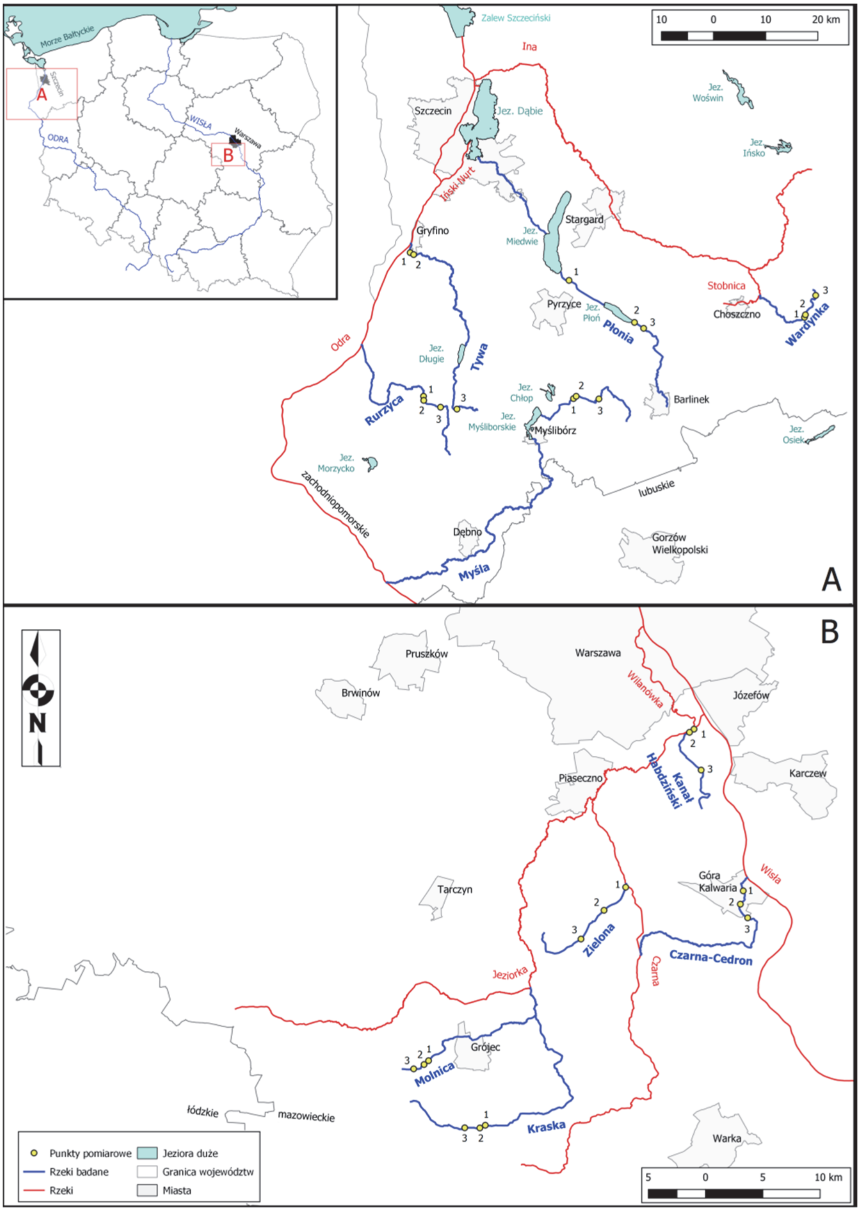

Fig. 1. Location of small rivers in the Odra (A) and Wisła catchments (B)

In the Płonia river catchment area 73.5% was agricultural, 5.2% was anthropogenic and 4.7% was water area. In the catchment areas of the Tywa and Wardynka rivers, apart from agricultural areas (constituting over 65%), forested areas (approx. 30%) and a small amount of anthropogenic areas were annotated. However, despite the fact that the river basin Myśla and Rurzyca dominated by agricultural land (over 56%), a significant part they are also forests and natural ecosystems.

Characteristics of individual rivers are shown in Table 1.

Table 1. Characteristics of small watercourses of the Odra and Wisła catchments

Name of the watercourse	Total surface of the watercourse [km^2]	Total length of the watercourse [km]	Average decrease for positions [‰]	Average depth* [m]	Abiotic type of surface waters (according to the Regional Inspectorate for Environmental Protection Szczecin and Warsaw
Odra catchment					
Płonia	1 129.0	73.0	2.7	0.84	23
Myśla	1 298.0	104.0	3.6	0.31	20
Tywa	264.5	47.9	1.9	0.40	16
Rurzyca	430.7	44.4	2.3	0.44	24
Wardynka	101.2	21.3	2.8	0.20	18
Wisła catchment					
Kanał Habdziński	28.1	9.9	0.9	0.43	17
Zielona	37.0	11.6	1.1	0.16	17
Czarna-Cedron	71.0	15.5	0.5	0.70	17
Kraska	36.0	11.5	3.7	0.21	17
Molnica	59.0	15.5	3.9	0.07	17

*own measurement (average of all positions)

3. Material and methods

Field examinations were conducted within the 2018 vegetation period (Apr to Oct). Temperature and pH of water were measured directly in the field, using the multi-parameter mobile measuring instrument HACH, also dissolved oxygen (DO) content was measured (multi-parameter measuring instrument Multi 3400 by WTW with oxygen probe type Cellon 323 was used). Also, field measurements were accompanied by taking water samples (3 samples from each station) every 30 days from rivers subject to study. Test samples were taken in compliance with the applicable standards. Concentration in water was determined: $N\text{-}NO_3^-$, $N\text{-}NH_4^+$ and $P\text{-}PO_4^{3-}$. Concentrations of nitrogen and phosphorus forms were determined by the Environmental Chemistry Research Laboratory of ITP in Falenty by colorimetric method, using automatic flow analyzer manufactured by Skalar. In addition, depth was determined at individual measuring stations, using measuring staff.

Water quality indices have been evaluated with reference to requirements included in the Regulation by Minister of Environment of July 21, 2016 on classification of the state of uniform parts of surface waters and on environmental quality standards for priority substances (JoL 2016 item 1187). Water test results were statistically processed in the software tool Statistica 12.5 PL. Since the data obtained failed to meet the assumptions necessary to conduct the variance analysis (i.a. no normal distribution, no homogeneity of variance), Kruskal-Wallis test ($p < 0.05$) has been used to determine statistically significant differences.

4. Results and discussion

Physical and chemical properties of river waters change in time and space, resulting in continuity of ecological processes and gradient nature of river zones, so-called river continuum (Vannote et al. 1980, Neal et al. 2006). Width and depth of river bed, inflow of biogens, temperature, general suspended matter, oxygen content, as well as the water flow rate change continuously from the riverhead to the river mouth (Kanclerz et al. 2018). Since matter and energy are transferred with the flow of a water course, gradual increase in concentration of substances dissolved in water is natural. Such factors as change in decline and flow rate, land improvement related reshaping of river bed, contamination of waters, hydro-engineering structures may interfere with the concept of river continuum. Small watercourses – tributaries to higher-order river, may supply waters of such river with organic matter and pollutants.

When analyzing results of water quality tests from waters of five (5) rivers within Odra river basin, four water quality indicators out of seven, namely conductance, dissolved oxygen, $N\text{-}NO_3^-$ and $P\text{-}PO_4^{3-}$ concentration, were elevated and failed to meet the requirements as per Regulation by ME of 21/07/2016 (Tab. 2). The highest, 15-fold excess of the permitted content of phosphate phosphorus (≤ 0.101 mg $P\text{-}PO_4 \cdot dm^{-3}$ for water quality class II) was recorded in waters of Płonia river. It is probably connected with local dumping of fertilizer compounds, noted in its upper course. Differences between obtained concentrations of phosphate phosphorus were statistically significant from those recorded for rivers Myśla, Tywa and Rurzyca. In the latter one, however, nearly 4-fold exceeding of permitted $N\text{-}NO_3^-$ content (≤ 1.7 mg $N\text{-}NO_3^- \cdot dm^{-3}$ for water quality class II) was observed. Elevated values of $N\text{-}NO_3^-$ and $P\text{-}PO_4^{3-}$ has impact on low content of oxygen dissolved in waters of examined rivers. It was in the range 1.16 $mg \cdot dm^{-3}$ (item 3, river Myśla) to 6.27 $mg \cdot dm^{-3}$ (item 2, river Tywa) and at no point did it meet the requirements of water quality class II (Tab. 2). In the context of the regulation in force, considering mean values of electrolytic conductance of waters from those 5 rivers, a slight exceeding of limit value for water quality cat. II, which has been observed in, Tywa and Wardynka, and in Myśla and Rurzyca the limit value has been exceeded by 53.3 and 73.6% respectively. Values of remaining indices, as per requirements in the regulation, were not exceeded and complied with requirements for water quality class I and II (Tab. 2).

Having assessed the quality of those 5 rivers, it is waters of Rurzyca river that carry the largest quantities of pollutants. This is probably due to local dumping of municipal sewage recorded by stations 1 and 2, whereas station 3 was located at the municipal sewage treatment plant.

Table 3 presents the results of water quality analysis for small rivers of Wisła river basin. As is the case with Odra river basin, indices that complied with the requirements of water quality class I and II in Regulation by ME of 21/7/2016 were temperature, pH and $N\text{-}NH_4^+$ content. Considering mean values of electrolytic conductivity, the highest mean value was observed in waters of river Kraska (813 µs/cm), and the lowest in waters of Czarna Cedron (519 µs/cm) and only in the latter water course values obtained complied with requirements for water quality class I as per the a.m. regulation (≤ 549 µs/cm). Small quantity of oxygen dissolved in water was observed in all watercourses of the Wisła river basin. Mean values were in the range 3.96 to 5.63 $mg \cdot dm^{-3}$ and differences between them were not statistically significant (Tab. 3).

Table 2. Average values and standard deviation (SD) of physico-chemical parameters at individual research stations located on selected watercourses of the Odra river catchment

Water-course	P	Temp °C	pH	EC [µs/cm]	O_2 [mg·dm^{-3}]	N-NO_3^- [mg·dm^{-3}]	P-PO_4^{3-} [mg·dm^{-3}]	N-NH_4^+ [mg·dm^{-3}]
Płonia	1	16.0	7.9	552	4.85	3.973	1.230	0.169
	2	15.0	7.9	555	5.25	4.530	1.278	0.123
	3	14.4	7.9	585	5.52	4.385	2.008	0.114
	avg.	**15.2^{bc} ±0.8**	**7.9^{a} ±0.1**	**564^{a} ±18**	**5.21^{a} ±0.34**	**4.296^{ab} ±0.289**	**1.505^{b} ±0.437**	**0.135^{a} ±0.030**
Myśla	1	15.8	8.0	656	5.68	2.983	0.417	0.090
	2	14.2	7.5	772	4.13	5.645	0.453	0.091
	3	15.0	7.4	954	1.16	2.023	0.335	0.070
	avg.	**15.0^{bc} ±0.8**	**7.7^{a} ±0.3**	**794^{bd} ±150**	**3.66^{a} ±1.90**	**3.550^{a} ±1.877**	**0.401^{a} ±0.006**	**0.084^{a} ±0.012**
Tywa	1	13.7	7.9	606	6.0	4.632	0.420	0.087
	2	15.0	8.1	601	6.27	5.597	0.597	0.111
	3	13.5	7.6	879	3.99	2.103	0.650	0.080
	avg.	**14.0^{ac} ±0.8**	**7.7^{a} ±0.2**	**695^{ab} ±159**	**5.42^{a} ±1.25**	**4.101^{ab} ±1.793**	**0.555^{a} ±0.120**	**0.092^{a} ±0.016**

Table 2. cont.

Water-course	P	Temp °C	pH	EC [µs/cm]	O_2 [mg·dm^{-3}]	$N\text{-}NO_3^-$ [mg·dm^{-3}]	$P\text{-}PO_4^{3-}$ [mg·dm^{-3}]	$N\text{-}NH_4^+$ [mg·dm^{-3}]
Rurzyca	1	14.8	7.4	886	3.07	6.997	0.533	0.127
	2	14.2	7.6	855	4.97	8.428	0.703	0.672
	3	14.0	7.5	740	3.84	6.537	0.470	0.251
	avg.	**14.5^{bc} ±0.4**	**7.5^{a} ±0.1**	**828^{bd} ±77**	**3.96^{a} ±0.96**	**7.321^{b} ±0.987**	**0.643^{a} ±0.247**	**0.350^{a} ±0.285**
Wardynka	1	12.8	7.8	594	5.96	4.375	1.183	0.089
	2	12.2	8.0	627	6.19	4.000	1.073	0.093
	3	12.4	7.5	608	2.57	2.903	0.510	0.221
	avg.	**12.5^{a} ±0.3**	**7.8^{a} ±0.3**	**610^{ae} ±16**	**4.90^{a} ±2.0**	**3.759^{a} ±0.765**	**0.922^{ab} ±0.361**	**0.134^{a} ±0.075**

Colour coded: green – values conforming to requirements concerning water in water quality class I, yellow – in class II, red – above class II. Variance analysis ANOVA $p < 0.05$; mean values in verses marked with the same do not differ statistically significantly at $p > 0.05$ (Kruskal-Wallis post-hoc test)

Table 3. Average values and standard deviation (SD) of physico-chemical indicators determined at individual research stations located on selected watercourses of the Wisła river basin

Waterco-urse	P	Temp °C	pH	EC [µs/cm]	O_2 [mg·dm^{-3}]	N-NO_3 [mg·dm^{-3}]	P-PO_4^{3-} [mg·dm^{-3}]	N-NH_4^+ [mg·dm^{-3}]
Kanał Habdziński	1	17.6	7.4	611	5.32	5.295	0.980	0.520
	2	17.2	7.4	558	5.71	4.893	0.615	0.162
	3	15.7	7.0	519	3.52	4.297	0.958	0.198
	avg.	**16.8^{ab} ±1.0**	**7.3^{a} ±0.3**	**562^{abc} ±46**	**4.85^{a} ±1.17**	**4.828^{a} ±0.502**	**0.851^{b} ±0.205**	**0.293^{a} ±0.197**
Zielona	1	18.8	7.4	529	6.02	3.892	0.083	0.084
	2	18.1	7.5	566	5.72	4.422	0.752	0.111
	3	17.2	7.3	671	5.16	2.315	0.553	0.083
	avg.	**18.0^{b} ±0.8**	**7.4^{ab} ±0.1**	**589^{abc} ±74**	**5.63^{a} ±0.44**	**3.543^{a} ±1.096**	**0.462^{ab} ±0.344**	**0.093^{a} ±0.016**
Czarna Cedron	1	17.7	7.3	543	5.18	2.990	0.060	0.164
	2	18.8	7.2	527	3.88	2.363	0.069	0.073
	3	19.0	7.2	486	3.64	2.598	0.037	0.107
	avg.	**18.5^{b} ±0.7**	**7.2^{a} ±0.1**	**519^{a} ±29**	**4.23^{a} ±0.83**	**2.651^{a} ±0.317**	**0.055^{a} ±0.017**	**0.115^{a} ±0.046**

Table 3. cont.

Watercourse	P	Temp °C	pH	EC [µs/cm]	O_2 [mg·dm^{-3}]	$N\text{-}NO_3$ [mg·dm^{-3}]	$P\text{-}PO_4^{3-}$ [mg·dm^{-3}]	$N\text{-}NH_4^{+}$ [mg·dm^{-3}]
Kraska	1	15.4	7.7	835	3.98	3.495	0.288	0.118
	2	15.5	7.7	782	4.71	4.303	0.352	0.117
	3	15.0	7.6	822	3.44	3.923	0.871	0.119
	avg.	**15.3^{a} ±0.3**	**7.7^{ab} ±0.1**	**813^{c} ±28**	**4.04^{a} ±0.64**	**3.907^{a} ±0.404**	**0.503^{ab} ±0.320**	**0.118^{a} ±0.001**
Molnica	1	16.7	7.7	621	4.53	7.638	2.253	0.049
	2	16.8	7.6	988	2.46	4.478	1.753	0.084
	3	15.2	8.0	609	4.88	3.160	2.063	0.088
	avg.	**16.2^{ab} ±0.9**	**7.8^{b} ±0.2**	**739^{abc} ±215**	**3.96^{a} ±1.31**	**5.092^{a} ±2.301**	**2.023^{c} ±0.252**	**0.074^{a} ±0.022**

Markings as in Table 1

Very high excesses were noted for concentrations of $N\text{-}NO_3^-$ and $P\text{-}PO_4^{3-}$. The highest mean value of $P\text{-}PO_4^{3-}$ was obtained for Molnica river. It exceeded the limit value for water quality class II as much as 20-fold ($P\text{-}PO_4^{3-} \leq 0.101$ mg·dm^{-3} for water quality class II). This small watercourse was fully covered by aquatic vegetation, which often accumulates charges of nitrogen and phosphorus (Ilnicki 2014). Also, the depth of Molnica river was the smallest, reaching on average as little as 0.07 m (Tab. 1). In Czarna Cedron river, the concentration of $P\text{-}PO_4^{3-}$ was small – 0.055 mg·dm^{-3}, and consistent with requirements for water quality class I (Tab. 3). The lowest concentration of $N\text{-}NO_3^-$ has been determined also in waters of Czarna Cedron river and the value determined exceeded permitted value 3.4 mg·dm^{-3} for water quality class II (Tab. 3). The highest mean value of this index was obtained for river Molnica, and in item 1 the quantity of $N\text{-}NO_3^-$ was exceeded two times, considering requirements included in Regulation by ME of 21/7/2016. The whole course of this small river runs through agricultural areas, in sections adjacent to farm households. During the study period the growth of aquatic plants there was intense, completely covering the watercourse surface, which combined with the outflow of biogenic components, could have accelerated eutrophication of the watercourse subject to study.

Summarizing the values of water quality indices for examined water it may be concluded that river Molnica is the most contaminated watercourse in the Wisła river basin, whereas river Czarna Cedron is the least contaminated one.

In the spring and summer season phytoplankton and macrophytes inhabiting rivers increase their absorption of nutrients, while higher availability of light and higher temperatures promote and intensify nitrogen and phosphorus absorption processes (Jarvie et al. 2013). Increase in biogen concentration during the vegetation season, observed in the study, may be the testimony to anthropogenic contamination of waters, originating in farming and industrial operations running in the area.

5. Summary

Study completed confirmed the assumed thesis on contamination of small, lowland watercourses going through agricultural land. Analyzed samples from all rivers demonstrated elevated content of phosphate phosphorus. Material exceeding of $P\text{-}PO_4^{3-}$ in Zachodniopomorskie region has been recorded for river Płonia (1.505 mg·dm^{-3} on average), whereas in Mazowsze region the highest excess has been recorded for Molnica watercourse (2.023 mg·dm^{-3} on average). Despite those two rivers being so different in length and surface area of river basin, local dumping of fertilizer compounds and intensive farming use of the land adjacent to the river were observed in both cases. Also the highest content of nitrate nitrogen were recorded in Molnica river (2.023 mg·dm^{-3} on average), which may be explained by intense growth of aquatic plants in the watercourse. In addition, the smallest quantity of water (0.07 m on average) was observed in the watercourse, which could trigger biogenic charges in bottom deposits. The highest content of the same compound in waters of Western Poland has been determined in Rurzyca river (7.321 mg·dm^{-3} on average), probably due to local dumping of municipal sewage. In both examined areas the situation was better with contamination of small rivers with ammonia nitrogen compounds – waters could be classified as water quality class I and II as per Regulation by ME of 21/7/2016. High content of biogenic compounds in examined waters translated into low oxygen concentration and elevated conductance. Aforementioned significant increase in phosphorus and nitrogen content in minor lowland watercourses may be the evidence for biogens ingress to major rivers, such as Odra and Wisła, and in the absence of control and monitoring measures, municipal sewage and fertilizer sewage dumping spots may be the significant source of contamination.

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Abstract

An important source of contamination of inland waters is the content of nitrogen and phosphorus compounds, which in agricultural areas constitute a significant threat by getting into flowing waters. The runoff of mineral substances from areas with high intensification of agriculture contribut to increase of nutrient content in rivers, which often causes disturbances in water quality, with excess nutrients supporting the growth of phytoplankton (algae receipts) and macrophytes and associated with it loss of habitats and desirable plant and animal species. The small rivers play an important role in the water quality of large rivers. The purpose of this work is to assess the quality of water in small lowland rivers, which are tributaries of the Odra and Wisła rivers, with particular emphasis on the content of biogenic compounds (nitrogen and phosphorus forms). The study was carried out on 10 small rivers from the Odra river basin (Płonia, Myśla, Tywa, Rurzyca and Wardynka River), and the Wisła river basin (Habdziński Channel, Zielona, Czarna-Cedron, Kraska and Molnica River). The analyzed water samples in all rivers had increased content of reactive phosphorus, which allows to classify the waters into non-class waters. The highest exceedences were recorded in the Płonia River (on average 1.505 mg $P\text{-}PO_4^{3-}$/L) in the Odra river basin, while in the in the Wisła basin the highest exceedances were recorded in the Molnica watercourse (average 2.023 mg $P\text{-}PO_4^{3-}$/L). Also high concentrations of the nitrate-nitrogen content were recorded, and the highest amounts of $N\text{-}NO_3^-$/L were found in the Rurzyca River (the Odra catchment – 7.321 mg $N\text{-}NO_3^-$/L) and in Molnica River (Wisła catchment – 5.092 mg $N\text{-}NO_3^-$/L). Lower values of ammonium nitrogen were found in all tested watercourses, classifying water to the first class of water quality according to Minister of the Environment Regulation (21.07.2016r.). Only increased concentrations classifying the examined waters up to the 2nd water quality class were recorded in the Rurzyca river (Odra catchment - 0.350 mg $N\text{-}NO_3^-$/L average, and in the Habdziński Channel (Wisła catchment - 0.293 mg $N\text{-}NO_3^-$/L). Significant increases in the content of biogenic compounds classifying tested waters to the 2nd class and above, were also conducive to low values of oxygen concentration in water and high conductance. For example in the Molnica river, high nitrate nitrogen and phosphate content influenced on low water oxygenation. In addition, there was a very low water level in the watercourse, which could have triggered nutrient loads in bottom sediments. Contamination of waters from agricultural areas with nitrogen and phosphorus compounds may pose a threat to larger rivers to which they can pass without proper monitoring.

Keywords:
watercourses, catchment, water quality, pollution

Analiza jakości wód wybranych małych cieków zlokalizowanych w zlewni rzek Odry i Wisły

Streszczenie

Istotnym źródłem zanieczyszczenia wód śródlądowych są zawartości związków azotu i fosforu, które na obszarach rolniczych stanowią znaczące zagrożenie przedostając się do wód płynących. Do nadmiernego wzrostu zawartości związków biogennych w rzekach przyczyniają się spływy substancji mineralnych z terenów o dużej intensyfikacji rolnictwa, co niejednokrotnie jest przyczyną zaburzeń jakości wody, przy czym nadmiar składników odżywczych sprzyja wzrostowi fitoplanktonu (zakwitów glonów) i makrofitów oraz związanej z tym utraty siedlisk i pożądanych gatunków roślin i zwierząt. Dużą rolę w kształtowaniu jakości wody dużych rzek pełnią niewielkie dopływy stanowiące małe cieki wodne. Celem niniejszej pracy jest ocena jakości wód w wybranych małych nizinnych ciekach wodnych będących dopływami rzeki Odry i rzeki Wisły ze szczególnym uwzględnieniem zawartości związków biogennych (formy azotu i fosforu). Badaniami objęto 10 niewielkich cieków z obszaru zlewni rzeki Odry (rzeki: Płonia, Myśla, Tywa, Rurzyca i Wardynka), oraz zlewni rzeki Wisły (Kanał Habdziński, Zielona, Czarna-Cedron, Kraska i Molnica). Analizowane próby wody we wszystkich rzekach

miały podwyższone zawartości fosforu fosforanowego, co pozwala zaklasyfikować badane wody do wód pozaklasowych. W zlewni rzeki Odry największe przekroczenia norm odnotowano w rzece Płonia (średnio 1.505 mg $P\text{-}PO_4^{3-}$/L), natomiast w zlewni Wisły największe przekroczenia zanotowano w cieku Molnica (średnio 2.023 mg $P\text{-}PO_4^{3-}$/L). Również wysokie stężenia odnotowano analizując wody pod kątem zawartości azotu azotanowego, a największe ilości $N\text{-}NO_3^-$ stwierdzono w rzece Rurzyca (zlewnia Odry – 7.321 mg $N\text{-}NO_3^-$/L) i w Molnicy (zlewnia Wisły – 5.092 mg $N\text{-}NO_3^-$/L). We wszystkich badanych ciekach stwierdzono niższe ilości azotu amonowego, klasyfikując wody do I klasy czystości wg Rozp. MŚ z 21.07.2016r. Jedynie podwyższone stężenia klasyfikujące badane wody do 2 klasy czystości wód zanotowano w rzece Rurzyca (zlewnia Odry – średnio 0.350 mg $N\text{-}NH_4^+$/L, oraz w Kanale Habdzińskim (zlewnia Wisły – 0.293 mg $N\text{-}NH_4^+$/L). Znaczące podwyższenia zawartości związków biogennych klasyfikujące badane wody do II klasy i powyżej II klasy czystości wód sprzyjały również niskim wartościom stężenia tlenu w wodzie oraz wysoką konduktancją. Przykładem jest tu rzeka Molnica, w której wysokie zawartości azotu azotanowego oraz fosforanów przekładały się na niskie natlenienie wody i wysokie przewodnictwo właściwe. Ponadto w cieku była bardzo niski stan wód, co mogło uruchomić pokłady ładunków biogennych w osadach dennych. Zanieczyszczenia wód z terenów rolniczych związkami azotu i fosforu mogą stanowić zagrożenie dla większych rzek, do których bez odpowiedniego monitoringu mogą się przedostawać.

Słowa kluczowe:
cieki wodne, zlewnia, jakość wody, zanieczyszczenie

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Cytotoxic Effects of Two Parabens Determined in Surface Waters and Sewage Sludge on Normal (Senescent) Human Dermal Fibroblasts

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1. Introduction

Parabens, i.e. esters of p-hydroxybenzoic acid (also referred to as nipagins or aseptins), are commonly known preservatives frequently used in cosmetics and medicines due to their broad spectrum of antimicrobial activity (Andersen 2008; Cashman & Warshaw 2005; Dębowska 2016; Muszyński & Ratajczak 2009; Soni et al. 2005). Another advantage of nipagins is their low toxicity and activity over a wide pH range (4-8). As parabens do not demonstrate drug incompatibilities, they can be added to medicines.

Parabens are used to preserve such cosmetic products as creams, soaps, perfumes and deodorants, hair care products, shaving and depilation products, makeup products, nail care products, and agents with UV filters. Almost all leave-on cosmetic products (intended to stay in prolonged contact with skin) are preserved with parabens. They are also frequently found in rinse-off cosmetic products (Bojarowicz et al. 2012).

Mixtures of parabens (in particular methyl paraben and propyl paraben due to the synergism of their actions) are most frequently used.

A concentration of a single paraben in cosmetic products in EC must not exceed 0.4%, while the maximum permitted content of a paraben mixture is 0.8%, according to the Annex V of EC Regulation on cosmetics (Regulation (EC) No 1223/2009 of the European Parliament and of the Council). The most commonly used preservative mixture is a combination of 0.2% methyl paraben with 0.1% propyl paraben.

The use of esters of p-hydroxybenzoic acid in cosmetics may be also due to their properties other than an antimicrobial action; e.g. in soaps they also serve as anti-perspirants, and in shampoos they are used as anti-dandruff agents as well.

Methyl and propyl esters of p-hydroxybenzoic acid have also been used in ophthalmic medicines at concentrations of 0.065-0.15%, and in ointments and oral medicines at a concentration of 0.5%.

Widespread use of parabens is bothering because concerns include endocrine disruption, carcinogenicity (specifically breast cancer), neonatal and perinatal exposure risks, fertility, spermatogenesis disturbance, emotional disorders, and environmental impact (Fransway et al. 2019).

Parabens are present in the natural environment as its significant contaminant, although data on their dissemination in the environment and the secondary sources of exposure to both humans and animals are scarce.

Kijeńska et al. (2016) report that the total content of (methyl, ethyl, propyl and benzyl) parabens amounted to 10.43 ng/g dry matter in sewage sludge collected from five Polish municipal sewage treatment plants. The highest content in all analysed sewage sludge samples was noted for methyl paraben (2.31-2.83 ng/g dry matter).

In surface waters, paraben concentrations ranging from 15 to 400 ng/l were observed (Brausch & Rand 2011), and it should be noted that parabens contaminating surface waters may pose a hazard to aquatic organisms since even their low levels may exhibit estrogenic effects (Dobbins et al. 2009). In the muscle tissue of marine fish inhabiting the Manila Bay waters, a concentration of methyl paraben ranging from 605 to 3,450 ng/g was determined, while that of propyl paraben ranged from 46 to 1,140 ng/g (Haman et al. 2015).

Methyl paraben and propyl paraben were also detected in human urine at concentrations of 43.9 and 9.05 ng/ml, respectively (Ye et al. 2006).

For this reason, studies into toxic effects of parabens on human cells may also be of significance in terms of the environmental exposure of humans to these 4-hydroxybenzoic acid derivatives.

This article presents the results of the study into the cytotoxic effects of (methyl and propyl) parabens of the normal fibroblasts isolated from human skin.

2. Material and methods

2.1. The analysed parabens, cell line, reagents and culture medium

A study was carried out on two esters of p-hydroxybenzoic acid, namely methyl paraben (MePB) (CAS 99-76-3) and propyl paraben (PrPB) (CAS 94-13-3).

The control group included cells incubated in a xenobiotic-free culture medium (untreated cells = 100% viability).

The cytotoxicity study was carried out on an ageing cellular line of diploid human dermal fibroblasts CCD-1136Sk (ATCC® CRL-2697™) purchased through LGC Standards, the exclusive European distributor of the American Type Culture Collection (ATCC) products. The study into the effects of preservatives on the cells were carried out on passages numbered from 8 to 20.

For cell culturing, the following were used: culture medium Iscove's Modified Dulbecco's Medium (ATCC® 30-2005™) with 10% of Foetal Bovine Serum (catalogue No. 10084-150) manufactured by Gibco BRL (Life Technologies Ltd. Paisley, Scotland), and a trypsin solution (0.25%) and EDTA (catalogue No T-4049) manufactured by Sigma (Sigma Chemical Company, St. Louis, Mo USA).

Cells were maintained in monolayer cultures, at 37°C in a humidified atmosphere with 95% air and 5% CO_2.

2.2. Cytotoxicity assessment methods

The cytotoxicity assessment was carried out in accordance with INVITTOX protocols No 17 and 64 for the MTT and NRU test, respectively (INVITTOX 1990 and 1992). The MTT test involves the assessment of the metabolic activity of cells, expressed by the capability of absorbing a dye, namely the yellow tetrazolium salt (MTT), and reducing it, mainly in the mitochondria with the participation of succinate dehydrogenase, to a formazan compound with a purple-navy blue colour.

The principle of the NRU test which assesses the cell membrane integrity is based on the viable, undamaged cells' capability of absorbing a dye, namely neutral red (3-amino-7-dimethylamino-2-methylphenazine hydrochloride) which accumulates in lysosomes.

Based on the MTT and NRU tests, the analysed substances' concentrations inhibiting the viability of cells by 50% (IC_{50}) were determined. IC_{50} values (median inhibitory concentration - concentration required for 50% inhibition of cells viability compared to the negative control, which was accepted as 100%: % cell viability = {(Absorbance value of treated cells - Absorbance value of blank)/(Absorbance value of untreated cells - Absorbance value of blank)} x100). The IC_{50} values for each compound were calculated with a computer program using curve interpolation (four-parameter logistics), Gen5™ Data Analysis, manufactured by BIO-TEK INSTRUMENTS, INC.

2.3. Methodology for statistical analyses of results

For testing of general hypotheses in the analysis of variance, F-Snedecor test was applied, while in multiple comparisons for simple effects, the Bonferroni test was applied.

3. Results and discussion

The obtained IC_{50} values for the analysed parabens on subsequent passage human dermal fibroblasts are presented in Fig. 1.

Having compared the cytotoxicity of both analysed parabens on CCD-1136Sk cells (ATCC® CRL-2697™) based on the IC_{50} values determined in the MTT and NRU tests, it was found that propyl paraben (PrPB) was more toxic; however, none of the tests found a consistent trend for a change in the cells' sensitivity to the analysed parabens as they passaging, that would be reflected in the determined IC_{50} values (Fig. 1).

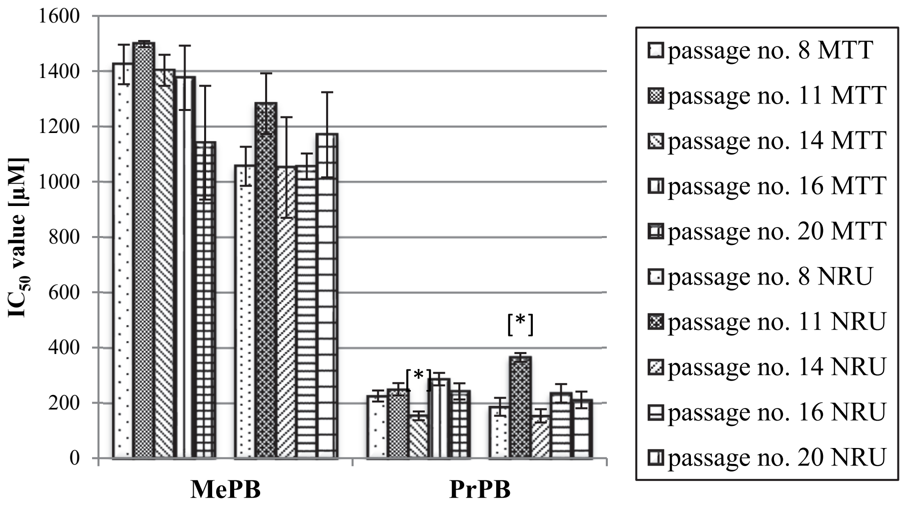

Fig. 1. The comparison of cytotoxicity of the analysed parabens based on the IC50 values determined on subsequent passages of CCD-1136Sk cells (ATCC® CRL-2697™) in the MTT and NRU tests. Each bar represents an average and a standard deviation from 9 measurements in 3 independent experiments. Statistically significant averages ($p < 0.05$) are marked

On the other hand, having analysed the course of the curves of relationships between the cell viability and the preservative concentration, it was found that the exposure of normal dermal fibroblasts to methyl paraben assessed using the NRU test (Fig. 2) indicates a stronger effect of the preservative at a concentration of 50 and 200 µg/ml on the earliest cells passage (no. 8) compared to the subsequent passages of these cells. At the same time, the compound with a concentration of 50 and 800 µg/ml was the least toxic to the latest passage cells (no. 20). No such changes were noted in the MTT test (Fig. 3) except for a weaker effect of the compound at a concentration of 800 µg/ml on the older passage cells (no. 20) compared to the earlier cell passages.

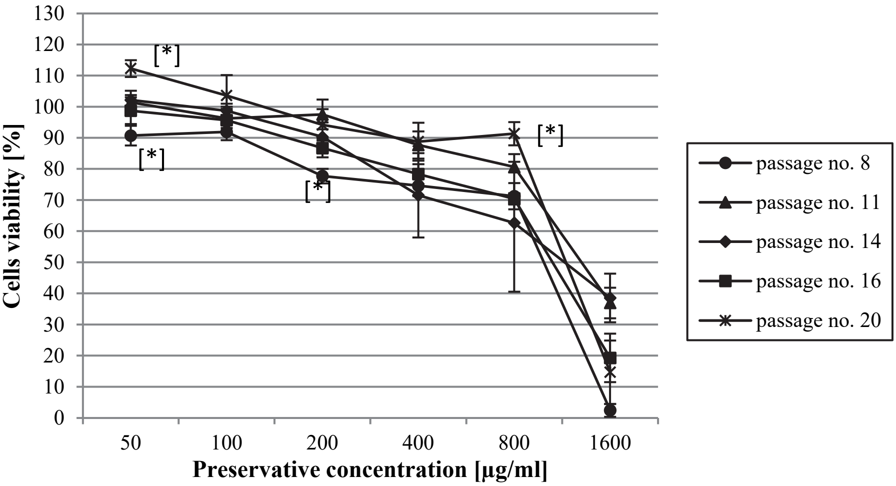

Fig. 2. The effect of methyl paraben on the viability of CCD-1136Sk cells (ATCC® CRL-2697™) determined using the NRU test. Each point represents an average and a standard deviation from 9 measurements in 3 independent experiments. Statistically significant averages ($p < 0.05$) are marked

No different sensitivity of consecutive passages of cells was noted at the exposure of CCD-1136Sk fibroblasts to propyl paraben in any of the two tests.

The obtained results enable the conclusion that propyl paraben exhibits a stronger cytotoxic effect on normal (senescent) diploid human fibroblasts CCD-1136Sk (ATCC® CRL-2697™) than methyl paraben.

These results are consistent with those obtained by Carvalho et al. (2012), who found that propyl paraben exhibited a stronger cytotoxic effect on human dermal fibroblasts (HDF) than methyl paraben, as the IC_{50} value for propyl paraben in the NRU test was determined at a level of 0.25%, while for methyl paraben this value amounted to 2.35%.

The results of the comparison of toxicity of MePB and PrPB, carried out in this study, are also consistent with the Cosmetic Ingredient Review (2008) according to which propyl paraben exhibits a stronger cytotoxic effect than methyl paraben; a study carried out on the cells of a specified cell line originating from the cervical cancer cells (HeLa) determined the IC_{50} values for methyl paraben and propyl paraben at a level of 1.3 mM and 0.22 mM, respectively. The cited IC_{50} value for propyl paraben falls within the range of the values determined in this project on dermal fibroblasts.

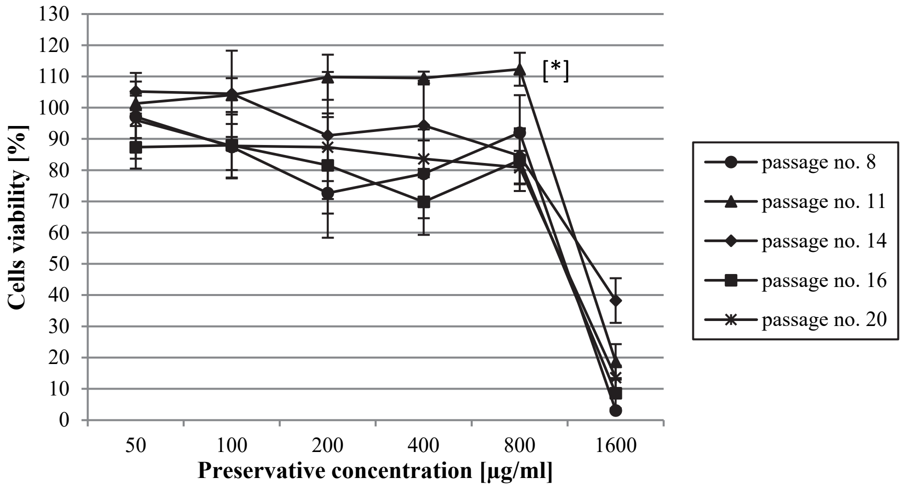

Fig. 3. The effect of methyl paraben on the viability of CCD-1136Sk cells (ATCC® CRL-2697™) determined using the MTT test. Each point represents an average and a standard deviation from 9 measurements in 3 independent experiments. Statistically significant averages ($p < 0.05$) are marked

Taking into account the course of the curves of relationships between the cell viability and the concentrations of the analysed preservatives, it can be observed that these compounds may exert various effects on the cells of the same line which differ in age (the early and late passage).

Having considered the comparison of the sensitivity to cytotoxic effects of parabens between the younger cell passages and the older passages, it was found that the CCD-1136Sk cells of the early passages were characterised by a greater sensitivity to the cytotoxic effects of methyl paraben, which was evident at the exposure to the two lowest of the applied concentrations of the compound. As the cells were passaged, a phenomenon of their increased resistance to the effects of the analysed preservatives occurred; however, it concerned only one of the higher analysed paraben concentrations.

It should be noted that even the cells of immortalised lines that are maintained for a long time may respond differently to the same xenobiotic due to the occurrence of mutations which change the cells' characteristics found in the early passages of a particular line (Wenger et al. 2014). Inter alia, changes (aberrations) in the cell caryotype (a set of cell chromosomes) were found, namely duplications of a chromosomal region and of entire chromosomes. The authors emphasise that the confirmation of the origin of a cell line, and its accurate characterisation (including the passage number) is a prerequisite for obtaining reliable results of experiments which can only be useful for other researchers only on this condition.

The number of passage at which changes occur in the cells is characteristic of a particular cell line. For the Syrian hamster embryo (SHE) cells, a “crisis” was found (Chang-Liu & Woloschak 1997) which occurred at passage 37 and continued to passage 49, and which was characterised by rapid changes in the number of colonies formed from a single cell (“plating efficiency”) and by changes in the cell growth parameters. In the testing carried out as part of this study, the phenomenon of the inhibition of the proliferation of CCD-1136Sk cells (ATCC® CRL-2697™) was observed at passage 27 (unpublished data).

The results obtained in this study confirm the findings of many authors about the heterogeneity and variability of the results of studies carried out on the cells of various age or origin. A review of the literature on the effects on the passage number on cell lines indicates that this effect is complex and highly dependent on many factors such as the cell line type, the tissue and species of its origin, the culture conditions (temperature, pH, appropriate mediums and culture additives, or the growth surface) and the uses for which a particular cell line is applied. For example, it was found (unpublished ATCC data) that older passages of Caco-2 cells exhibited the up-regulation of the reporter protein GFP (green fluorescent protein) following the transfection, while older passages of the MCF7 line, compared to the younger ones, exhibit a decrease in the GFP levels (Tech Bulletin of ATCC 2010).

In summary, it can be concluded that the presented results indicate that the analysed parabens used in the cosmetic and pharmaceutical industries may be toxic to skin cells, and their consecutive passaging may be associated with differences in the susceptibility to cytotoxic effects. It therefore appears necessary to take into account the possibility of different later and earlier passages cells’ reactivity when interpreting the results of studies into the effects of preservatives on the living body. Furthermore, it should be borne in mind that humans may be exposed to preservatives due to environmental contamination with their residues, although compared to other sources of exposure, such as the direct use of cosmetic products or medicines, neither water bodies nor the biota appear to be the main source of exposure for humans (Ramaswamy et al. 2011).

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Abstract

The aim of the study was to compare the cytotoxic effects of (methyl and propyl) parabens likely to be environmental contaminants on early and late passage fibroblasts isolated from human skin. The study was carried out on senescent diploid cell lines, namely normal (senescent) dermal fibroblasts CCD-1136Sk (ATCC®CRL-2697™). In order to assess the cytotoxic effect, the MTT test which determines the cells' metabolic activity and the neutral red uptake assay which assesses the cell membrane integrity (NRU test) were applied. Propyl paraben (PrPB) appeared to be more cytotoxic to the analysed dermal fibroblasts (since it reached lower IC_{50} values); however, none of the tests found a consistent trend for a change in the cells' sensitivity to the analysed parabens as they age, that would be reflected in the determined IC_{50} values. On the other hand, having analysed the course of the curves of relationships between the cell viability and the preservative concentration, it was found that at the exposure of CCD-1136Sk fibroblasts to propyl paraben, none of the two tests observed different sensitivity of late and early cell passages; however, the exposure of dermal fibroblasts to methyl paraben, determined using the NRU test, indicated a stronger effect of the preservative at a concentration of 50 and 200 μg/ml on the earliest cells passage (no. 8), compared to the subsequent passages of these cells. At the same time, the compound with a concentration of 50 and 800 μg/ml was the least toxic to the latest cells passage (no. 20). The presented results indicate that the analysed parabens used in the cosmetic and pharmaceutical industries may be toxic to skin cells; moreover, it is not excluded that with consecutive passaging, differences in the susceptibility to cytotoxic effects may occur. It therefore appears necessary to take into account the possibility of different later and earlier passages cells' reactivity when interpreting the results of studies into the effects of preservatives on the living body. Furthermore, it should be borne in mind that humans may be exposed to preservatives due to environmental contamination.

Keywords:
preservatives, methylparaben, propylparaben, cytotoxicity, senescent cells, in vitro

Cytotoksyczne działanie dwóch parabenów oznaczanych w wodach powierzchniowych i osadach ściekowych na normalne (starzejące się) ludzkie fibroblasty skórne w badaniach in vitro

Streszczenie

Celem badań było porównanie cytotoksycznego działania parabenów (metylu i propylu), mogących stanowić zanieczyszczenie środowiska naturalnego, na wczesne oraz późne pasaże fibroblastów wyprowadzonych ze skóry człowieka. Badania wykonano na starzejących się diploidalnych liniach komórkowych: fibroblastach skórnych CCD-1136Sk (ATCC® CRL-2697™). Do oceny cytotoksycznego działania zastosowano test MTT, który określa aktywność metaboliczną komórek oraz test pochłaniania czerwieni obojętnej oceniający integralność błon komórkowych (test NRU). Bardziej cytotoksyczny (osiągający niższe wartości IC_{50}) dla badanych fibroblastów skórnych okazał się propyloparaben (PrPB), jednak w żadnym z testów nie stwierdzono spójnej tendencji zmiany wrażliwości komórek na badane parabeny w miarę ich starzenia się, która znalazłaby odzwierciedlenie w wyznaczonych wartościach IC_{50}. Analizując natomiast przebieg krzywych zależności żywotności komórek od stężenia konserwantu stwierdzono, że przy narażeniu fibroblastów CCD-1136Sk na paraben propylowy nie zaobserwowano zróżnicowanej wrażliwości komórek późnych i wczesnych pasaży w żadnym z dwóch testów, natomiast narażenie fibroblastów skórnych na paraben metylowy oceniane testem NRU wskazało na silniejsze działanie konserwantu o stężeniu 50 i 200 µg/ml na komórki najwcześniejszego pasażu (nr 8) w porównaniu z kolejnymi pasażami tych komórek. Jednocześnie, związek o stężeniu 50 i 800 µg/ml był najmniej toksyczny dla komórek najpóźniejszego pasażu (nr 20). Przedstawione wyniki wskazują, iż badane parabeny stosowane w przemyśle kosmetycznym i farmaceutycznym mogą działać toksycznie na komórki skóry, nie wyklucza się także, że wraz z ich starzeniem się mogą być występować różnice w podatności na działanie cytotoksyczne. Konieczne zatem wydaje się uwzględnianie przy interpretacji wyników badań nad odziaływaniem substancji konserwujących na żywy organizm również możliwości odmiennej reaktywności komórek późniejszych i wcześniejszych pasaży. Nie należy ponadto zapominać o możliwości narażenia człowieka na substancje konserwujące wynikające z zanieczyszczenia środowiska naturalnego.

Słowa kluczowe:
konserwanty, paraben metylu, paraben propylu, cytotoksyczność,
starzejące się komórki, in vitro

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Water Needs of Asparagus Plants in the Different Regions of Poland

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1. Introduction

The researchers involved in the study of water requirements of the plants in Poland believe that asparagus (*Asparagus officinalis* L.), due to their deep and well-developed root system, are relatively resistant to the water deficits in the soil (Kaniszewski 2005, Kaniszewski 2006). On the other hand, asparagus plants grown on the light soil positively respond to irrigation treatments (Rolbiecki 2013). In the experiment published by Rolbiecki (2013), the micro-irrigation applied during the post-harvest period (June-August) significantly increased the marketable yield of asparagus spears collected in the next growing season (April-June). The studies on the water needs of asparagus in Poland are very rare. The exceptions are the results published by Rolbiecki (2013) that presented observations of many-years field experiments, in which irrigated asparagus plants were investigated. In these studies, using the Grabarczyk's formula (1976) that determines the reference evapotranspiration, the plant coefficients (kc) were evaluated for this vegetable species. Finally, as the result of the research the crop evapotranspiration i.e. the water needs of asparagus plants was determined. Generally, the crop evapotranspiration is used as the measure of plant water requirements of particular species (Doorenbos & Pruitt 1977, Doorenbos & Kassam 1979, Allen et al. 1998).

The purpose of this investigation was to determine the water requirements of asparagus plants cultivated in the five different regions of Poland.

2. Material and methods

The calculations of asparagus (*Asparagus officinalis* L.) water requirements, based on the precipitation measurements, were performed for the thirty-year period from 1981 to 2010. To estimate the needs of asparagus plants, considered as the crop evapotranspiration (Etp), the plant coefficients (kc) were applied (1):

$$\text{Etp} = \text{kc} \times \text{Eto} \tag{1}$$

The plant coefficients were determined for the Polish field conditions by Rolbiecki (2013) that based on the long-term field experiments, which included observations of the irrigated asparagus plants. The reference evapotranspiration (Eto) was calculated in accordance with the Grabarczyk et al. (1994) method (2):

$$\text{Eto} = \text{K} + \text{P}\,(1 - \text{k}) \tag{2}$$

where:
K – constant value characteristic for individual months and different regions of Poland
k – coefficient indicating the reduction value of water deficiencies as a result of precipitation equal to 1 mm, designated for individual months and different regions of Poland
P – monthly sum of atmospheric precipitation (mm).

The Grabarczyk's formula was chosen because it allowed estimating the reference evapotranspiration in a simplified way, i.e. based only on the rainfall measurements.

The precipitation deficiencies (N) were considered according to the Ostromęcki's method (Żakowicz et al. 2009). The rainfall deficit in the period, including months July and August that are critical in terms of the amount of water available to the plants, was calculated as the difference between the water needs of asparagus, expressed as the crop evapotranspiration for a considered month, and the total precipitation in this month (3):

$$\text{N} = \text{Etp} - \text{P} \tag{3}$$

The water needs of asparagus were determined for five agro-climatic regions of Poland (Łabędzki et al. 2013) with the representative meteorological stations located in Olsztyn, Bydgoszcz, Warszawa, Wroclaw and Krakow (Fig. 1).

Fig. 1. Agro-climatic regions of Poland with the representative meteorological stations (according to Łabędzki et al. 2013)

The results were statistically calculated by determining the values, such as maximum, minimum and median, as well as standard deviation and variation coefficient. The calculations were performed using Excel software.

3. Results

The highest variability of asparagus water needs was calculated in in July in the C-E region (Table 1). The variation coefficient was 8.4%. High value of the variability of asparagus water needs was calculated also in the C-N-W region of the Poland. The variation coefficient in July and August was 7.7% and 7.6%, respectively. Whereas the lowest variability of asparagus water requirements were observed in the S-W and S-E region of Poland.

Figure 2 presents the water needs of asparagus (expressed as the crop evapotranspiration) in the period from July 1 to August 31 in the different regions of Poland. The highest water requirements of asparagus plants were noted in C-N-W and C-E region (100 and 129 mm in July, and 100 and 128 mm in August, respectively). Finally, during both considered months, in total, the level of water needs of this vegetable species was by 228 mm. The lowest water requirements of asparagus were calculated in the N-E region of Poland (206 mm).

Table 1. Crop evapotranspiration of asparagus plants in the different regions of Poland

Specification	Region of Poland					Poland
	N-E	C-N-W	C-E	S-W	S-E	
July						
Minimum (mm)	70	79	66	77	71	75
Maximum (mm)	100	110	109	106	105	105
Median (mm)	89	100	101	98	97	96
SD (mm)	6.478	7.670	8.430	5.968	6.667	6.097
VC (%)	7.3	7.7	8.4	6.2	6.9	6.3
August						
Minimum (mm)	97	92	96	100	107	106
Maximum (mm)	130	141	141	135	134	134
Median (mm)	119	130	129	128	126	126
SD (mm)	8.350	9.725	8.899	7.732	6.362	6.311
VC (%)	7.1	7.6	7.0	6.1	5.1	5.1

SD – standard deviation; VC – variation coefficient

During the considered period from July 1 to August 31, the highest precipitation deficiencies were observed in the C-N-W and C-E region Poland, where the values of $N_{50\%}$, $N_{25\%}$ and $N_{10\%}$ were 91, 157 and 209 mm, respectively in the C-N-W region, and 89, 166 and 245 mm, respectively, in the C-E region (Table 2). In the S-E region, were noted the lowest rainfall deficiencies of 55, 125 and 160 mm, in average dry years, medium dry years and very dry years, respectively.

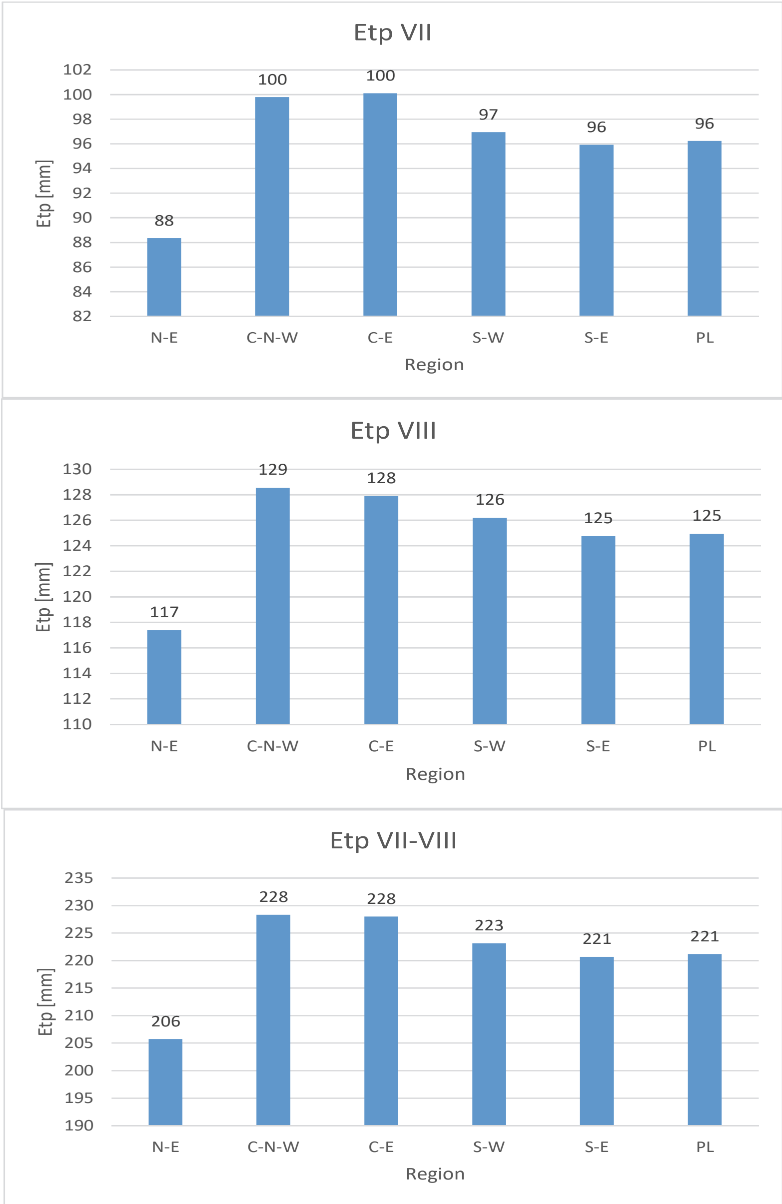

Fig. 2. Water needs (Etp) of asparagus, expressed as crop evapotranspiration, in the period from July 1 to August 31 in the different regions of Poland

Table 2. Rainfall deficit (mm) in the asparagus cultivation at the critical period (July-August) in the different regions of Poland

Year in terms of the amount of rainfall	Probability (p) of occurrence % of years	Region of Poland				
		N-E	C-N-W	C-E	S-W	S-E
July						
Average dry	50	14	22	23	17	8
Medium dry	25	56	76	72	53	57
Very dry	10	76	107	103	95	82
August						
Average dry	50	52	69	66	58	47
Medium dry	25	86	81	94	75	68
Very dry	10	131	102	142	92	78
July-August						
Average dry	50	67	91	89	75	55
Medium dry	25	142	157	166	128	125
Very dry	10	207	209	245	187	160

4. Discussion

In the present study, the reference evapotranspiration was calculated according to the formula reported by Grabarczyk et al. (1994) that based on the results of precipitation measurements. Usually, rainfall occurring during the summer is connected to the changes in other weather factors that affect the growth and development of plants. During precipitation, there is an increase in cloud cover and reduction in insolation, as well as a drop in air humidity deficits and, generally, fall of the temperature. The weather factors, mentioned above, determine the amount of reference evapotranspiration and thus establish the water needs and deficits in the period of intensive biomass growth (Doorenbos & Pruitt 1977, Doorenbos & Kassam 1979, Grabarczyk et al. 1994, Allen et al. 1998).

The largest water requirements of asparagus plants were estimated in the C-N-W and C-E region of Poland. Previously, similar observations were published by Rolbiecki et al. (2000 a, b), Rolbiecki & Rolbiecki (2008), Stachowski & Markiewicz (2011) and Żarski et al. (2013), which the greatest necessity to use irrigation treatments complementing rainfall shortages noted in the central Poland, i.e. in areas with high water deficits.

In the study reported by Paschold et al. (2004), the water consumption of asparagus plants evaluated in the lysimeter conditions ranged from 266 to 292 mm. In turn, according to Pardo et al. (1997) the seasonal water consumption of asparagus plants under lysimeter conditions was between 274 and 294 mm. In the present research, the total water needs of asparagus in the C-N-W and C-E region of Poland during the period from July 1 to August 31 was nearly 230 mm, while the precipitation deficits were 91 and 89 mm, 157 and 166 mm, and 209 and 245 mm, respectively, in average dry years, medium dry years and very dry years, respectively. The value of rainfall deficit in very dry years ($N_{10\%}$) that securing the plant water needs at p = 90%, is especially useful during planning and designing of the irrigation system (Żakowicz et al. 2009). According to Kaufmann (1977), the total water deficits (i.e. irrigation needs) in the cultivation of asparagus in the central Europe climatic conditions ranged from 20 to 160 mm, depending on the location of the crop. In turn, Paschold et al. (2001), based on the many-years experiment conducted at the Horticultural Institute in Geisenheim (Germany), noted that the irrigation needs of asparagus cultivated on sandy soil depend on the level and distribution of precipitation in the range from 48 to 153 mm.

In the study published by Rolbiecki et al. (2017), the comparison of water needs of the asparagus plants grown in the regions of Bydgoszcz and Wroclaw during the period from 1996 to 2015, demonstrate a tendency to raise the asparagus water needs observed in July in both considered regions. In July, the monthly amount of the asparagus crop evapotranspiration increased in every ten years by 12.3 mm in the region of Bydgoszcz and by 21.2 mm in the region of Wroclaw. The results presented by Rolbiecki et al. (2017) confirm the opinion published by Łabędzki (2009), who believes that the expected in the near future climate changes will increase the water needs most of the plants species. In order to get ready for the forecasted climate changes, it would be necessary to undertake the adaptation activities, such as the development of an irrigation program, the importance of which will grow with the increasing of the weather changes (Łabędzki 2009, Kuchar & Iwanski 2011, 2013, Żarski et al. 2013, Kuchar et al. 2015, 2017).

According to Rolbiecki et al. (2017), in the period from June 1 to August 31 observed during the twenty-year study, the average precipitation deficit in the asparagus cultivation was 128 mm in the region of Wroclaw and 87 mm in the region of Bydgoszcz. However, in August, the highest monthly rainfall deficiencies – 100 and 70 mm – in the Wroclaw and Bydgoszcz regions, respectively, were noted. In the present study, the highest precipitation deficits also in August were measured, although the values were much higher (126 and 129 mm in the Wroclaw and Bydgoszcz regions, respectively). On the one hand, these differences can be explained by a different period of research (1996-2015 in the study reported by Rolbiecki et al. (2017) and 1981-2010 in the present study). On the other hand, different methods of the reference evapotranspiration estimation were applied in both experiments; in the study published by Rolbiecki et al. (2017) the calculations based on the temperature and deficits of air humidity (Grabarczyk 1976), however in the present study the determination of reference evapotranspiration based only on the precipitations measurements (Grabarczyk et al. 1994).

5. Conclusions

1. The highest variability of asparagus water needs was calculated in July in the C-E region of Poland (variation coefficient 8.4%). High variability of the asparagus water requirements (7.7 and 7.6% in July and August, respectively) was also estimated in the central-north-west region of the country. While the lowest variability of asparagus water needs were find in the south-west and south-east region of Poland.
2. The highest water requirements of asparagus plants in the period from July 1 to August 31, on average 228 mm, were noted in the central-north-west and central-east region of Poland.
3. The highest rainfall deficit calculated for medium dry years, average dry years and very dry years were 91 and 89 mm, 157 and 166 mm, and 209 and 245 mm, respectively, in the central-north-west and central-east region of Poland, respectively.
4. In August, generally, were noted higher precipitation deficiencies than in July.

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Abstract

Asparagus (*Asparagus officinalis* L.), due to their deep and well-developed root system, are relatively resistant to the water deficits in the soil. On the other hand, asparagus plants grown on the light soil positively respond to the irrigation treatments. The aim of the present study was the determination of water needs of asparagus plants in the different agro-climatic regions of Poland. The calculations of asparagus water requirements, considered as the crop evapotranspiration, based on the precipitation measurements collected during the thirty-year period from 1981 to 2010. The estimations were achieved for the months, including July and August, critical in terms of the amount of water available to the plants. The calculation of asparagus water needs using the plant coefficients was performed. The plant coefficients for asparagus cultivated in the Polish field conditions were determined by Rolbiecki. Published by him calculations based on the long-term observations of the irrigated asparagus crop. The reference evapotranspiration was calculated according to Grabarczyk's method. The Grabarczyk's formula was chosen because it allowed estimating the reference evapotranspiration in a simplified way, i.e. based only on the precipitation measurements. The rainfall deficit was considered using the Ostromęcki's method. The precipitation deficit in the period from July 1 to August 31 was calculated as the difference between the water needs of asparagus, expressed as the crop evapotranspiration for a considered month and the total precipitation in this month. The water needs of asparagus plants were determined for five agro-climatic regions of Poland with the representative meteorological stations located in Olsztyn, Bydgoszcz, Warszawa, Wroclaw and Krakow. The highest variability of asparagus water requirements was calculated in the central-north-west (C-N-W) region of the Poland. The variation coefficient in July and August was 7.7% and 7.6%, respectively. In contrast, the lowest variability of asparagus water needs were find in the south-west (S-W) and south-east (S-E) region of Poland. The highest water needs of asparagus plants, on average 228 mm, in the period from July to August were noted in the C-N-W and central-east (C-E) region of Poland. The highest rainfall deficit, calculated for medium dry years, average dry years and very dry years, was 91 mm and 89 mm, 157 mm and 166 mm, and 209 mm and 245 mm, respectively, in the C-N-W and C-E region, respectively. Generally, higher precipitation deficiencies were noted in August than in July.

Keywords:
Asparagus officinalis L., crop evapotranspiration, rainfall deficiencies,
reference evapotranspiration, water requirements

Potrzeby wodne szparaga w różnych regionach Polski

Streszczenie

Szparagi (*Asparagus officinalis* L.), ze względu na swój głęboki oraz dobrze rozwinięty system korzeniowy, są roślinami uważanymi za stosunkowo odporne na niedobory wody w glebie. Z drugiej strony, rośliny szparagów uprawiane na glebie lekkiej bardzo pozytywnie reagują na przeprowadzone zabiegi nawadniające. Podstawowym celem niniejszej pracy było określenie potrzeb wodnych roślin szparagów w różnych regionach agro-klimatycznych Polski. Obliczenie zapotrzebowania roślin tego gatunku warzywnego na wodę, wyrażonego jako ewapotranspiracja potencjalna, wykonano na podstawie pomiarów opadów atmosferycznych przeprowadzonych w okresie trzydziestu lat licząc od 1981 do 2010 roku. Obliczenia wykonano dla dwóch miesięcy, dla lipca oraz dla sierpnia. Miesiące te stanowią okres krytyczny pod względem ilości wody dostępnej dla roślin. Potrzeby wodne roślin szparaga oszacowano przy użyciu współczynników roślinnych. Współczynniki roślinne dla roślin szparaga uprawianych w Polsce w warunkach polowych zostały ustalone przez Rolbieckiego w oparciu o długoterminowe obserwacje nawadnianych nasadzeń szparaga. Ewapotranspirację wskaźnikową obliczono zgodnie z metodą zaproponowaną przez Grabarczyka. Metoda Grabarczyka została wybrana do niniejszych badań, ponieważ pozwoliła ona na określenie ewapotranspiracji wskaźnikowej w uproszczony sposób, to znaczy tylko na podstawie pomiarów opadów atmosferycznych. Niedobory opadów zostały obliczone przy użyciu metody Ostromęckiego. Deficyt opadów w okresie od 1 lipca do 31 sierpnia obliczono, jako różnicę między potrzebami wodnymi roślin szparagów, wyrażonymi jako ewapotranspiracja potencjalna dla danego miesiąca, a sumą opadów atmosferycznych w tym miesiącu. Potrzeby wodne roślin szparaga określono dla pięciu różnych regionów agro-klimatycznych Polski wraz z reprezentatywnymi stacjami meteorologicznymi zlokalizowanymi na terenie Olsztyna, Bydgoszczy, Warszawy, Wrocławia i Krakowa. Największą zmienność potrzeb wodnych roślin szparaga obliczono w środkowo-północno-zachodnim (C-N-W) regionie Polski. Współczynnik zmienności w lipcu oraz w sierpniu wyniósł odpowiednio 7,7% i 7,6%. Natomiast najmniejszą zmienność potrzeb wodnych roślin szparaga stwierdzono w południowo-zachodnim (S-W), a także południowo-wschodnim (S-E) regionie Polski. Największe potrzeby wodne roślin szparagów, średnio 228 mm, w okresie od 1 lipca do 31 sierpnia, odnotowano w C-N-W, a także środkowo-wschodnim (C-E) regionie Polski. Największy deficyt opadów atmosferycznych, obliczony dla przeciętnie suchych lat, średnio suchych lat oraz bardzo suchych lat, wynosił odpowiednio 91 mm i 89 mm, 157 mm i 166 mm oraz 209 mm i 245 mm, odpowiednio w C-N-W i C-E regionie Polski. Podsumowując, większe niedobory opadów atmosferycznych odnotowano w sierpniu niż w lipcu.

Słowa kluczowe:
Asparagus officinalis L., niedobory opadów, potencjalna ewapotranspiracja, potrzeby wodne, wskaźnikowa ewapotranspiracja

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Determination of the Optimal Location of Sewage Sludge Installation for the Needs of Production of Fertilizer Products

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1. Introduction

The limited availability of natural resources and the needs of the economy and societies result in increased production costs and an increased demand for resources. The search for new sources of supply and the pressure associated with environmental protection caused an increase in the interest in products that partly lost their value − waste, by-products or secondary raw materials. This change is reflected in the new paradigm of management − a circular economy. The transformation towards the circular economy means that enterprises are increasingly implementing new technological solutions that would enable material, biological, raw or energetic recovery and use of values from defective products and closing the circulation of materials.

The essence of the circular model of the economy is to reduce the mass of waste produced while increasing their level of recovery. As a result, the waste is treated as a raw material for the implementation of current production and enabling the company's product range to be expanded by introducing new products obtained from waste to the market. The changing approach to the use of waste and by-products of industrial and domestic processes has led to the development of a specific group of entities involved in the process of closing the circulation, defined in other publications and papers as *Circular Economy Plants* (Barla et al. 2018). Their main goal is the transformation of waste generated from one industry to raw materials used by another. These objects therefore mediate and clear the material flows between the links of value chains. They apply the technology adapted to the selected type of recovery and operation in conditions of uncertainty resulting from the volatility of the supply stream of waste constituting the object of processing and the demand for recovery processes. Conducting operations under conditions of high uncertainty means that it is necessary to take a number of decisions covering both economic and environmental aspects that translate into competitiveness and profitability of operations. One of the key decisions in the functioning of such plants concerns logistics regarding the spatial configuration of the supply network, the participants of which will provide the necessary materials for their operations.

In Poland the management of sewage sludge especially in medium and small wastewater treatment plants is a significant problem and requires continuous activities. Furthermore, the problem of configuration of the logistics network for the optimization of activities in the circular economy is a new subject and relatively rarely discussed in literature, there is especially a lack of references (Jąderko 2018) concerning wastewater management and waste management such as sewage sludge.

The management of municipal sewage sludge depends on many factors, however, the key legal issues are the legal conditions that shape the activities of water and sewage companies. International (National Waste Management Plan 2022) and national (Directive 2008/98/EC on waste) conditions assume increased sludge recycling and their application in agriculture, horticulture, green areas and land reclamation processes. Sludge recycling technologies within the framework of organic recycling have many advantages, which include loss of waste status, possibility of storing fertilizer and free transport as well as generating an additional source of income for the company or obtaining an appropriate level of organic recycling. It should be emphasized that the implementation of such solutions should be justified from the technological and logistical point of view and correspond to the idea of sustainable development.

The issue of supply chain modelling for effective management of sewage sludge corresponding to the concept of circular economy is a complex issue including both logistics and environmental engineering (Jąderko and Białecka 2015, Dos Santos 2019, Jąderko 2018), which requires:

- analysis of material flows in the waste management system (Makarichi et al 2018),
- processing of data related to the operational activities of waste management plants (Burger et al 2018),
- eco-design of biological wastewater treatment technology (Zhao et al 2019), energy waste utilization technology (Simeone et al 2016),
- use of logistic models of configuration and management of the logistics network.

The development of an integrated decision model supporting network management processes is an important and current research problem, which requires conducting a number of research works and testing various variants of solutions. The conducted study of the subject literature showed the need to develop decision models in the selection of optimal locations for circular plants, the main purpose of which is to treat rainfall as a raw material (Jąderko and Białecka 2016). So far, the only criterion for selecting the location of waste management facilities was to minimize costs (Merkisz-Guranowska 2012) while environmental and logistic factors were treated as complementary. The increase of entrepreneurs' demand for raw materials and problems related to ensuring the efficiency of their processing systems, in particular configuration aspects for logistics systems of sediment management, causes the need to develop a solution based on a systemic approach, taking into account a multi-criteria analysis. The research problem formulated in this way is the starting point for the considerations presented in the article.

2. Methods

The centre of gravity method (Łupicka 2002) is a classical method used in logistics for pre-locating production and storage facilities. It was applied in the tests in order to determine the optimal location of sewage sludge installation. The basic assumption of the method makes it possible to indicate the best location of the facility, taking into account the geographical coordinates of supply sources, transport costs and the volume of the shipped cargo. It is basically very simple to apply, but it also leads to a number of disadvantages including issues with stativity. Nevertheless, it has a wide application in determining the base solution and is a starting point for its further improvement (Krawczyk 2001).

From the point of view of the conducted research, the determination of optimal locations for sewage sludge transformation facilities requires a holistic approach that takes into account the interaction of a number of related elements. The adoption of the logistic concept of land for waste management (including sewage sludge), including in particular optimization methods and tools, allows streamlining the management of material flows, in this case waste with the simultaneous effective involvement of resources and capital.

The purpose of the article was to develop a decision model for the selection of the optimal location of sewage sludge installation on the example of Silesia, Poland. The following works were carried out successively:

- identification of key elements of sewage sludge management system,
- analysis and quantitative-qualitative assessment of sewage sludge streams and other substrates necessary for the production of fertilizer granules,
- analysis of criteria excluding the selection of the installation location,
- gathering spatial data resulting from defined criteria,

- determination of the optimal location for the installation (using the method of determining optimal solutions for the location of objects − centre of gravity),
- analysis of the possibilities of technology adaptation in the analysed region.

The decision-making model developed on the basis of the presented research stages, taking into account the optimization of the installation location, allowed to include technological and logistical, ecological, infrastructural, economic-legal and social criteria as part of the planning process of the circular economy plant location.

3. Identification of key system elements

The stabilized municipal sewage sludge (waste code 19 08 05) is created in wastewater treatment plants. Their quantity and quality depend on the content of pollutants in sewage, the technology adopted and implemented, and the degree of decomposition of organic substances in the process of so-called stabilization.

At present, the dominant trend for the management of municipal sewage sludge is the use (according to data: Local Data Bank, data for 2017):

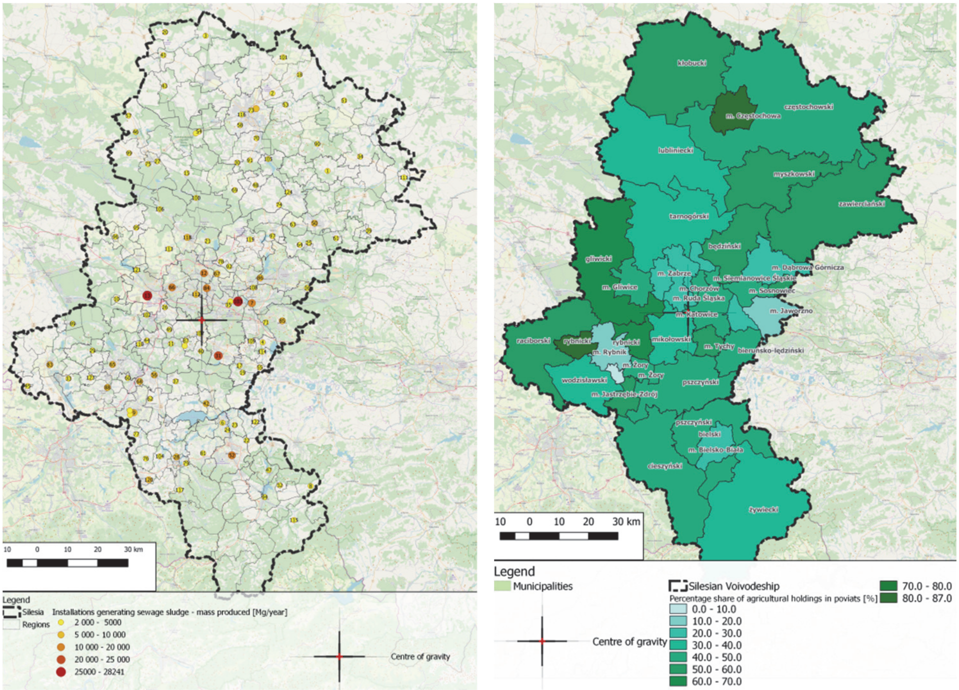
- in agriculture: 2 513 Mg s.m.,
- for the reclamation of land, including land for agricultural purposes: 2 482 Mg s.m.,
- for growing plants intended for the production of compost: 5 322 Mg s.m.,
- by thermal transformation: 5 428 Mg s.m.,

and:

- are stored together: 64 Mg s.m.,
- and the remaining ones are accumulated in the treatment plant.

In Silesia, there are currently 26 (Voivodship reports on waste management 2017)waste recovery or disposal installations, including municipal sewage sludge. The inventory of sources of sewage sludge production constituting a potential source of supply has shown that in 2017 in Silesia, 340,315.24 Mg (64 039 Mg s.m.) of (Local Data Bank, data for 2017) municipal sewage sludge was generated (waste code 19 08 05). The mass of generated sewage sludge in Silesia compared to the total capacity of the waste management installation of this group of waste (265,576.62 Mg/year), confirms the necessity to increase the efficiency or implementation of technologies allowing sludge management.

The identification of key elements of the system allowed to indicate: (1) installations producing sewage sludge in Silesia as sources of technology for the production of organic fertilizers from sewage sludge (124 facilities included in the analysis) and (2) the share of agricultural holdings constituting the fertilizer market. Geographical data is presented in Figure 1.



(1) (2)

Fig. 1. (1) Installations generating sewage sludge (2) surface share of farms in Silesia
Source: Own elaboration

Using the centre of gravity method to determine the optimal location required the collection of spatial and quantitative data corresponding to individual waste holders. The collected data made it possible to adapt the designs to a specific group of materials – waste, and allowed to determine the geographical coordinates for the optimal location of the sludge treatment plant in organic fertilizers.

The optimal location was determined according to the following formula:

$$\boldsymbol{X}^* = \frac{\sum_{i=1}^{I} M_i X_i}{\sum_{i=1}^{I} M_i} \tag{1}$$

$$\boldsymbol{Y}^* = \frac{\sum_{i=1}^{I} M_i Y_i}{\sum_{i=1}^{I} M_i} \tag{2}$$

where:
(Xi, Yi) − coordinates of the i-th source of sewage sludge − waste holder
Mi − the mass of generated sediments from the i-th source of sewage sludge − waste holder.

Table 1 Data summary
Source: Own elaboration

Ite m	Waste holder (*)	Mass of generated waste [Mg]	Geographical coordinates	
			X	Y
1	Rejonowe Przedsiębiorstwo Wodociągów i Kanalizacji S.A.	16756.51	50.2603059	19.13713299999995
2	Jastrzębski Zakład Wodociągów i Kanalizacji S.A.	8,145	49.94133730000001	18.602509499999996
3	Przedsiębiorstwo Wodociągów i Kanalizacji Sp. z o.o.	28240.92	50.281858	18.66275189999999
…	….	…	…	…
124	Waste holder no. 124	M_{124}	X_{124}	Y_{124}

(*) due to the wide range of data, selected items developed for the needs of database research were presented

4. Results and discussion

Considering the necessity to include the spatial mapping of the studied area, where the installation will eventually be created, the spatial layers should contain the following thematic maps to select a group of proposed location options for the implementation of technology, including the administrative map of the region; topographic map; hydrological map; road network map; map of residential buildings; map of protected areas; map of sources of supply of substrates necessary for the production of fertilizers from sewage sludge.

According to the adopted methodology and the centre of gravity method applied, the optimal location of sewage sludge installation for the production of fertilizer products is Mikołów (geographical coordinates: 50,21057311; 18,90949076). The point determining the optimal location has been presented on the map.

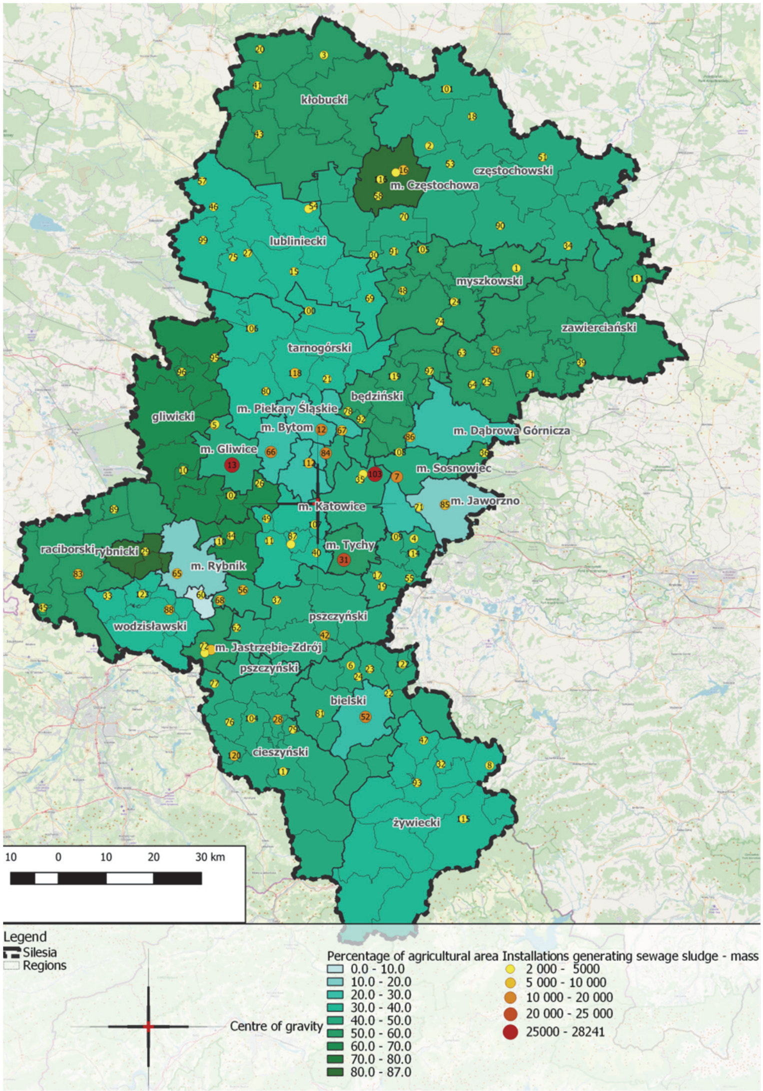


Fig. 2. Optimal installation location
Source: Own elaboration

The optimal location of the installation has also been presented on the thematic maps, which are the main determinants of choosing the best solution and exclusion criteria. It should be emphasized that the centre of gravity method presents the predisposed area for the construction of the facility or implementation of the installation, however, making a final decision requires detailed analyses allowing to determine a set of location variants as starting points for further research. An important advantage of the method used is the possibility of including the distance to the collection points of waste, which from the point of view of both economic and ecological issues is one of the key selection criteria.

(1) (2)

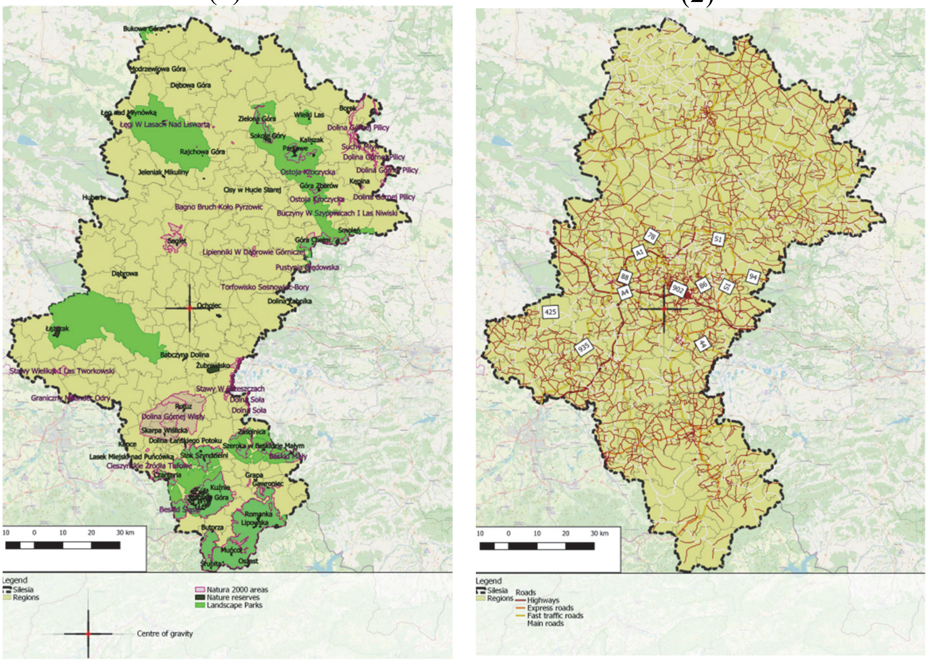


Fig. 3a. (1) Protected areas, (2) Road network
Source: Own elaboration

(3) (4)

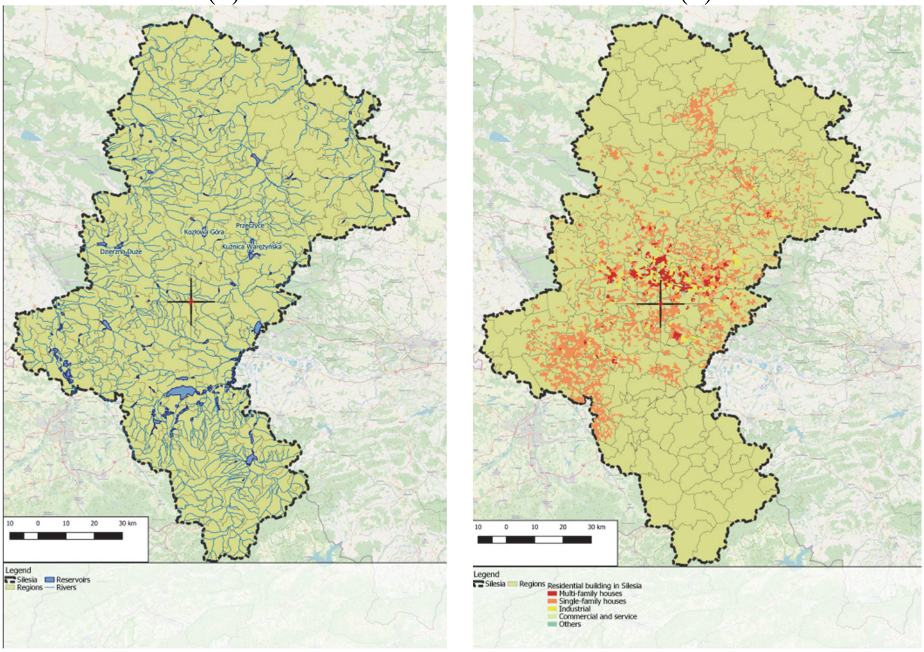


Fig. 3b. (3) Hydrographic network, (4) Residential building in Silesia
Source: Own elaboration

In terms of the spatial data analysed, the designated centre of gravity is characterized by the following geographical features:

1. The owner of the waste (supplier)
   - The owner of the waste (supplier) nearest to the place is Zakład Inżynierii Miejskiej Sp. z o.o. in Mikołów (6.3 km from the designated point). Importantly, the designated point is located between the largest producers of sewage sludge – Katowickie Wodociągi S.A. producing over 27 thousand Mg of sediment (about 19 km from the point), Regionalne Centrum Gospodarki Wodno-Ściekowej S.A. in Tychy, which produces over 22 thousand Mg of sediment (about 16 km from the point) and Przedsiębiorstwo Wodociągów i Kanalizacji in Gliwice, generating annually over 28 thousand Mg sediments (about 28 km from the point).
2. Agricultural holdings (recipient)
   - the centre of gravity is located in the Mikołów region, where the percentage of farms is 30-40%.

3. Areas of residential and industrial development
   - the designated point is located approximately 1.6 km from single-family buildings and 1.3 km from industrial areas.
4. Hydrographic network
   - the designated point is located approximately 800 m from the Stragniec water reservoir.
5. Recreation area
   - the designated point is located approximately 800 m from the holiday resort Stragniec.
6. Forms of nature protection
   - the closest reserve − Ochojec, located approximately 6.26 km from the designated point,
   - the nearest landscape park − Cistercian Landscape Compositions Rudy located approximately 13.08 km from the designated point,
   - the nearest protected landscape area − the Bujaków Stream, including the tributaries, located approximately 9.61 km from the designated point,
   - the closest nature and landscape complex − the Jamno Valley, located approximately 0.87 km from the designated point,
   - NATURA 2000 Special Protection Areas − Ponds in Brzeszcze PLB120009 located approximately 23.57 km from the designated point,
   - NATURA 2000 Special Protection Areas − Podziemia Tarnogórsko-Bytomskie PLH240003 located approximately 19.36 km from the designated point,
7. Post-mining areas
   - the designated point is located approximately 1 km from Hałda Panewnicka.

The presented outline of the terrain characteristics allows to define those elements that may affect the exclusion of selected areas, such as the close location of recreation and housing areas and valuable natural areas − the natural and landscape complex of the Jamno Valley.

In order to determine the full balance of the key components of the sludge management system (suppliers − sludge owners, producers/distributors of other substrates and fertilizer users), it is necessary to identify potential location options around the designated centre of gravity. This will allow taking into account relevant transport rates that are important from the point of view of profitability analysis.

The development of a full model of the optimization of the location of installations for processing sewage sludge with the desired level of detail is connected with a detailed analysis of determinants affecting the effectiveness of the implementation of the solution. The following factors can be included:

- **Infrastructural**, including the space for the construction of the facility along with the accessibility of access roads and other infrastructure elements that are related to securing the construction and supply of necessary utilities.
- **Social**, which consists of both the possibilities of providing human resources as well as social acceptance related to the implementation of projects that may significantly affect the environment.
- **Ecological**, which covers all elements related to environmental resources that strongly affect and which may be affected by the construction of the installation.
- **Economic and legal**, which regulate all legal issues and provide indicators of economic effectiveness of investments, which allow to determine whether the investment is justified from the point of view of its profitability.
- **Logistics and technology** – including the spatial characteristics of the installation location and factors limiting the implementation of technologies that can significantly affect the environment, raw material potential of available sewage sludge streams taking into account the quantitative and qualitative characteristics (type and nature of – related to the source of supply, quantity and quality, availability, regularity , diversification of supplies depending on the season), location of other raw materials (fillers) necessary for the production of fertilizers, location of potential collection points for fertilizers. A set of technological indicators covering basic technological parameters, efficiency, recovery level, technological possibility of increasing recycling.

In the process of selecting the location of the installation, the centre of gravity method was used as an element supporting optimal object placement in space (Jąderko and Białecka 2016). The basis for the selection was the raw material potential of sources of supply – understood as the mass of produced sewage sludge. Due to the complexity of the sewage sludge management system and the multidimensionality of the criteria necessary for the analysis, key assumptions of the decision model were developed and presented in the form of an algorithm.

The general description of the structure of the decision model allows to clearly highlight the need for a comprehensive and systematic approach to the problem of selecting the optimal location variant. Based on recognized variables including technological parameters, logistics parameters, geographical coordinates and the raw material potential of sewage sludge, it is possible to network the waste flows and thus to create a comprehensive view of sewage sludge management system with an indication of real demand for the implementation of waste management installations.

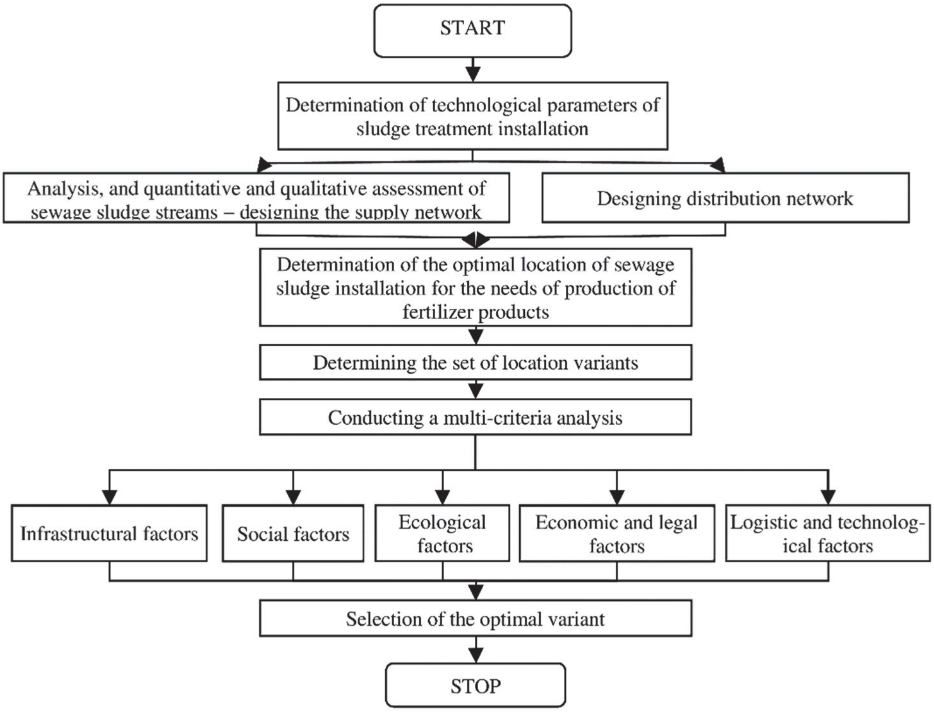


Fig. 4. Algorithm of the decision model
Source: Own elaboration

5. Conclusion

The centre of gravity method is one of the oldest and most frequently used methods to determine the location of objects. Due to the high degree of generalization in economic practice, it finds application primarily in the determination of location variants – predisposed areas. The determination of the base location by means of the said method can be included in the most important stages of the initial analysis, which will indicate the material potential of the designated area taking into account the mass of sewage sludge constituting the key substrate for the production of fertilizers. It should be emphasized, however, that the choice of location depends on a number of factors, hence another important step is to conduct a detailed multi-criteria analysis of the target location options.

Additionally, the decision model should be of a staged and procedural nature, including:

- analysis of areas predisposed for the construction of the installation together with the assessment of the impact on the environment;

- multi-criteria analysis along with its assessment (analysis of costs and benefits, eco-effectiveness, social and economic effects of investments);
- impact on competitiveness, growth and employment.

Spatial data included in the process of determining the optimal location allows for a comprehensive approach to the research problem only when a multi-criteria analysis is carried out including the assessment of factors excluding construction of the location (e.g. close proximity to valuable natural areas and residential areas). An especially important aspect in the perspective shape of the decision model for the selection of the optimal location of sewage sludge installation is to ensure the possibility of simulating the efficiency of the fertilizer sludge production process taking into account the quality properties of sediments supplied from various sources. This approach will enable the development of a universal model that is part of a comprehensive decision support system related to the objectives of the circular economy.

The study was carried out in the Department of Water Protection of the Central Mining Institute in Katowice, within the framework of the statutory work of the Ministry of Science and Higher Education.

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Abstract

The objective of this article was to develop a structure of a decision-making model for selection of optimal locations of sewage sludge installation on the example of the Silesian Voivodeship. Selection of locations for waste treatment facilities belongs to complex multicriteria decision-making problems.

Taking into account the problems of modelling the supply network for the effective management of sewage sludge corresponding to the concept of circular economy, the paper presents the application of the centre of gravity method for determining the optimal locations for the sewage sludge treatment plant based on the fertilizer production process.

The research carried out for the purpose of this study included identification of key elements of the sewage sludge management system, analysis and quantitative and qualitative assessment of sewage sludge streams, analysis of criteria excluding the selection of installation locations, gathering spatial data resulting from defined criteria, determination of optimal location for installations (using the method of determining optimal solutions for the location of objects – the centre of gravity method). All spatial data are presented on thematic maps prepared with the use of QGIS software.

The result of the research is a description of the decision-making model structure based on optimization of installation location and including technological and logistic, ecological, infrastructural, economic and legal and social criteria in the process of planning the location of a circular economy plant.

Keywords:
waste logistics, sewage sludge, circular economy, decision support, centre of gravity method

Wyznaczenia optymalnej lokalizacji instalacji zagospodarowania osadów ściekowych na potrzeby produkcji produktów nawozowych

Streszczenie

Celem artykułu było opracowanie struktury modelu decyzyjnego dla wyboru optymalnej lokalizacji instalacji zagospodarowania osadów ściekowych na przykładzie województwa śląskiego. Wybór lokalizacji dla obiektów przetwarzania odpadów należy do złożonych wielokryterialnych problemów decyzyjnych.

Biorąc pod uwagę problematykę modelowania sieci dostaw dla efektywnego zagospodarowania osadów ściekowych odpowiadających koncepcji gospodarki obiegu zamkniętego w artykule przedstawiono zastosowanie metody środka ciężkości dla wyznaczania optymalnej lokalizacji dla zakładu przekształcania osadów ściekowych w nawozy.

Przeprowadzone na potrzeby niniejszej pracy badania obejmowały m.in. identyfikację kluczowych elementów systemu zagospodarowania osadów ściekowych, analizę i ocenę ilościowo-jakościową strumieni osadów ściekowych, analizę kryteriów wykluczających wybór lokalizacji instalacji, zgromadzenie danych przestrzennych wynikających ze zdefiniowanych kryteriów, określenie optymalnej lokalizacji dla instalacji (z wykorzystaniem metody wyznaczania optymalnych rozwiązań dla lokalizacji obiektów – metody środka ciężkości). Wszystkie dane przestrzenne zostały przedstawione na mapach tematycznych opracowanych wykorzystaniem oprogramowania QGIS.

Opracowany na podstawie prac badawczych opis struktury modelu decyzyjnego uwzględniający optymalizację lokalizacji instalacji pozwolił na uwzględnienie kryteriów technologiczno-logistycznych, ekologicznych, infrastrukturalnych, ekonomiczno-prawnych oraz społecznych w ramach procesu planowania lokalizacji zakładu gospodarki cyrkularnej.

Słowa kluczowe:
logistyka odpadów, osady ściekowe, gospoda obiegu zamkniętego,
wspomaganie decyzji, metoda środka ciężkości

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Method of Formation of Thermophysical Properties of Porous Materials

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1. Introduction

Investigation and control of the processes of structure formation of materials are difficult tasks, which are still unsolved. Clear understanding of the mechanism of structure formation makes it possible to develop a methodological basis of new technologies, including the technology of production of thermal insulating materials with predictable thermal properties.

However, the ways of formation physical properties of the material were not found. A lot of experimental data show the relationship between the porosity of the material and its thermal properties (Pavlenko & Koshlak, 2015, Nimmo, 2004, Shpac et al., 2005). It is obvious that the structure of the materials, in particular the porosity, determines their properties. But in the mentioned works this impact is shown in different ways. For example, in the (Shpac et al., 2005) the thermal conductivity of Fe (58.19 W/(m · K)) and of clay (3.26 W/(m · K)) differ by 18, but the thermal conductivity of insulation structures, which are made from granules of Fe and granules of clay with the same porosity are almost equal – 0.0403 W/(m · K) and 0.0402 W/(m · K). Such results show that not only porosity, but also size and shape of the pores affect the properties of the material. Since any material has an own characteristic distribution of the pore size, it is obvious that various researchers obtained conflicting information about the nature of the influence of pore size on the thermal properties of these materials. Current technologies of structure formation do not provide the prediction of the geometric structure, which means that there is no possibility to predict the properties of materials.

2. Literature analysis and the problem statement

In (Pavlenko & Koshlak, 2015, Nimmo, 2004, Shpac et al, 2005, Shpac, et al., 2005, Freire-Gormaly, 2013) the dependence of the thermal properties of porous materials on a structure was discussed, but recommendations about optimal structure were not given. In (Eom, et al., 2013, Komissarchuk et al., 2014, Bajare et al., 2013) the dependence of the mechanical properties on a structure of porous materials was analyzed and recommendations about structure formation with predicted properties were given, but there was no information about the thermal properties.

In (Lopez-Pamies et al., 2012) the influence of internal pore pressure on closed-cell elastomeric foams was explored. Changes of internal pore pressure with different hydrostatic loads were

considered. Obtained results show that this pressure can significantly change macroscopic reaction and stability of closed-cell elastomeric foams. Also it shows that elastomeric foams with internal pore pressure have a higher stiffness, even with atmospheric pressure, than without it. But the method of calculating the internal pore pressure was not given. Also pressure was taken only as a function of density. In (Vesenjak et al., 2005) changes of the structure with a closed porosity under compression and extension, with different initial pressures in the pores, were researched. Experiment results show, that internal pressure has a positive effect under compression and negative under extension. The impact of deformation on the structures with closed porosity can lead to high initial pressure in the pores, which increases the total energy absorption and stiffness of the material under the process of deformation. But nothing was said about the methods of achieving certain pressure in the pores of the material and its calculation.

In (Aboudi et al., 2013) the micromechanical analysis of the porous material with internal pressure in the pores was made, the polymer BX-265 was taken as experimental material. The influence of initial pore pressure on the predicted elongation of the sample and the influence of the applied load (with pressure in the pores and without it) on the predicted break of the sample were shown. But nothing was said about the calculation methods of internal pore pressure.

In (Pavlenko & Szkarowski, 2018) the dependencies of thermal characteristics from the structure of materials were compiled and the task of the controlled pore formation by adjustable heat treatment of the raw gel-like mixture was formulated. In (Pavlenko & Koshlak, 2017, Pavlenkoet al., 2019, Pavlenko, 2018) the main physicochemical formation processes of the gas-vapor area (pores) were analyzed, which were taken as a basis in this work.

All mentioned works have one main idea that materials structure affects their properties. But there are no practical recommendations about formation of specific material structure.

Above information cannot be generalized, because it's contradictory. That's why existing technologies of the thermal swelling (structure formation) can't give the required structure.

3. The purpose and objectives of the research

The purpose of this work is the research of regularities of gas-vapor phase formation in liquid mixtures, which are in a state of thermodynamic equilibrium. To achieve this purpose, next objectives must be solved:

– to simulate the condition of thermodynamic phase equilibrium in the liquid mixture to control the process of pore formation;
– to determine the energy parameters of the swelling process (the pressure of the pore former agent gas inside the closed spherical pore, the conditions of thermal balance);
– to determine the overheating temperature of the liquid mixture to assess the growth dynamics of the gas-vapor area;
– to research the growth dynamics of the gas-vapor phase (pores).

4. Materials and methods of research

Carrying out the practical research into raw mass, we added the chamotte clay or pure structural clay, the composition of which is shown in the table1.

The research was performed by the use of differential thermal analysis (DTA) of the thermal bloating process for the raw mixture.

Trails are performed at a constant rise of temperature with recording the temperature difference on the chart paper as a function of temperature. The result is a curve DTA (Fig. 1-4). At processing the experiment's results, the horizontal axis should be graded by temperature. According to the position of peak of the endothermic process, the temperature interval of phase transitions can be found.

Table 1. The chemical composition of fire-clay

No	Clay	The content of oxides, %									
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3	Lost on ignition
1	Structural clay	44.59 54.14	27.13-35.85	1.48-2.47	1.14-1.97	0.38-0.81	0.23-0.42	0.21-0.60	0.25-0.45	1.34-3.62	11.48-13.86
2	Chamotte clay	46.80	36.80	1.58	-	0.20	0.76	0.34	0.18	-	13.6

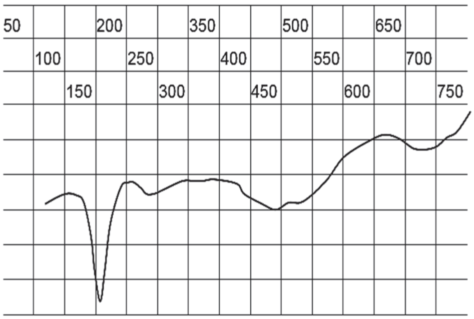

Fig. 1. DTA of raw material mixture with a content of 75 mass fractions of clay No. 1 (Table 1)

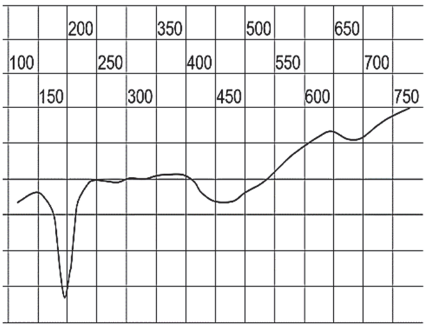

Fig. 2. DTA of raw material mixture with a content of 75 mass fractions of clay No. 2 (Table 1)

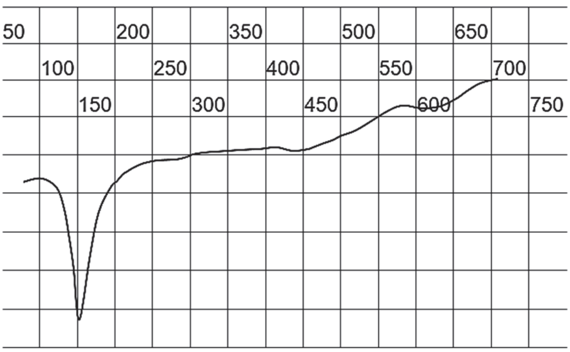

Fig. 3. DTA of raw material mixture with a content of 160 mass fractions of clay No. 1 (Table 1)

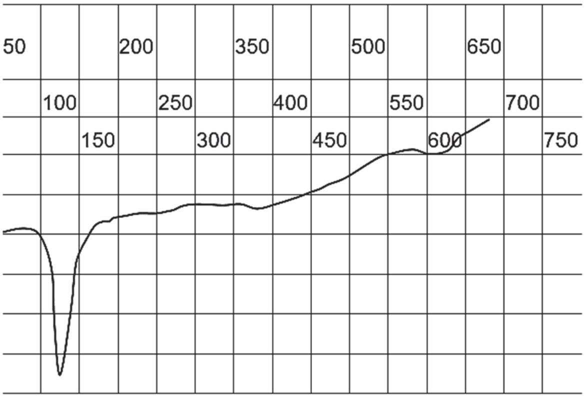

Fig. 4. DTA of raw material mixture with a content of 160 mass fractions of clay No. 2 (Table 1)

Changes, which had the place during the heating, showed three endothermic effects: 146, 450, and 720. A large endothermic effect due to the removal of absorbed water is at 146°C, and the observed step at 300°C on the curve says about removal of interpacket water. The second effect (450-550°C) corresponds to the removal of the constitutional water (bound into the form of OH). The endothermic effect at 720°C, it explains the removal of OH-ions. As it can be seen from the data chart, the optimum temperature range for dehydration of the mixture is within 146-720°C. It should be defined the connection of temperature intervals with the structure of bloated material, and, consequently, with the useful application properties (strength, conductivity, heat resistance, water absorption). For this, changing the composition of the initial mixture, the measurements were repeated under method presented above.

On the obtained DTA curves for all experimental samples in the investigated temperature intervals a number of phenomena associated with thermal effects is observed:

1) up to 100°C – evaporation of chemically unbound water;
2) 100...170°C – a sudden loss of mass and strongly expressed endothermic effect that is related to the partial dehydration of gel and phases of different composition;
3) 450...550°C – endothermic effect that corresponds to the decomposition of portlandite with water vapor emission;
4) 700...900°C – a minor loss of mass and weak endothermic effect, which is related to the decomposition of carbonate minerals (calcite, dolomite), and late-stage dehydration of gel and hydro aluminates.

The morphology and porosity of the samples were determined by optical methods. According to this method, the macroscopic parameters of porosity inside metric interval with a lower bound of 10 µm and upper bound of 5 mm are determined. The specified interval characterizes the strength parameters of the substance and parameters of heat and mass transfer.

The characteristic feature of the obtained data is that graphs for different types of clay are almost the same. Significant differences are in reading for different temperature minimums. So, for the first endothermic minimum, we received the bloated material with small and almost spherical pores (Bajare et al., 2013, Lopez-Pamies, 2012). Most of them had a minimum size. The bloating of the raw material mixture in the second endothermic minimum provides a mixed porosity (spherical cellular and channel). The material becomes less solid. When there is bloating in the conditions of the third endothermic minimum the channel porosity is mainly formed. This material has the lowest strength. You should expect the reducing in thermal conductivity with increasing temperature of bloating.

The obtained material has a low thermal conductivity even at temperatures of 1000-1200°C (Fig. 1). The thermal conductivity of the material was determined by thermal conductivity meter IT – λ – 400. Samples with a cylindrical form (height 5 mm, diameter 15 mm) were put inside the meter and were processed by temperature influence from 200 to 700°C. In this temperature range, the thermal conductivity of the material was determined according to the standard method, which is described in the device manual.

Fig. 5 shows the experimental dependence of thermal conductivity on the temperature of the material, for technologies of which the main technological stages were simulated.

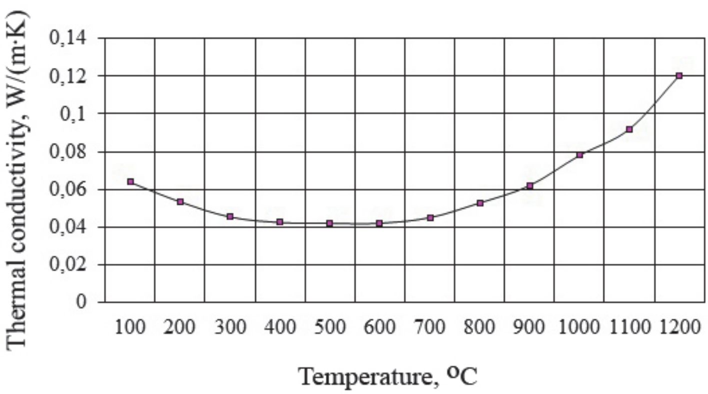

Fig. 5. Dependence of thermal conductivity on the temperature

5. Equilibrium conditions of the pore agent in the material, during the formation of the porous structure

As the dynamic characteristic, which determines the direction of size changes in vapor pore, tension difference was taken, which was caused by the pressure in the vapor area and by the resistance of the boundary surface of the pore. The equation, which characterizes the dynamics of growth or reduction of the vapor bubble (Pavlenko & Szkarowski, 2018).

$$\frac{dw}{d\tau}=-\frac{1,5\rho w^2+P_г-P_n(T)}{\rho_г R}=-\frac{1,5\rho w^2}{\rho_г R}+\frac{P_n(T)-P_г}{\rho_г R}. \quad (1)$$

where:
w – speed of growth of the vapor bubble,
τ – time of bubble growth,
ρ – density,
$P_г$ – pressure inside the vapor area,
P_n – pressure in the surrounding liquid,
T – temperature,
R– radius of the vapor bubble.

Increasing, decreasing and stabilization of the bubble sizes can be represented by three cases:

$$\begin{cases} w=\dfrac{\alpha\left[\left(w_0-\alpha\right)e^{-\frac{1,5\rho\tau}{\rho_г R}}+w_0+\alpha\right]}{w_0+\alpha-\left(w_0-\alpha\right)e^{-\frac{1,5\rho\tau}{\rho_г R}}} ;\alpha=\sqrt{\dfrac{P_n(T)-P_г}{1,5\rho}};\dfrac{P_n(T)-P_г}{1,5\rho}\succ 0, \\ w=\dfrac{\sqrt{\left|\dfrac{1,5\rho}{P_n(T)-P_г}\right|}w_0-tg\dfrac{1,5\rho\tau}{\rho_г R}}{\sqrt{\left|\dfrac{1,5\rho}{P_n(T)-P_г}\right|}+\left|\dfrac{1,5\rho}{P_n(T)-P_г}\right|w_0 tg\dfrac{1,5\rho\tau}{\rho_г R}};\quad \dfrac{P_n(T)-P_г}{1,5\rho}\prec 0, \\ w=\dfrac{w_0\rho_г R}{1,5\rho w_0\tau-\rho_г R};\qquad P_n(T)-P_г=0. \end{cases} \quad (2)$$

In the last case, when $P_n(T) - P_г = 0$,– the gas-vapor area (pore) doesn't change in volume. In the technological aspect, relations between energetic parameters, which characterize the predicted pore size (average), were achieved. Therefore, thermophysical parameters also were achieved, including thermal conductivity.

The equation for finding the speed of size changing of the pore, can be written as:

$$\frac{dR}{d\tau} = \frac{w_0 \rho_г R}{1{,}5 \rho w_0 \tau - \rho_г R}. \tag{3}$$

w_0 – the initial velocity of the boundary of the vapor region (accept 1).

When solving the equation (3), duration of the swelling process can be found. Since the average value of the pore size is one of the main factors, which determine thermophysical properties of the sample, it this method gives a chance to predict the discussed properties (Fig. 6).

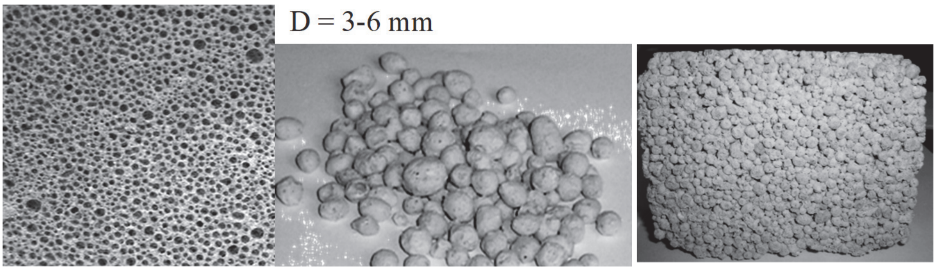

Fig. 6. New materials for thermal protection of buildings

6. Conclusions

The solution of creating new porous thermal insulation materials and technologies of their production is inextricably related to scientific research in energy transferring of porous structure during the stages of bloating, hardening and drying under the condition of providing the lowest thermal conductivity and density.

The indicated material properties are determined by a rate of their porosity, the ratio of micro and macro porosities, properties of interporous material that form a kind of supporting structure, which in its turn is determined by the production technology, type of raw materials and conditions of their preparation. All mentioned above impose the special requirements to the formation of material structure to ensure its relatively high strength and durability.

With the help of differential thermal analysis, the modes of heat treatment have been studied; the rational parameters of thermal bloating has been defined that allows to implement the process with minimal energy consumption and the predicted thermal properties of obtained materials.

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Abstract

The study of the porosity of thermal insulation made of refractory materials is an important task for the power industry, since the thermal conductivity of porous materials depends on the shape and especially the location of the pores.

An analytical review of existing technologies shows that research in this area is not enough to simulate the process of heat and mass transfer in porous alumina material. Experimental determination of the characteristics of heat and mass transfer in porous materials during the formation of a porous structure is a pressing scientific problem.

This article analyzes the influence of the composition of materials on the formation of pores, as well as the effect of various impurities and temperature on the thermal conductivity of the material.

Keywords:
porous materials, composite insulation materials, alkaline silicate, thermal bloating

Metoda formowania właściwości termofizycznych materiałów porowatych

Streszczenie

Porowatość izolacji termicznej wykonanej z materiałów ogniotrwałych jest ważnym zadaniem dla energetyki, ponieważ przewodność cieplna materiałów porowatych zależy od kształtu, a zwłaszcza od lokalizacji porów.

Analiza analityczna istniejących technologii pokazuje, że badania w tej dziedzinie nie są wystarczające do symulacji procesu przenoszenia ciepła i masy w porowatym materiale z tlenku glinu. Eksperymentalne określenie charakterystyki transferu ciepła i masy w materiałach porowatych podczas tworzenia struktury porowatej jest palącym problemem naukowym.

W artykule przeanalizowano wpływ składu materiałów na powstawanie porów, a także wpływ różnych zanieczyszczeń i temperatury na przewodność cieplną materiału.

Słowa kluczowe:
materiały porowate, kompozytowe materiały termoizolacyjne, krzemiany alkaliczne, termiczne wzdęcia

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Current Status and Possibilities of Implementing Green Walls for Adaptation to Climate Change of Urban Areas on the Example of Krakow

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1. Introduction

Extreme weather conditions such as: high temperatures, heat waves, torrential and heavy rains, strong winds or floods are increasingly frequent symptoms of climate change. As predicted by climatologists, they would keep occurring more and more often and their intensity would increase. Expansion of the cities resulting in a continuous annexation of biologically active areas under housing developments, parking lots, recreation and educational centers, shopping centers etc. is considered as the main cause of climate change. By 2050, almost 70% of the world's population (around 6.4 billion people) is to live in cities and urban areas, meaning that the number of city dwellers will almost double (International Organization for Migration 2015). Modifications of the climate, caused by urbanization and industrialization, become the topic of concern mainly because of increased air pollution, radiation (changes in components of a radiation balance), thermal and humidity conditions, air circulation (change of direction and speed of wind) and precipitation.

Each city faces particular climate threats, specific to its structure and conditions, e.g. high temperatures (a regular increase of the average annual temperature is observed, e.g. by 1.2°C in the period 1951-2010), volatile rains (increase of annual rainfall by 10-15%). Climate changes cause also water deficit and a development of invasive species, which pose a threat to human health. The higher number of illnesses is also associated with i.e. heat waves – the results of Polish research show an increase of mortality by 18% due to cardiovascular diseases, as a result of extremely high temperatures (Institute of Environmental Protection – National Research Institute 2017).

Since 1850, 13 out of the 14 warmest years fall on the 21st century and each of the last three decades has been warmer than the previous one (World Meteorological Organization 2014). Flooding and floods are the biggest threats to the agglomeration. They pose a great danger not only directly to residents' property, but also cause severe economic losses, e.g. during a temporary interruption of a production process.

Cities are an unique kind of ecosystem where people, infrastructure and nature should co-exist in a harmony. The challenge, however, is to direct the city development so as it positively impacts all areas of life, including the quality of the natural environment. The main strategic activities for cities should be included in plans for their spatial development. The plans should underline the need to increase green areas and waterways as well as ventilation corridors. Urban adaptation plans should take into account rainwater management and higher retention.

In the era of modern cities, sustainable spatial planning becomes a considerable challenge for urban planners. The need to adapt existing urban areas to climate change is also not an easy task. This is particularly difficult in historic city centers, where implementation of many technical solutions is very much limited. Adaptation of cities to climate change, and in particular to its effects, is described in (Ministry of the Environment 2014) as a stronger resilience of society and the economy to negative effects of current and anticipated climate change. The document (The Intergovernmental Panel on Climate Change IPCC 2014) defines adaptation as the process of adjustment to actual or expected climate and its effects. In Poland, the first strategic document on the issue of adaptation to climate change was the “Strategic adaptation plan for sectors and areas sensitive to climate change by 2020 with the perspective of 2030” (so-called SPA 2030), developed on the basis of the KLIMADA research project (Ministry of the Environment 2014).

One of the proposed solutions for adapting cities to climate change is introduction of various forms of green infrastructure. Water and greenery, so called blue and green infrastructure, perfectly fit into the urban space; it deals with adverse symptoms of climate change in a very positive way, based on the forces of nature.

The source (Ministry of the Environment 2015) gives an example how the area at risk of urban flooding can adapt to climate change by namely growing green infrastructures, especially green roofs and walls. This is a "win-win" option, which means that additional social, ecological or economic benefits are also obtained in mitigating the effects of climate change (Ministry of the Environment 2015).

Green roofs have been a topic of research and numerous scientific studies for many years. In the scientific literature (Perini & Rosaco 2013, Sheweka & Magdy 2011, Djedjig et al. 2017) one can also find studies on living walls, although this topic is not as popular as green roofs. Designing of green roofs on the existing buildings in the urbanized area is not an easy task since it has to consider e.g. the strength of the building's structure. It should be noted that since there is less horizontal surfaces in the city than vertical ones and since the green wall can also be installed on fences or screens – there is a great potential for placing them in public places. Linear or pocket parks, that have been recently popular, are a good example how green walls can find their place in the city space.

The paper analyses the role of green walls in the adaptation of urban space to climate change. The authors developed a map of locations of this type of green infrastructure in the city to indicate potential sites for new plantings.

2. Definition of green walls

There are many definitions of green walls in the technical literature and scientific studies. There are also various definitions of vertically grown vegetation. These include names such as: green facades, living walls and vertical gardens. For example, according to (City Council of Wrocław 2015), a vertical garden is an installation with perennial plants located on the substrates enabling their multi-season vegetation. According to (Future Cities Adaptation Compass 2018), the green wall is a wall covered with vegetation. It should be noted that the term "wall" can mean a wall made from bricks or stones or a fence. According to (Kania et al. 2013), the term "vertical plants" can refer to both walls covered with vines planted in the ground, as well as plants mounted vertically in special constructions. Usually, the authors explain the definition to which they refer in their work. Terminology needs to be further thought out and organized in this respect, but such approach requires a broad scientific discussion and consultation or even adopting a legal act (standard).

The authors suggest that all kinds of vertical structures and partitions covered with vegetation should be treated as green walls. This type of construction can include building walls, various types of fences – stone walls, fences or wire mash fences, as well as noise barriers, trusses, frames, balustrades, retaining walls and shed walls. Also a special kind of green walls, where the plants are arranged vertically on an individual construction, is considered as a vertical garden. Among the accepted green walls concept, outdoor and indoor walls can be included.

In the paper, only outdoor walls are be considered, as they may be an important element of adaptation of the city to climate change. The outdoor green walls can be attached to a building structure or just free-standing (all fences, pergolas or screens). It should be added that there are also special racks, installed in such a way as to maintain a certain distance between plants and a building.

There are also hanging green walls, e.g. from balconies or billboards. They do not related in part to any surface. Another issue are lighting poles, trees or advertising poles covered with vegetation. In their case, green poles seems a more accurate term.

3. Role of green walls

Vertical gardens combine many functions and are a good practice in developing of an urban space. They are natural elements of the urban environment that have a positive impact on many aspects (Burszta-Adamiak 2015, Cahill 2012, Kania et al. 2013).

The importance of green walls for the design of urban space is also determined by the fact that proposal of technical standard for them can be found in the technical literature (Tedesco et al. 2016, Giordano et al. 2017).

Green walls create a healing environment and green plants accelerates a process of recovery for hospital patients (shorter hospital stay). They bring solace, improve well-being and create a healthy atmosphere in the room. Ailments, such as eye irritation, headaches, sore throat or fatigue are significantly reduced in these areas. In offices with a lot of greenery, a noticeable drop in absences caused by diseases has been observed.

Vertical gardens can provide an interesting decorative element, as well as hide old and ugly walls.

They compensate for green areas lost during city development and introduce vegetation to the city center, without taking up the land surface.

Green systems such as green facades or living walls may contribute to reduction of effects of the urban heat island and improve air quality (Perini & Rosaco 2013). As each greenery, they improve the air quality and therefore they are called "city lungs ". Plants located on green walls filter dust that fly in the air and convert CO_2 into oxygen.

Green walls are an excellent acoustic isolator. According to research (Azkorra et al. 2015), a weighted sound reduction index for the tested type of green wall was obtained at the level of 15 dB.

Green walls provide a thermal insulation of building facades, so electricity bills for air-conditioning can be much lower. They also help to eliminate negative effects of the urban heat island. A detailed literature review on these issues can be found in (Sheweka & Mohamed 2012). In turn, (Djedjig et al. 2017) describes an experiment carried out to understand the thermal and hydrological behavior of green walls.

Thanks to vertical gardens biodiversity in the environment is expanding; plants growing on green walls provide a perfect shelter for birds, butterflies and other insects.

In water management, blue-green infrastructures, including vertical gardens, are an important element of effective rainwater management in the city both in case of water excess or shortage. Green and blue infrastructures work closely together: vegetation is a biological reservoir of water while water is essential for a vegetation growth. In addition, plants that are one of the elements of the blue-green infrastructure, uptake a certain amount of water from the root zone and evaporate it into the air (evapotranspiration). Green walls, although to a limited extent, but play a role in managing rainwater in cities (Burszta-Adamiak 2015). They stop, among others, runoff water (Januchta-Szostak 2011).

Vertical gardens are a solution that reduces and slow down the outflow of rainwater to sewage systems. Too fast and sudden discharge to a sewage network is currently the most important problem of rainwater management in the cities.

Positive impact of vertical gardens on the urban environment may not be as important as green roofs, but assuming their use on a large scale – the effect may multiply.

4. Scope

The aim of the research was to find locations of green walls in the city of Krakow and then visually assess their spatial structure and density. On the basis of this data, areas for potential growing of green infrastructures in a selected settlement unit were identified.

The authors also created a map of green walls in Krakow along the main communication routes. The map is made up of spatial data in a digital form, as two vector layers linked with the city map.

5. Materials and methods

The research material comprised the map of Krakow and information obtained during a preliminary inventory of the Krakow's green walls.

Due to a large number of green walls in Krakow, the scope of work was limited only to the first, second and third ring around the city (existing sections) and to major roads and their immediate vicinity.

The first ring included the following streets: St. Idzi, Podzamcze, F. Straszewskiego, Podwale, J. Dunajewskiego, Basztowa, Westerplatte and St. Gertruda and their closest vicinity. The second ring comprised the streets: M. Konopnickiej from the Mateczny roundabout, the Alleys of Trzech Wieszczy, part of the Alley of 29 Listopada, W. Stwosza and A. Lubomirskiego, Powstania

Warszawskiego, Kotlarska, G. Herlinga-Grudzińskiego, S. Klimeckiego, Powstańców Wielkopolskich, the Alley of Powstańców Śląskich, part of H. Kamieńskiego up to the Mateczny roundabout. The third ring comprised: part of Armii Krajowej, street of J. Conrada from the Ofiar Katynia roundabout, streets: Opolska and Lublańska, the Alley of general T. Bór-Komorowski, streets of I. Stella-Sawickiego and Nowohucka. The remaining part of this ring is just planned and currently does not exist. The only exception is the section covering streets: Nowosądecka and W. Witosa, which was also included in the research.

In addition to the rings, some major city routes were also taken into account, including the streets: Mogilska, the Alley of Jan Paweł II, the streets R. Kuklińskiego – Lipska – J. Surzyckiego – Rybitwy – Ch. Botewa, the streets Młyńska and J. Meissnera, the Alley of 29 Listopada up to the general T. Rozwadowski overpass, Armii Krajowej, streets: S. Grota Roweckiego, M. Bobrzyńskiego – K. Bunscha, and also the Alley of Pokoju, the streets: H. Kamieńskiego and Wielicka (up to Nowosądecka) and their closest vicinity.

The map of Krakow's green walls has been completed on the basis of cartographic data from OpenStreetMap.org (Geofabrik 2018, OpenStreetMap 2018). In addition, the materials form the state geodetic and cartographic resources were used. The data from the state register of boundaries and the area of units of territorial divisions of the country were collected (Head Office of Geodesy and Cartography 2018). The map was developed using the QGIS program – version 2.4.0 (QGIS 2015).

New spatial data has been added to the map. Two vector layers in a form of points were created. The first layer corresponds to buildings (or other constructions) with green walls, the other one marks free-standing green walls, i.e. fences or acoustic screens. Each point is described by the list of specific features, including the ordinal number, the name of the street where the wall is located, the wall number (if there is more than one) and any other comments. Due to the use of two separate layers, it is possible to create two separate maps (with specific types of green walls) or one combined map.

Green walls attached to balustrades of terraces or balconies were classified as green walls of buildings. In the case of streets with a large number of screens, it was assumed that each sequence of screens with vegetation corresponds to one point on the map. When there were more screen sequences or gaps in between, then another point on the map was added with a corresponding annotation in the table of features. The maps do not include green walls at public transport stops.

The research was conducted for a long period of time and over different seasons. A photographic documentation was collected for the green walls, showing vegetation during both a growing and a resting season.

6. Discussion of results

In the studies, a relatively large number of external green walls was spotted along the streets in question (Fig. 1).

There were just a few plant species planted on the green walls, mainly ivy like, e.g. ivy and Boston ivy. However, a large variety of constructions on which vegetation occurred was observed. Creepers were found on noise barriers, wire mesh fences, fence walls, retaining walls, special racks, as well as billboards and street lamps. In the case of buildings, the plants also covered balustrades and balconies. Both evergreen and the plants losing leaves were represented. Figures 2 and 3 show a green wall during resting and vegetation periods. The plants that change color rather than flourish have been observed more often. On the other hand, there were no green outdoor walls in the public space, such as vertical gardens.

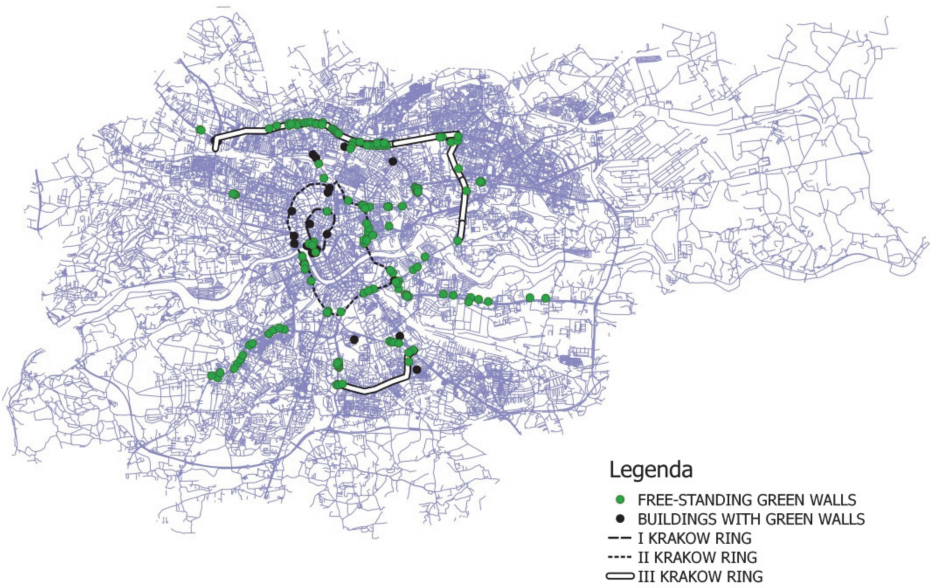

Fig. 1. Map with a location of green walls along the major routes in Krakow. Study based on own data and data from (Geofabrik 2018, Head Office of Geodesy and Cartography 2018, OpenStreetMap 2018)

Fig. 2. Green wall in a resting season (author's photo)

Fig. 3. Green wall in a vegetation season (author's photo)

Along the first ring (a sequence of streets surrounding the Old Town) vegetation can be found only on individual structures (walls, fences, screens) mainly in the south-western part of the area. There are also few vines on the walls of buildings. Green walls can be mainly found on many historic buildings located at the Wawel Hill. There are not many examples of green walls in this area, however there are other different forms of greenery e.g. Planty surrounding the Old Town and numerous gardens. Therefore, it does not seem necessary to set up new green walls, although each new plant in urban space generates additional environmental gains. The layout of the green walls along the first ring is shown in Figure 4.

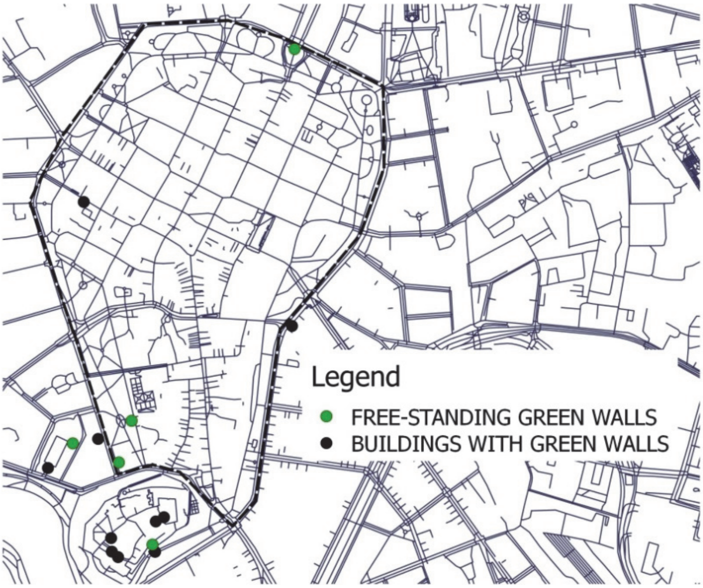

Fig. 4. Green walls along the first Krakow ring – Study based on own data and data from (Geofabrik 2018, Head Office of Geodesy and Cartography 2018, OpenStreetMap 2018)

The second ring is a series of city streets along which green walls can be seen. The green walls are placed quite evenly in fragments of this ring of roads, with an exception of the northern part. Almost every street in this district has green walls on buildings or as a detached structure. However, they are quite rare. The evergreen wall on the Mogilskie roundabout, incorporated into the historic fort ruins, deserves a special attention in this area. Figure 5 shows the city map with the green wall locations along the second ring.

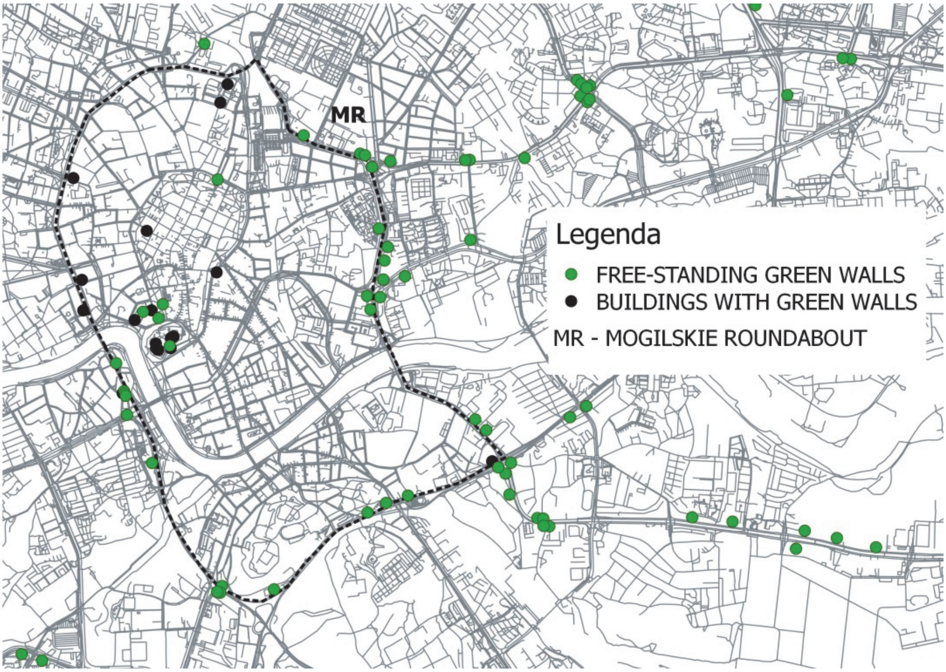

Fig. 5. Green walls along the second Krakow ring – Study based on own data and data from (Geofabrik 2018, Head Office of Geodesy and Cartography 2018, OpenStreetMap 2018)

It is therefore proposed to densify the existing green infrastructure, especially in the northern and north-western parts of the second ring road. The potential location of green walls in this area may be tenement houses along Słowackiego Avenue and Mickiewicza Avenue (if the condition of their facades is good). A characteristic feature of these buildings is the large facade surface. The buildings of technical universities (AGH University of Science and Technology, Cracow University of Technology, University of Agriculture) located in this area can also be a location for new green walls. It can be added that in the analysed region of the second Krakow ring there is greenery along the Avenues of the Three Poet – Prophets, but every new form of greenery in the built-up city center is important. In the south-west part of the second road ring, green walls can be introduced in the new housing estate on the Wilga River, while in the east and south part of the second beltway it is suggested to introduce vegetation on all existing sound absorbing screens. In addition, the city has already attempted to introduce green walls at public transport stops around the second ring road, but they were not included in the maps due to their very small size.

Among the existing sections of the third ring, a beautiful corridor of green walls along the Opolska Street can be noticed. The street has two roadways with three lanes in each direction. The roadways are separated by a green belt and partly by noise barriers. Vegetation covers noise barriers on both sides of each roadway. Another green walls (on screens and fences) are placed also along the next street (continuation of this section). The roads constitute the central part of the northern part of the third ring. Single screens are located in the north-eastern part of the ring and at both ends of the existing southern section. Moreover, single fences covered with vegetation were observed along the third ring.

A striking lack of greenery was observed on the western section of the northern ring. The green walls should be mainly considered in this area – for example on numerous shopping centers located in this area or their fences. The use of green walls should also be considered on the eastern section of the northern part of the ring, also with shopping centers. It is proposed to introduce green walls or green roofs for Krokus and Serenada shopping centers, Galeria Bronowice and a large furniture store located near the northern part of the third road ring. Along the eastern part of the third ring more green fences should be placed as well as more noise barriers covered with vegetation. It is also proposed to build green walls along the southern section of the third ring. Figure 6 shows the city map with the green wall locations along the third ring.

Among the more important communication routes, there are single green walls on fences or screens. Particularly noteworthy are sequences of screens planted with vines stretching from Kuklinski street to Botewa street and from Grot-Rowecki street to Bunsch street. It seems that the greening of all noise barriers along the city's main communication routes is the right direction. It is possible to try to encourage property owners along the city's major routes to introduce vegetation on theirs fences.

A worth mentioning cluster of green walls can be found around the University of Agriculture, where creepers are present on a long noise barrier, on the walls of a sports hall, and also on two fences, located nearby. Green walls are also present on several objects located at the campus of the Cracow University of Technology.

Fig. 6. Green walls along the third Krakow ring - Study based on own data and data from (Geofabrik 2018, Head Office of Geodesy and Cartography 2018, OpenStreetMap 2018)

7. Conclusions

Installation of green roofs on existing buildings is very limited due to strength of their construction. For this reason, it is extremely important to pay more attention to the issue of green walls in urban space.

The map of green walls along the most important communication routes in Krakow allowed to identify potential places for new plantings and to assess a spatial structure of green infrastructure. The spatial structure of the green walls is diverse in Krakow. In the entire city, it can be assumed that a spatial distribution of green walls associated with buildings or other structures is rather random and in some areas numerous structures can be observed (e.g. the Wawel Hill, the University of Agriculture and the campus of the Cracow University of Technology). Greenery growing on sound-absorbing screens along roads is arranged in a planned manner and its spatial structure can be treated as even (at selected street routes).

More than 140 green free-standing walls and nearly 30 such facilities attached to buildings or other structures were listed in the study. There is a large number of green walls in the city, but their density is not large, yet. There are many places that are potential locations for greening. Particular attention should be paid to shopping centers, as there are many ways to introduce this form of green infrastructure in their area. The sheds of public transport stops are also a space that can be developed through vegetation. It would be a very good solution, especially in the built-up city center. The green stops can be used especially where the implementation of green walls on other objects is difficult. It is advisable to introduce vegetation on all sound-absorbing screens. It is also worth considering the possibilities of persuading property owners to introduce greenery on fences along roads. In the discussion of the results, the areas for greening were suggested in detail, and the proposed specific locations of objects where it is worth considering the use of green walls.

Only if at a high density, greenery will help to overcome effects of climate change in the city. Creepers are the perfect plants for planting in cities. They produce green elevations, embellish buildings and isolate residents from traffic nuisances. They become green screens among the city's buildings.

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Abstract

Extreme weather events such as: high temperatures, heat waves, torrential and heavy rains, strong winds or floods are increasingly frequent symptoms of climate change. As predicted by climatologists, they would keep occurring more and more often and their intensity would increase. Flooding and floods are the biggest threats to the agglomeration. They pose a great danger not only directly to residents' property, but also cause severe economic losses, e.g. during a temporary interruption of a production process.

Adaptation to climate change can be supported not only by new technologies, but also by some trends in spatial planning, i.e. activities related to installation of green infrastructure throughout the city. Water and green perfectly fit into an urbanized space.

The article investigates how green walls can participate in adaptation of the city of Krakow to climate changes. The term of the green wall was also discussed and the own its definition was proposed.

The aim of the research was to find locations of green walls in the city of Krakow and then visually assess their spatial structure and density. On the basis of this data, areas for potential growing of green infrastructures in a selected settlement unit were identified.

The research material comprised the map of Krakow and information obtained during a preliminary inventory of the Krakow’s green walls. The map of Krakow's green walls has been completed on the basis of cartographic data from OpenStreetMap.org. In addition, the materials form the state geodetic and cartographic resources were used. The map was developed using the QGIS program – version 2.4.0.

The authors created a map of green walls in Krakow along the main communication routes. The map is made up of spatial data in a digital form, as two vector layers linked with the city map. There were just a few plant species planted on the green walls. However, a large variety of constructions on which vegetation occurred was observed.

The map of green walls along the most important communication routes in Krakow allowed to identify potential places for new plantings and to assess a spatial structure of green infrastructure.

There is a large number of green walls in the city, but their density is not large, yet. There are many places that are potential locations for greening. Particular attention should be paid to shopping centers, as there are many ways to introduce this form of green infrastructure in their area. Only if at a high density, greenery will help to overcome effects of climate change in the city.

Keywords:
rainwater, green infrastructure, green wall

Stan obecny i możliwości implementacji zielonych ścian w celu adaptacji do zmian klimatu terenów zurbanizowanych na przykładzie miasta Krakowa

Streszczenie

Ekstremalne zjawiska pogodowe takie jak okresy wysokich temperatur, fale upałów, ulewne i nawalne deszcze, silny wiatr czy powódź to coraz częściej występujące objawy zmian klimatu. Zgodnie z przewidywaniami klimatologów będą występowały częściej, a ich intensywność będzie wzrastać. Największym niebezpieczeństwem dla aglomeracji są podtopienia i powodzie. Mają one negatywny wpływ nie tylko na stan mienia mieszkańców, ale mogą także powodować dotkliwe straty gospodarcze, np. w postaci czasowych przerw w produkcji.

Adaptacji do zmian klimatu sprzyjają zarówno nowe technologie, jak i trendy w planowaniu przestrzennym takie jak działania związane z instalacją infrastruktury zielonej w mieście. Woda i zieleń doskonale wpisują się w zurbanizowaną przestrzeń miejską. W artykule przedstawiono stan obecny i możliwości implementacji zielonych ścian w celu adaptacji miasta Krakowa do zmian klimatu. Przedyskutowano także definicję zielonej ściany i zaproponowano własną.

Celem prowadzonych badań było określenie lokalizacji zielonych ścian na terenie miasta Krakowa oraz ocena wizualna struktury przestrzennej i zagęszczenia tego typu obiektów. Na tej podstawie określono obszary do potencjalnego zazielenienia tego typu formą zielonej infrastruktury w wybranej jednostce osadniczej.

Materiał do badań stanowiła mapa Krakowa oraz informacje pozyskane na podstawie prowadzonej wstępnej inwentaryzacji zielonych ścian Krakowa. Mapa zielonych ścian Krakowa została opracowana na podstawie danych kartograficznych pochodzących z OpenStreetMap.org. Ponadto do przygotowania mapy wykorzystano także materiały państwowego zasobu geodezyjnego i kartograficznego. Mapę opracowano z wykorzystaniem programu QGIS w wersji 2.4.0.

Określone cele osiągnięto poprzez stworzenie mapy zielonych ścian na terenie Krakowa wzdłuż głównych ciągów komunikacyjnych. Opracowana mapa stanowi dane przestrzenne w formie cyfrowej w postaci dwóch warstw wektorowych połączonych z mapą miasta. Gatunki stosowanych roślin wykazywały niewielkie zróżnicowanie. Zaobserwowano natomiast dużą różnorodność konstrukcji, na których występowała roślinność. Analiza opracowanej mapy lokalizacji zielonych ścian wzdłuż ważniejszych ciągów komunikacyjnych Krakowa pozwoliła na wskazanie potencjalnych miejsc dla nowych nasadzeń oraz ocenę struktury przestrzennej tego typu formy zielonej infrastruktury.

W mieście występuje duża liczba zielonych ścian, ale ich zagęszczenie nie jest jeszcze duże. Istnieje wiele miejsc będących potencjalnymi lokalizacjami do zazielenienia. Szczególną uwagę należy zwrócić na centra handlowe., gdyż w ich okolicy istnieje wiele możliwości do wprowadzenia tej formy zielonej infrastruktury. Zieleń w mieście pozwoli na uzyskanie niwelacji skutków zmian klimatu dopiero przy dużym jej zagęszczeniu.

Słowa kluczowe:
woda deszczowa, zielona infrastruktura, zielona ściana

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Selected Biological Properties of the Soil in a Burnt-Out Area under Old Pine Trees Three Years after an Fire

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1. Introduction

Fires, on account of their emotional, economic and cognitive aspects, are of interest to numerous researchers, and their impact is often unpredictable and difficult to investigate. They are among some of the most dynamic factors shaping terrestrial ecosystems (e.g. Bowman et al. 2009). They destroy vegetation and alter the physicochemical and biological properties of soils (e.g. Hauke-Pacewiczowa and Trzcińska 1980, Querner et al. 2010), including those of forest soils (e.g. Certini 2005). They affect the hydrological and thermal properties of the soil, the rate of mineralization, circulation of nutrients, and accelerate soil erosion (e.g. Certini 2005, Köster et al. 2011, Hewelke et al. 2018).

Under the influence of fires, not only vegetation but also litter and the organic soil layer are destroyed (e.g. Certini 2005). Fires affect living organisms directly (causing their death) and indirectly, transforming their living environment (affecting food availability and quality, heterogeneity of the environment, pH increase, etc.) (e.g. Kim and Jung 2008).

Fires significantly influence the abundance of microorganisms and taxonomic biodiversity of bacteria and fungi (e.g. Dooley and Tresender 2012, Knelman et al. 2015), and soil animals, such as springtails and mites (Wikars and Schimmel 2001, Kim and Jung 2008, Malmström et al. 2009).

Soil mesofauna, including springtails and mites, is an important element of the trophic network of every ecosystem, especially forest soils (e.g. Petersen and Luxton 1982, Carrillo et al. 2011). The animals of the mesofauna affect the development and spreading of microorganisms (bacteria and fungi) (e.g. Wallwork 1983, Tiunov and Scheu 2005) and thereby indirectly influence the processes of decomposition of dead organic matter, thus affecting the circulation of nutrients (e.g. Seastedt 1984, Carrillo et al. 2011). The interdependencies between the decomposition processes resulting from the activity of microorganisms, mesofauna and vegetation are the basis for the functioning of ecosystems (e.g. Van der Putten et al. 2001, Eisenhauer and Schadler 2011).

The impact of a fire is manifold, being dependent on, among other things, its intensity, the time of year it occurs, and the incidence rate (Querner et al. 2010, Gongalsky et al. 2012). The fire itself is controlled by many factors, such as the type and moisture content of the fuel, temperature and humidity of the air, wind speed, and the topography of the terrain (Certini 2005). Like the effects of a fire, the restoration of ecosystems after a fire is also influenced by the intensity and frequency of fires, weather conditions, vegetation type, and the physicochemical and biological properties of the soil (e.g. Malmström et al. 2008, Malmström 2010).

It is believed that the restoration of communities of soil organisms takes 2-7 years (e.g Huta et al 1967, Malmström et al. 2008, Kim and Jung 2008, Saifutdinov et al. 2018), and even longer (Malmström 2012, Auclerc et al. 2019). Different groups of soil organisms respond differently to fire-induced disturbances and have different abilities to restore their communities (e.g. Lindberg and Bengtsson 2006, Malmström 2012).

Restoration of communities of soil organisms depends primarily on their chances of surviving a fire and their migration abilities, as well as on the presence of areas unaffected by fire (‘islands’, unburnt areas within the site of the fire, ‘corridors’) (e.g. Gongalsky et al. 2012). Also important are: the intensity of the fire, the time of year when it occurred, and weather conditions (e.g. Malmström et al. 2008).

However, despite many studies, the rate at which communities of soil organisms are restored is still not well known, especially in areas burnt out by anthropogenic fires, which, due to climate change and human activity, occur more and more often (Olejniczak et al. 2017, Górska et al. 2018).

The research on soil microorganisms and mesofauna was conducted in burnt-out areas resulting from anthropogenic fires of different intensity, in the Kampinos National Park in the third year after the fires (which occurred in May and June 2015) in a 200-year-old forest stand.

The aim of the research was to determine the degree of restoration of the abundance of microorganisms and mesofauna in the areas burnt out by fires of different intensity in a two-hundred-year-old pine stand. It had been assumed that: 1) the restoration of mesofauna communities was correlated with the restoration of microbial communities, 2) the restoration of communities of soil organisms can occurs similarly regardless of the intensity of the fire.

2. Study areas and methods

The study was carried out in the Kampinos National Park near Warsaw, in its north-eastern part, in the Kaliszki protection zone. The research sites included a 200-year-old pine stand (fresh coniferous forest habitat, *Peucedano-pinetum*) (Zaniewski and Otręba 2017) located on rusty soils (Brunic Arenosol) with fresh moder-mor humus (Biały et al. 2000, FAO 2015).

In August 2018, three years after fire of different intensity, nine test plots (10×10 m) were selected. The degree of burn-out of the organic layer was adopted as the criterion of fire intensity (Zaniewski and Otręba 2017). In the areas affected by the strong fire (**S**), the fire had tough impact and almost all the organic layer burnt and in the areas of the weak fire (**W**), the fire had only partially damaged the organic layer. The test plot in the unburnt areas was located 20 m away from the fire boundary.

The plots were designated on each burnt-out site: after a weak fire (**W**) and after a strong fire (**S**), and also in adjacent unburnt, control (**C**) areas.

The soil samples were collected in the organic layer (down to a depth of 5 cm) and mineral layer (from a depth between 5 cm and 25 cm). Soil samples were collected from six randomly selected points for each of the plot and a collective sample prepared for each of the layer.

Total organic carbon was measured using a Shimadzu TOC-V analyser with a solid-sample module (Shimadzu TOC 5000 A) by a non-dispersive infrared method. Nitrogen level was determined using the Kjeldahl method (analyser Kjeltec-Tecator). The soil pH in H_2O and in 1 m KCl was measured potentiometrically, while the soil moisture content was gravimetrically determined.

The physicochemical properties of the soils are given in Table 1.

Microbiological analysis

Microbiological samples were collected from the same each test plot into sterile containers, making sure aseptic conditions were maintained. The samples were taken from 6 randomly selected points of each plot, separately from the organic layer (0-5 cm) and the mineral horizon (5-25 cm) of the soil. The soil and litter were subjected to microbiological analyses to determine the total number of culturable heterotrophic soil bacteria on the Bunt and Rovira medium (Bunt and Rovira 1955) and of microscopic fungi on Martin's medium (Martin 1950) by bottom inoculation in agar. The abundance (number) of microorganisms was expressed in colony forming units (cfu) per kg dry litter or soil.

Table 1. Physical and chemical properties of the soils in the organic and mineral layers in the test areas: unburnt (control, **C**), burnt out by the weak fire (**W**), and burnt out by the strong fire (**S**)

Study area	Soil pH		$C\ g \cdot kg^{-1}$	$N\ g \cdot kg^{-1}$	C:N	Soil moisture content $g \cdot g^{-1}$
	pH_{KCL}	pH_{H2O}				
Soil organic layer						
Control (C)	3.11	3.68	419.2	16.38	26	38.35
Weak Fire (W)	3.09	3.76	326.2	14.39	23	30.14
Strong Fire (S)	3.18	3.91	296.4	13.21	22	34.53
Soil mineral layer						
Control (C)	3.31	3.61	24.11	1.13	21	7.19
Weak Fire (W)	3.26	3.57	38.15	1.85	21	11.70
Strong Fire (S)	3.63	3.83	22.02	0.94	24	5.14

Analysis of soil mesofauna

As in the case of microorganisms, 6 samples were taken from each test plot separately from the two layers, organic (0-5 cm) and mineral (5-10 cm), using a 10 cm^2 steel corer. A total of 108 samples were collected. The collected soil samples were used to extract mesofauna – mites (*Acari*) and springtails (*Collembola*), in a MacFadyen's apparatus, which were then preserved in 70% ethanol.

Mathematical analysis

The results of microbiological tests were verified by one-way analysis of variance; homogeneous groups were distinguished by the Tukey test for $\alpha = 0.05$ using the Statgraphics ver. plus 4.1 program.

The principal component analysis (PCA) was used to investigate the interdependencies between the examined traits and multi-trait variations among the objects studied.

3. Results

The abundance of bacteria and microscopic fungi in the soil and litter, three years after the fires, in the soil genetic horizons depended on the intensity of the fire (Tab. 2).

Table 2. Numbers of microorganisms and mesofauna in the test areas on the following sites: unburnt (control – C), burnt out by the weak fire (W), burnt out by the strong fire (F), in the soil organic layer (0-5 cm) and mineral layer (0-25 cm, in the case of mesofauna 5-10 cm), and the effect of fire intensity on the abundance of the studied edaphone groups in the tested soil layers (homogeneous groups were distinguished by the Tukey test for $\alpha = 0.05$)

Study area	Heterotrophic bacteria cfu $\cdot 10^6 \cdot kg^{-1}$ DW_s	Microscopic fungi cfu $\cdot 10^6 \cdot kg^{-1}$ DW_s	Mites *Acari* N $\cdot 10^3 \cdot m^{-2}$	Springtails *Collembola* N $\cdot 10^3 \cdot m^{-2}$
Soil organic layer				
Unburnt (**C**)	2 000.0 b	1 514.0 a	13.1 a	3.2 a
Weak Fire (**W**)	1 120.0 a	1 593.0 a	8.2 a	4.2 a
Strong Fire (**S**)	1 350.0 a	1 480.0 a	10.0a	2.8 a
Soil mineral layer				
Unburnt (**C**)	127.0 a	117.0 a	3.0 a	0.2a
Weak Fire (**W**)	239.0 b	257.0 b	0.7a	0.1a
Strong Fire (**S**)	335.0 c	143.0 a	1.4a	0.3a

In the organic soil layer in the burnt-out areas, irrespective of fire intensity, lower bacterial abundance were still recorded three years after the fire, in comparison with the control (unburnt) areas. In contrast to the bacteria, the numbers of microscopic fungi did not differ significantly in the burnt-out and unburnt areas (Tab. 2). The soil mineral layer from the areas affected by the weak fire and strong fire in the old pine-tree stand was characterized by a significantly higher number of heterotrophic soil bacteria, compared with the control soil (Tab. 2). The abundance of fungi in the soil mineral horizon, three years after the fire, was the highest in the soil in the areas affected by the weak fire, compared with the soils in the other test areas (Tab. 2).

In the case of soil mesofauna, there was no significant effect of fire intensity on the abundance of invertebrates three years after the fire (Tab. 2). The numbers of springtails and mites were many times lower in the mineral layer than in the organic layer, regardless of the strength of the fire (Tab. 2).

The PCA analysis revealed that in the organic soil layer the number of fungi showed a negative relationship with soil acidity (Fig. 1). By comparison, the numbers of bacteria were strongly correlated with high soil moisture, C and N contents, and the C/N ratio (Fig. 1). Based on the PCA analysis, contrary to bacteria, the occurrence of fungi in the soil mineral layer was strongly positively correlated with the C and N contents, and with the highest moisture content of the humus layer (Fig. 2).

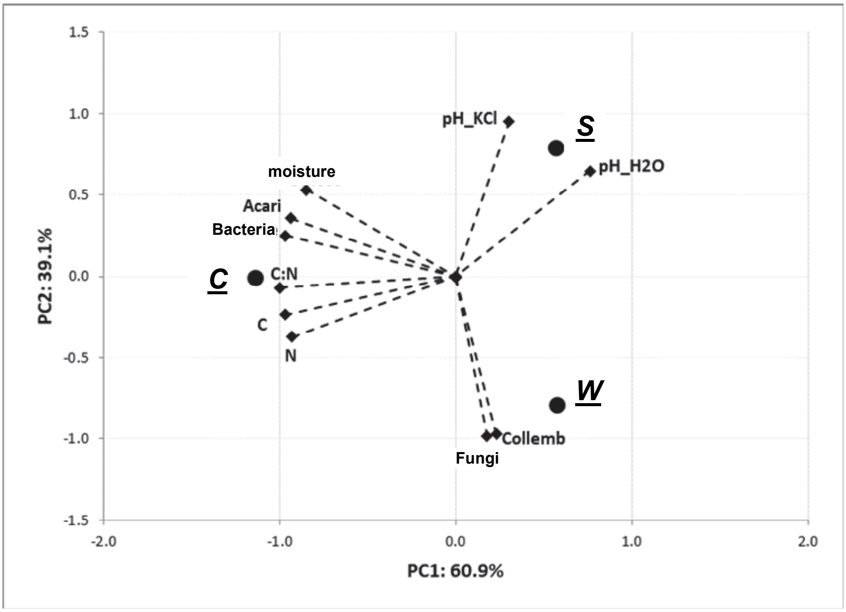

Fig. 1. Differences among the test areas in terms of the traits examined: soil properties (C and N contents, soil pH, moisture), abundance of microorganisms (bacteria and fungi) and of mesofauna (*Acari* and *Collembola*) in the soil organic layer, three years after the fire. **C** – control, **W** – weak fire, **S** – strong fire

In the organic layer, the numbers of springtails (*Collembola*) were strongly positively correlated with those of fungi and negatively correlated with soil pH, which was also the case with fungi (Fig. 1). However, the occurrence of mites (*Acari*) and bacteria was strongly positively interrelated, as well as being positively correlated with the level of moisture, C and N contents, and C : N ratio (Fig. 1). In the case of soil mineral layer, the occurrence of mites and springtails was strongly positively interrelated, as well as being positively correlated with soil acidity (pH) (Fig. 2).

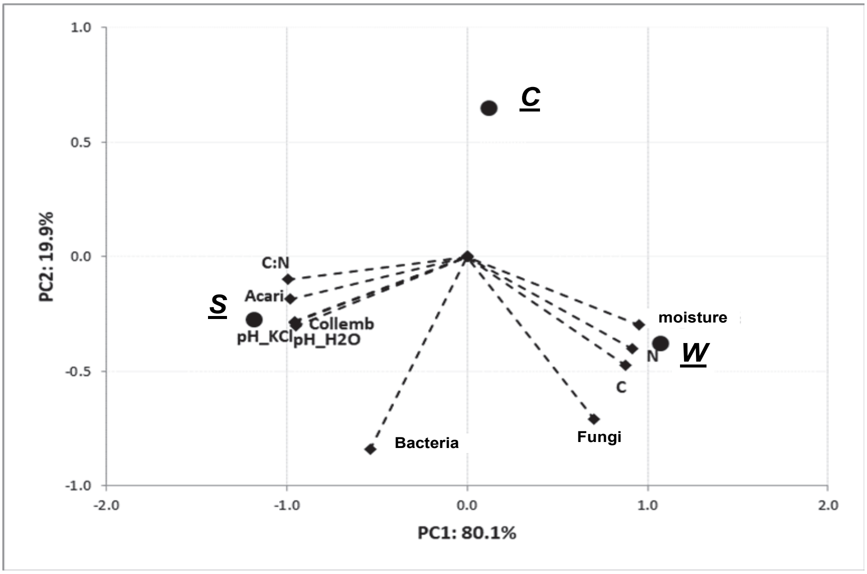

Fig. 2. Differences among the test areas in terms of the traits examined: soil properties (C and N contents, soil pH, moisture), abundance of microorganisms (bacteria and fungi) and of mesofauna (*Acari* and *Collembola*) in the soil mineral layer, three years after the fire. **C** – control, **W** – weak fire, **S** – strong fire

4. Discussion

The dependence of the abundance of bacteria and microscopic fungi in the soil and litter, three years after fire may be attributed to various factors, such as changes in soil chemical properties, as well as in the composition of the flora recolonizing the areas tested and of the various exudates discharged by their root system.

In the areas burnt out by the strong fire, three years after the fire, the mineral layer of the soil was found to contain a significantly greater number of bacteria relative to the areas affected by the weak fire, and which was almost twice as large as that for the unburnt (control) areas. Many factors may have contributed to this, including the amount and chemical composition of root secretions of the plants recolonizing the soil after the fire, as well as competition for an ecological niche of heterotrophic bacteria, which, in contrast to fungi, multiply much faster in a substrate with a lower moisture content. One of the abiotic factors that can limit the development of microorganisms in burnt forest stands is the availability of water. It was observed that the organic layer in the unburnt area had 25% more moisture than on the site where there had been a weak fire and 10% more in relation to the site of the strong fire. On the surface of the site of the strong fire, the fire had almost completely burnt the litter, and on the site of the weak fire, the fire had considerably damaged the organic layer. After the removal of (damage to) the insulating layer of moss, the soil in the burnt forest stand dries faster after a rainfall. Soil microorganisms in burnt-out areas experienced greater stress associated with lack of moisture. This claim is confirmed by studies in which significant decreases in soil moisture were recorded after forest fires (Harden et al. 2006, Holden et al. 2015).

The amount of organic carbon in the soil affected by fire can be higher or lower, than immediately after the fire, depending on the nature of the fire, soil type and moisture, as well the nature of the burned materials (González-Pérez et al. 2004). In the area of the strong fire, in the third year after fire, the contents of organic matter in the organic soil layer, were approximately 70% lower than in control plots and in areas with weak fire 77% than in the control organic soil layer.

The highest abundance of fungi in the soil mineral layer after the weak fire may have been influenced by the strongly acidic soil pH, as well as the high organic carbon content of the substrate, which create optimal conditions for the growth and development of microscopic fungi. The contents of organic carbon in that plot were over 50% higher than in control one. In addition, the amount of moisture in that soil layer was more than twice as high as that in the area of the strong fire and over 1/3 higher in relation to the control area. Our data suggest that one of the abiotic factors that can have an influence on increasing the abundance of fungi in burnt forest stands is the availability of water.

It is known that fires, especially very intense ones, have a significant impact on communities of soil microorganisms (Fioretto et al. 2005, Knelman et al. 2015). It has been shown that even a weak fire significantly affects microorganisms (Dooley and Treseder 2012). The rate of regeneration of microorganisms, apart from the environmental conditions of the soil, may also be determined by their ability to survive fires.

Wang et al. (2015) had shown that microorganisms were characterized by considerable resistance to high temperatures. Therefore, it can be assumed that the microorganisms on the burnt-out sites examined in this study may have survived the fires, especially the weak one. A no less important factor contributing to the restoration of microbial communities is their ability to move around. But even poor colonizers, such as microorganisms, are able to restore their communities relatively quickly on burnt-out sites (Jalaludin 1969). In summary, in the case of the presented study, it can be concluded that the communities of bacteria in the soil after the fires had been regenerated, thanks to endospores, cysts and conidial spores, among others, or could have been deposited from the regenerating flora and/or leaves brought in from other areas by air movements.

Rodriguez et al. (2018) found that the restoration of organic matter and bacterial and fungal populations in areas burnt out by a strong fire occurred 2-3 years after the fire. Prieto-Fernandez et al. (1998) had found that the regeneration of microbial communities lasted at least 4 years. Also in the study presented here, the communities of microorganisms, three years after the fires, were found to be at a highly advanced stage of regeneration.

The hight abundance of soil mesofauna in the soil organic layer is not unusual because springtails and mites inhabit mainly the top soil layers and forest litter (e.g. Bardgett and Cook 1998).

Rutigiano et al. (2013) had found that the abundance of mesofauna was affected by the availability of food. Although springtails are considered to be food generalist, their diet consists predominantly of fungi (e.g. Rusek 1989, Petersen 2002), which may be an explanation for the strong correlation with the fungi observed in the study, in soil organic layer Mites include various trophic groups. The moss mites (Oribatida), which were only recorded in the studied areas, similarly to the springtails can feed on fungi, but also on bacteria (Schneider et al. 2004). The eating-up of fungi by springtails and moss mites was undoubtedly conducive to the development of bacteria. So, the strong correlation between bacteria and mites, observed in the forest areas examined, may be the result of not only food availability but also competition. The results of the PCA indicate the possibility of competing springtails with mites for food that would be fungi. Abiotic factors such as soil pH, moisture and temperature affect the abundance of mesofauna (e.g. Hågvar 1984, Huhta and Häninen 2001). Hence the correlation between the abundance of mesofauna and moisture, or the degree of wetting and soil pH, observed in the tested forest areas. It is believed that the restoration of communities of soil organisms takes 2-7 years (e.g Huta et al. 1967, Malmström et al. 2008, Kim and Jung 2008, Saifutdinov et al. 2018). The similarity in the abundance of mesofauna on burnt-out sites (irrespective of fire intensity) and sites unaffected by fire may be evidence that three years after the fire those invertebrate communities had probably been restored (in terms of numbers). This is within the range of results obtained by other researchers. For example, Metz and Farrier (1971), investigating the impact of the incidence of fires on the restoration of mesofauna communities, had found that springtail and mite communities would become restored when fires occurred every 4 years. While, Malmstrom (2010) found that the rate at which the abundance of mesofauna became restored depended on the strength of the fire and the restoration could still continue 5 years after the fire. Saifutdinov et al. (2018) found that the restoration of springtail communities in boreal forests lasted 5-6 years after a surface fire of moderate intensity.

The restoration of springtail and mite communities on burnt-out sites undoubtedly depended on their chances of surviving the fire (e.g. individuals escaping into deeper layers of soil) (e.g. Gongalsky et al. 2012). Life strategies and the ability to spread around were obviously of vital importance in the restoration of the mesofauna (e.g. Petersen 1995). Springtails can recolonize burnt-out areas by actively migrating from nearby unaffected areas or unburnt parts of the fire site (e.g. Shaw 1997). These invertebrates have great migration abilities and can cover large distances in a short time (even more than a dozen centimetres in a week) (Hågvar 1995). However, what is also very important in the recolonization of fire-affected areas, and thus in the possibility of restoring communities of springtails and mites, the latter, unlike the former, having limited migration abilities, is passive spreading, i.e. by wind or water, or thanks to a phoretic relationship (e.g. Dighton et al. 1997, Ouarner et al. 2010). Wherein, the presence of unburnt areas, the so-called migration corridors is important in colonization the burnt areas by mesofauna, (e.g. Zeitsev et al. 2014).

In summary, three years after the fire, the communities of soil mesofauna are seen as becoming restored in the burnt-out areas, at least in terms of numbers. Ecosystem restoration research re-quires a long-term, interdisciplinary commitment and special attention based on an understanding of the environmental conditions and processes that shaped the evolution of species structure of the soil organism communities.

5. Conclusions

1. The communities of microorganisms, three years after the fires, were found to be at a highly advanced stage of regeneration.
2. The restoration of soil organisms in terms of numbers is to a large extent advanced, especially true for soil mesofauna.
3. The presented research confirmed the hypothesis that the restoration of microbial communities and the restoration of mesofauna are interrelated, which is also affected by the environmental conditions of the soils after a fire.
4. The hypothesis that the restoration of soil organisms occurs similarly regardless of the intensity of the fire was partially confirmed in the presented study. It was true for mesofauna and only for the soil microorganisms inhabiting soil organic layer. It seems that the reconstruction of microorganisms inhabiting the mineral soil layer proceeds with a fire strength gradient.

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Abstract

Fires, on account of their emotional, economic and cognitive aspects, are of interest to numerous researchers, and their impact is often unpredictable and difficult to investigate. They are among some of the most dynamic factors shaping terrestrial ecosystems. They destroy vegetation and alter the physicochemical and biological properties of the soil. Fires significantly influence the abundance and biodiversity of soil microorganisms and soil mesofauna, which are important elements of soils of every ecosystem, especially forest soils. Restoration of communities of soil organisms takes place at different rates and depends on, among other things, the intensity of the fire. The aim of the research was to determine the degree of restoration of the abundance of microorganisms and mesofauna in areas burnt out by anthropogenic fires of different intensity in an old pine forest. The research was conducted in a two-hundred-year-old pine stand (Peucedano-Pinetum), in the Kampinos National Park (near Warsaw, central Poland). In August 2018, three years after the fires, 3 test areas (10×10 m) were designated on each burnt-out site: after a weak fire (W) and after a strong fire (S), and also in adjacent unburnt (control, C) areas. In each test area, 6 samples were taken both from the organic layer (0-5 cm) and the mineral layer (5-25 cm – for microorganisms, and 5-10 cm for mesofauna) of the soil using standard methods for microorganisms and mesofauna. It was found that three years after the fires, the restoration of communities of soil organisms in terms of numbers was at an advanced stage (this was especially true for soil mesofauna). Based on the PCA analysis, it was found that the restoration of microbial communities and of the communities of mesofauna were interrelated, which was also influenced by the environmental conditions of the soils after the fires, in particular the physicochemical soil properties resulting from the intensity of the fire.

Keywords:
soil microorganisms, soil mesofauna, fire, Brunic Arenosol, forest soil

Wybrane właściwości biologiczne gleby na wypalonym obszarze pod starodrzewami sosny trzy lata po pożarze

Streszczenie

Pożary, ze względu na emocjonalne, ekonomiczne i poznawcze aspekty, są przedmiotem zainteresowań licznych badaczy, a ich wpływ często jest nieprzewidywalny i trudny do zbadania. Należą do jednych z najbardziej dynamicznych czynników kształtujących ekosystemy lądowe. Niszczą roślinność, zmieniają fizykochemiczne i biologiczne właściwości gleby. Pożary w istotny sposób kształtują liczebność i bioróżnorodność mikroorganizmów glebowych i mezofauny glebowej, będących istotnymi elementami gleb każdego ekosystemu, zwłaszcza gleb leśnych. Odbudowa zespołów organizmów glebowych zachodzi w różnym tempie i zależy między innymi od siły pożaru. Celem badań było ustalenie stopnia odbudowy liczebności mikroorganizmów i mezofauny w obszarach wypalonych po pożarach antropogenicznych o różnej sile w starodrzewie sosnowym. Badania prowadzono w dwustuletnim drzewostanie sosnowym (Peucedano-Pinetum), w Kampinoskim Parku Narodowym (koło Warszawy, centralna Polska). W sierpniu 2018, trzy lata po pożarach wyznaczono po 3 powierzchnie badawcze (10x10 m) na pożarzyskach: po słabym pożarze (W) i mocnym pożarze (S) oraz przyległych obszarach niewypalonych (kontrolnych, C). Na każdej powierzchni badawczej pobierano po 6 prób w warstwie organicznej (0-5 cm) i mineralnej gleby (5-25 cm – w przypadku mikroorganizmów i 5-10 cm w przypadku mezofauny) stosując standardowe metody dla mikroorganizmów i mezofauny. Stwierdzono, że po trzech latach po pożarze odbudowa zespołów organizmów glebowych pod względem liczebności jest w dużym stopniu zaawansowana (dotyczy to zwłaszcza mezofauny glebowej). Na podstawie analizy PCA stwierdzono, że odbudowa zespołów mezofauny i mikroorganizmów są powiązane ze sobą, na co mają wpływ także warunki środowiskowe gleb po pożarze, zwłaszcza właściwości fizykochemiczne gleby, wynikające z siły pożaru.

Słowa kluczowe:
mikroorganizmy glebowe, mezofauna glebowa, pożar, Brunic Arenosol, gleba leśna

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Movement of Chemical Elements in Ash on the Example of a Process of Combustion Corn Straw Briquettes in a Low Power Boiler

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1. Introduction

In Poland, the use of plant biomass for energy purposes is gaining importance. At the same time, the popularity of dendromass, despite changes in regulations increasing its supply for energy purposes, promotes an increased interest in a biomass of agricultural origin. This trend is associated not only with professional energy industry, that is obliged to use biomass for energy production in the processes of its direct combustion or co-combustion with fossil fuels, but also depends on the increase in demand for different assortments of solid biofuels in single-family housing or municipal buildings, where coal boilers are replaced by modern heating devices powered by a biomass under the "anti-smog" program (Kamińska 2018, Wąsowicz 2018).

The barrier with the use of solid biofuels in the aspect of emission standards for low-power heating devices, is their diversification in terms of volatile parts and the contents of carbon, hydrogen, nitrogen and sulfur. These parameters depend on the physiological characteristics of different plant species and varieties, as well as their development phase, plant parts, habitat, date and method of harvesting, transport, storage and other factors (Demirbas 2004, Graham et al. 2016, Jenkins et al. 1998, Krzyżaniak et al. 2014, Szyszlak-Bargłowicz et al. 2006, Wang et al. 2011).

The plant biomass also contains some amount of mineral substance, which after combustion is the main part of the ash, not exceeding 6% (Demirbas 2004, Kalembasa 2006, Kowalczyk-Juśko 2017, Shao et al. 2012). Chemical composition of ash (tendency to form sinters) affects the course of the combustion process, the choice of technology, emission of solid particles and after combustion – manner of its use. However, the management of ash is determined by its chemical properties. Ashes obtained from the combustion of straw, compared to biofuels with dendromass, contain relatively little calcium, a lot of potassium and silicon (Kraszkiewicz et al. 2017, Obernberger et al. 2006, Róg 2011, Uliasz-Bocheńczyk & Mokrzycki 2018). At the same time, longer vegetation period of trees than other plants used for energy purposes is conducive to the accumulation of other metals. Among wide range of biomass fuels, corn straw is an attractive raw material. Maize is one of the main cereal crops grown in Poland, and its straw is considered an interesting source of biomass for energy purposes (Karcz et al. 2013, Niedziółka & Zuchniarz 2006). While analyzing the combustion process and explaining the mechanism of burning straw from maize on a fixed bed contributes to its clean and efficient use as an energy source.

Metals contained in the biomass, evaporate or remain in ash during the combustion process and consequently get into the natural environment (Li et al. 2015, Rybak 2006). Kalembkiewicz and Chmielarz (2013) [after (Ram & Masto 2010, Pandey & Singh 2010, Johnson et al. 2010, Ahmaruzzaman 2010, Pandey et al. 2009, Reijnders 2005, 2007, Onisei et al. 2012, Dong et al. 2010, Syc et al. 2012)] indicate in their work that various applications of ash (reclamation, construction of embankments, production of building materials, flue gas desulphurization, production of ceramics, membranes and geopolymers) cause that knowledge of heavy metals distribution within ash as a mobile fraction is necessary before their use. The problem of heavy metals division between waste streams during combustion of Virginia mallow also draws attention of Szyszlak-Bargłowicz and Zając (2015), who indicate the need to analyze the problem in low power installations using biomass fuels, referring at the same time to the results obtained in this area by researchers dealing with industrial installations, in which fossil fuels were combusted.

Combustion is a complex phenomenon. It consists of many physical and chemical phenomena of thermal decomposition and combustion of fuel, occurring in a given space and time. Analysis of the combustion process requires knowledge of the properties of fuels and their impact on its course (Van Loo & Koppejan 2008, Villeneuve et al. 2012, Juszczak 2014, Liu et al. 2013, Ozgen et al. 2014). The type of pollution generated in the biomass combustion process depends not only on the process factors, heating equipment used, but also on the type of biomass being combusted (Zając et al. 2017, Konieczyński et al. 2017).

The aim of the conducted research was to assess the migration of elements within the ash during the combustion process of maize straw briquettes in the low power boiler in the aspect of their impact on the natural environment, and taking into account directions and possibilities of potential management of ashes.

2. Material and methods

Maize straw briquettes were used during the tests. The material for the study was obtained from an agricultural farm in the eastern part of Lublin province. Compaction process was carried out in a hydraulic briquetting machine with a cylindrical barrel with a diameter of 50 mm. For the obtained biofuels, basic physical and chemical properties were determined in three repetitions, applying the following methods:

- moisture content – by weight method according to the norm PN-EN 18134-3:2015,
- density – calculated on the basis of the mass, diameter and length of the briquettes from the randomly selected sample of 10 pieces, using the following formula:

$$\rho_w = \frac{4 \cdot 10^6 \cdot m}{\pi \cdot d^2 \cdot l} \ (\mathrm{kg \cdot m^{-3}}) \qquad (1)$$

where:
ρ_w – density of briquttes ($\mathrm{kg \cdot m^{-3}}$),
m – mass (g),
d – diameter (mm),
l – length (mm).

- carbon, hydrogen, sulfur – by means of IR absorption;
- nitrogen – by the katharometer method;
- net calorific value – calculated after previous determination of the heat of combustion according to the norm PN-EN 18125:2017;
- ash – according to the norm PN-EN18122:2016;
- chemical composition of the ash was made by plasma spectrometry using the Thermo iCAP 6500 Duo ICP device.

The combustion tests of the collected research material were carried out using a test bench (Figure 1), the integral element of which was a upper-combustion boiler with a fixed grate periodically loaded, in which the fan directed the air stream under the grate with the speed of 1.5 $\mathrm{m \cdot s^{-1}}$.

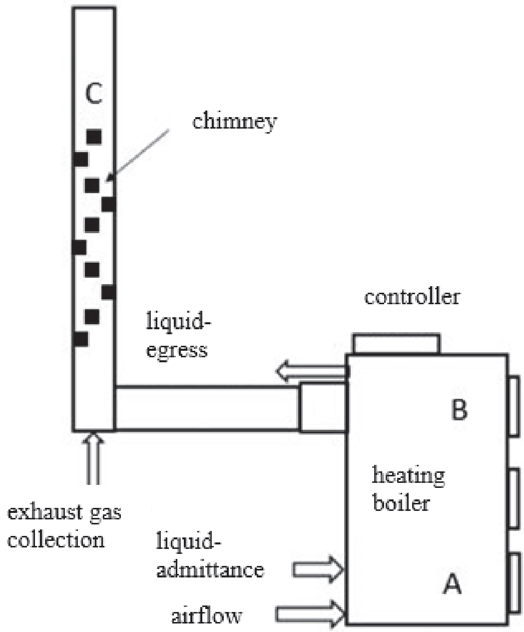

Fig. 1. Schematic of the measurement system (place for ash sampling: A ash pan, B heat exchanger, C chimney shelves marked with a black square)

Capacity of the combustion chamber to the exchanger part was 35.1 dm^3 (0.26 m × 0.3 m × 0.45 m). Above the combustion chamber, there was a heat exchanger with horizontal partitions with water channels. The ash chamber was below the water grate, in which the ash container was placed. The fuel was loaded and ash removed manually. Water capacity of the water jacket was 30 dm^3, and the storage tank 400 dm^3. Such a system was supposed to ensure similarity to real chambers and enable combustion process, as in low-power heating devices. The exhaust gases were taken through the chimney at a distance of 1 m from the boiler flue. The measuring probe was connected to the exhaust gas drier PGD-100 (Madur Eljack Electronics), from which the exhaust gases were sent to the flue gas analyzer. During the tests, a Photon portable gas analyzer, from the same company as the gas dryer, was used. It is a device operating on the basis of infrared sensors (NDIR) for the following gases: CO, CO_2, NO, SO_2 and electrochemical sensor for O_2. The temperature measurement was carried out using a K type thermocouple. The first of them was located in the middle part of the combustion chamber height at its outer wall, while the second one was to measure the temperature of the flue gas in the chimney and was located near the flue gas collection point.

The tests consisted of burning 20 portions of 1 kg of previously mentioned briquettes. Measurements of the exhaust gas composition were carried out continuously from the moment of the fuel lining to the stabilized layer of heat until the reaction extinguished. Results of the discussed parameters were automatically recorded by the analyzer's database every 4 s, with the simultaneous recording of the data recording time. The database created in this way was transferred to a PC computer after the tests were completed.

The ash for laboratory tests was taken from three points of the combustion installation: from the ash pan of the boiler, heat exchanger and chimney, in which 10 metal shelves of 20 mm × 20 mm were arranged on the circumference of the chimney every 120° on the 50 cm section, were installed to collect the ash (Figure 1). Prepared portions of ash, after previous preparation (digestion and dilution), were tested using SpectroBlue ICP OES spectrometer at the Regional Center for Environmental Research, Agricultural Technology and Innovation, the Pope John Paul II State School of Higher Education in Biała Podlaska. The analytical curves were prepared by diluting the VHG SM68-1-500 Element Multi Standard 1 in 5% HNO_3. Operating parameters were as follows: number of measurements: 3; pump speed: 30 rpm; coolant flow: 12 $dm^3 \cdot min^{-1}$; auxiliary flow: 0.90 $dm^3 \cdot min^{-1}$; nebulizer flow: 0.78 $dm^3 \cdot min^{-1}$.

3. Results and discussion

The average values of the obtained results (from three replications) characterizing the biofuels used are presented in Tables 1 and 2.

Table 1. Physical and chemical properties of briquettes made of maize straw

Parameter	Symbol	Unit	Value
Length	L	mm	23
Diameter	D	mm	50
Density	–	$kg \cdot m^{-3}$	900
Total moisture	W_t^r	%	8.00
Elemental composition	C	%	45.0
	H	%	5.50
	N	%	0.70
	S	%	0.18
Calorific value	Q_s^a	$MJ \cdot kg^{-1}$	18.81
Net calorific value	Q_i^r	$MJ \cdot kg^{-1}$	17.58
Ash	A^a	%	6.77

Table 2. Chemical composition of ash from briquettes made of maize straw

Chemical element	Unit	Value
Si	$g \cdot kg^{-1}$ dry mass ash	270.67
P		16.24
K		147.70
Ca		41.71
Mg		10.08
Na		2.37
S		7.34
Fe		9.61
Al		13.80
Mn		0.70
Ba		0.18
Ti		1.47
Sr		0.18

The produced briquettes were characterized by comparable physico-chemical features to other biofuels based on maize straw, thus meeting the assumptions of appropriate quality standards (Demirbas 2004, Eisenbies et al. 2016, Obernberger 2006). The elemental composition of ashes obtained after combustion at 550°C by a standardized method (PN-EN 18122: 2016) varied. In the structure of elements determined with this method, particularly high silicon (Si) content was observed – 50% compared to the other elements and 28% potassium (K). Following elements had a few percentages: phosphorus (P), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), and aluminum (Al). The remaining ash constituents made up small shares of less than 1% (Na, Mn, Ba, Ti, Sr). At the same time, the content of macro- and micronutrients in the ash from the analyzed biofuels was comparable to those from the literature data (Jewiarz & Kubica 2012, Kalembasa 2006).

The average values of CO, NO, SO_2, O_2 content in the flue gases and flue gas temperatures are presented in Table 3.

Interpretation of the obtained results concerning the content of CO, NO and SO_2 in the exhaust gas refers to the adopted combustion criteria, the characteristic feature of which was the use of a grate combustion system with fuel ignition from below and distribution of air under the grate. The obtained values of these compounds varied due to the periodicity of fuel feed to the boiler and phase of the combustion process. Immediately after lining the 1 kg of fuel along with a stabilized layer of heat, the temperature was increased and evaporation of volatiles from the fuel was mainly represented by maximum values of CO, NO and SO_2. Stabilization of the combustion process represented by minimum O_2 value led to a decrease in the value of these compounds in the exhaust gas, and for CO, it was acceptable for this type of boiler, falling into the 3rd class according to PN-EN 303-5: 2012. The analyzed components of exhaust gases during the tests were similar to the literature values (Jewiarz & Kubica 2012, Kordylewski 2008, Szyszlak-Bargłowicz et al. 2017).

Table 3. The content in the flue gas of CO, NO, SO_2, O_2 and the temperature of the exhaust during the combustion of the briquettes concerned

Parameter	Unit	Minimum	Maximum	Average	At min. O_2
CO	ppm	0	9925	3892	3396
CO at 10% O_2	$mg \cdot m^{-3}$	0	39311	7713	4408
NO	ppm	0	243	152	217
NO at 10% O_2	$mg \cdot m^{-3}$	0	413	288	303
SO_2	ppm	0	141	51	65
SO_2 at10% O_2	$mg \cdot m^{-3}$	0	382	172	194
O_2	%	10.44	20.95	13.66	10.44
Exhaust gases temperature	°C	9.8	397.2	285.0	389.8

Among the pool of 34 analyzed elements, for 12 (Cd, Ce, Cr, Gd, Ho, In, La, Lu, Na, Sm, Y, Yb) the recorded results were below the measuring range of the device. The remaining values of elements determined in ash are shown in Table 4.

For 12 elements, the content in the ash from the chimney was much larger than in the ash from the other two sampling points within the boiler. These elements were: Al, Co, Cu, Fe, Mn, Ni, Pb, Rb, Sc, Tl, V and Zn. The observed differences were from several to several hundred percent. Observed results partially coincide with the classification of elements migration in ashes deposited at various places of the installation presented by Meij and Winkel (2007). This classification contains 3 groups, in which group 1 are elements accumulating in ash, group 2 are elements concentrating in fly ash, while the third group are the most easily evaporating elements, often present in the gaseous phase in the exhaust gases (they were not determined during the tests). In the conditions of own research, following elements were convergent with this classification in group 1: Ca, K, Mg, Sr, Th, while in group 2: Co, Cu, Ni, V, Pb, Tl, Zn. Differences that appeared in comparison with this classification (especially in group 1: Al, Fe, Sc) may indicate some anomalies that appeared during tests in the assumed combustion conditions.

Table 4. Chemical composition of ash depending on the sampling point

Chemical element	Sampling point			Chemical element	Sampling point		
	ashpan	exchanger	chimney		ashpan	exchanger	chimney
	in mg·kg^{-1} d.m. ash				in mg·kg^{-1} d.m. ash		
Al	4061.27	3693.95	**20916.93**	Ni	0.00	6.69	**91.41**
Ba	**3988.44**	22.93	186.20	P	14965.32	**15307.01**	7964.32
Ca	**35968.21**	32149.68	16940.10	Pb	564.16	75.48	**603.39**
Co	10.98	1.59	**90.89**	Rb	13.58	11.46	**368.23**
Cu	38.15	50.00	**125.26**	Sc	0.00	9.55	**383.59**
Er	0.00	**750.64**	375.52	Sr	**289.31**	247.77	149.22
Fe	4376.01	10716.24	**12162.60**	Th	30.92	**31.53**	24.22
K	**690.75**	660.19	0.00	Tl	33.53	35.99	**269.27**
Mn	623.41	733.76	**2211.46**	U	91.33	**142.36**	0.01
Mg	**12085.26**	11489.81	6425.26	V	51.73	49.36	**72.66**
Nd	**26.88**	21.02	14.58	Zn	1574.28	497.77	**20054.17**

* The maximum values are marked in bold

4. Summary

Under the test conditions, the fuel used in the form of maize straw briquettes did not differ from other fuels of this type. The combustion criteria adopted during the tests, the characteristic feature of which was the use of a grate combustion system with bottom fuel ignition and air distribution under the grate, was acceptable in the scope of CO emissions for this type of boiler, falling into the 3rd class according to PN-EN 303-5: 2012. Loading the environment with gaseous components: CO, NO and SO_2, is significantly affected by combustion technology, combustion conditions and nitrogen content in the fuel. Choosing biofuels with the lowest nitrogen content for combustion should contribute to the reduction of NO emissions, which becomes another criterion for allowing heating devices to be marketed (Commission… 2015).

Despite varied chemical composition, the ashes analyzed in terms of the macro-, micronutrients and heavy metals load do not tend to exceed the limits set by relevant standards. The experimental results indicate that in low-power boilers fed with briquettes of maize straw, the ash components move. Anomalies that appeared for Al, Fe, Sc are particularly important. This process is important from the point of view of environmental protection, boiler durability and the possibility of using furnace wastes. Low-power boilers, that do not have exhaust gas treatment installations, in which biomass fuels are used, may be a source of harmful emissions.

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Abstract

In Poland, the use of plant biomass for energy purposes is gaining importance. At the same time, the popularity of dendromass, despite changes in regulations increasing its supply for energy purposes, promotes an increased interest in a biomass of agricultural origin. This trend is associated not only with professional energy industry, but also depends on the increase in demand for different assortments of solid biofuels in single-family housing or municipal buildings, where coal boilers are replaced by modern heating devices powered by a biomass under the "anti-smog" program. Biomass combustion is treated as a process neutral to the environment through the prism of CO_2 emissions. However, under certain conditions, the combustion of biofuels in individual heating systems can cause serious risks on the local scale for the environment and human health. The aim of the study was to assess the migration of elements in the ash during the burning process of maize straw briquettes in the low power boiler in the aspect of their impact on the natural environment, taking into account the directions and potential for the potential management of ashes. In the test conditions, the fuel used in the form of briquettes from maize straw does not differ from other fuels of this type. The combustion criteria adopted during the tests, whose characteristic feature was the use of a grate combustion system with fuel ignition from below and distribution of air under the grate, at minimum content O_2, was acceptable in the scope of CO emissions for this type of boiler, falling into 3rd class according to the standard PN-EN 303-5: 2012. The burning of the gas components CO, NO and SO_2 is significantly affected by combustion technology, combustion conditions and nitrogen content in the fuel. Choosing to burn biofuels with the lowest nitrogen content should contribute to the reduction of NO emissions, which becomes another criterion for allowing heating devices to be marketed. Despite the varied chemical composition, the ashes analyzed in terms of the macro environment, microelements and heavy metals do not tend to exceed the limits set by the relevant standards. The experimental results indicate that in low-power boilers fed with briquettes of maize straw, the ash components move. Anomalies that appeared for Al, Fe, Sc are particularly important. This process is important from the point of view of environmental protection, boiler durability and the possibility of using furnace wastes. Low-power boilers, which do not have exhaust gas treatment installations in which biomass fuels are used, may be a source of harmful emissions.

Keywords:
biomass combustion, emission, ash composition

Przemieszczanie się pierwiastków w popiele na przykładzie procesu spalania brykietów ze słomy kukurydzianej w kotle małej mocy

Streszczenie

W Polsce wykorzystanie biomasy roślinnej na cele energetyczne zyskuje na znaczeniu. Jednocześnie popularność dendromasy, pomimo zmian w przepisach zwiększających jej podaż na cele energetyczne, sprzyja zwiększonemu zainteresowaniu biomasą

pochodzenia rolniczego. Trend ten wiąże się nie tylko z energetyką zawodową, ale również koresponduje ze wzrostem zapotrzebowania na różne sortymenty biopaliw stałych w budownictwie jednorodzinnym lub komunalnym gdzie wymieniono kotły węglowe na nowoczesne urządzenia grzewcze zasilane biomasą na mocy programu „antysmogowego”. Spalanie biomasy, jest traktowane jako proces neutralny dla środowiska w kontekście emisji CO_2. Jednak w pewnych warunkach spalanie biopaliw w indywidualnych systemach grzewczych, może powodować poważne zagrożenie w skali lokalnej dla środowiska i zdrowia ludzi. Celem przeprowadzonych badań była ocena przemieszczania się pierwiastków w popiele podczas procesu spalania brykietów ze słomy kukurydzianej w kotle małej mocy w aspekcie ich wpływu na środowisko przyrodnicze uwzględniając tym samym kierunki i możliwości potencjalnego zagospodarowania popiołów. W warunkach badań wykorzystane paliwo w postaci brykietów ze słomy kukurydzianej nie odbiegało od innych paliw tego typu. Przyjęte podczas badań kryteria spalania, którego charakterystyczną cechą było wykorzystanie rusztowego systemu spalania z zapłonem paliwa od dołu i dystrybucją powietrza pod ruszt, przy minimalnej zawartości O_2, była akceptowalna w zakresie emisji CO dla tego typu kotła mieszcząc się w 3 klasie według normy PN-EN 303-5:2012. Na obciążenie środowiska składnikami gazowymi CO, NO i SO_2 wyraźny wpływ ma technologia spalania, warunki spalania i zawartość azotu w paliwie. Wybór biopaliw o jak najmniejszej zawartości azotu powinien przyczynić się do zmniejszenia emisji NO, która staje się kolejnym kryterium dopuszczającym urządzenia grzewcze do obrotu. Pomimo zróżnicowanego składu chemicznego analizowane popioły pod kątem obciążenia środowiska makro-, mikroelementami i metalami ciężkimi nie wykazują tendencji do przekroczenia wartości granicznych określonych odpowiednimi normami. Wyniki eksperymentalne wskazują, że w kotłach małej mocy zasilanych brykietami ze słomy kukurydzianej zachodzi przemieszczanie się składników popiołu. Szczególnie istotne są anomalie, które pojawiły się dla Al, Fe, Sc. Proces ten jest istotny z punktu widzenia ochrony środowiska, trwałości kotłów oraz możliwości wykorzystania odpadów paleniskowych. Kotły małej mocy, nieposiadające instalacji oczyszczania spalin w których stosuje się biopaliwa stałe mogą być źródłem emisji substancji szkodliwych.

Słowa kluczowe:
spalanie biomasy, emisja, skład popiołu

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Migration of Cadmium and Antimony from Zinc Oxide Emitted from a Sintering Machine in Zn and Pb Pyrometallurgical Process into Environment

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1. Introduction

The Miasteczko Slaskie Zinc Smelting Plant is the only zinc and lead manufacturer in Europe that uses the ISP (Imperial Smelting Process) pyrometallurgical process. The basic production departments of the smelting plant include Sinter Unit and Shaft Furnace (Zhao 2013, Guo et al. 2002, Habashi 1986).

A number of wastes are generated in the manufacturing process, such as: dusts, sludges, dross and slag.

Due to the diversity of the feed materials, i.e. mixture of zinc and lead concentrates with materials recycled from the process, these wastes differ widely in chemical and mineral composition (Gregurek et al. 2015, Rao 2006).

It is estimated that approximately 48 Mg of dust are emitted annually from the process (Adamczyk et al. 2010). The dust contains many toxic elements that may have an adverse environmental impact (Kitamura and Kubota 2000).

The subject of the study were the dusts emitted from the Sinter Unit because of the accompanying elements, including antimony and cadmium, that are present in Zn and Pb ores. The dust separation efficiency of filters at the Sinter Unit is very high at 99.99%, which strongly reduces dust emissions into the air. This, however, is not enough to completely eliminate Sb and Cd emissions with these dusts. These emissions are as follows: Cd – 0.0045 Mg/year, Sb – 0.0039 Mg/year.

Studies of the possibility of migration of chemical elements contained in the dust emitted to the soil and water environment by the Miasteczko Slaskie Zinc Smelting Plant forms a basis for determining the mechanisms of pollutant transformations in that environment.

Based on the data on the mean chemical composition of the dust from the Sintering Machine and on the results of dust phase composition determination

(Adamczyk et al. 2010, Nowińska et al. 2015) the fraction of zinc oxide among all other phase components (zinc sulphide, lead sulphide, lead sulphate, iron oxide and lead oxide) is 4.25 wt. %.

Zinc oxide grains are not uniform in terms of phase composition - they contain inclusions of other phases (Ruetten 2009). The latter include PbO and FeO which, on the average, constitute 0.54 wt. % and 1.95 wt. %, respectively, of the zinc oxide (Adamczyk and Nowińska 2015) Zinc oxide grains contain admixtures of trace elements, such as: Si, Al, Mn, Mg, Ca, K, Ag, As, Cd, Cu, Se, Sb and Sn. These elements most probably constitute substituents of the main elements in grains composed of ZnO, PbO and FeO. The total content of these elements is 1.629 wt. %. on the average (Adamczyk et al. 2015). These elements may form admixtures both in zinc oxide, as well as in the phases that constitute inclusions therein. Therefore, when considering the possibility of migration of these elements into the environment after the decomposition of zinc oxide, the content of these elements in inclusions, i.e. in PbO and FeO, should be indicated (Borch et al. 2010, Barakat 2003, Cabała et al. 2013, Voliante 2010).

The aim of the study was to determine the possibility of migration of Cd and Sb released from zinc oxide emitted by the Sintering Machine to the environment.

Both cadmium and antimony are toxic. Toxicity of cadmium comes from its high affinity with many chemical groups which are biologically important. This element forms covalent and ionic bonds with oxide, hydrogen and sulphur atoms, which create a number of compounds in plant and animal cells (Kaczyńska et al. 2015).

Antimony has high biogeochemical affinity with arsenic, wherein the antimony compounds are less toxic. Toxicity of Sb increases with decreasing of its oxidation state, toxicity of Sb (III) is tenfold higher than of Sb (V).
However, it needs to be emphasised that toxicity of elements depends on many parameters such as the considered organism, the route of exposure, or the presents of other contaminants (Diatta et al. 2008, Filella et al. 2009, Nadgórska-Socha et al. 2013, Niedzielski et al. 2000).

2. Methods

The estimation of the load of Cd and Sb introduced into ground waters as a consequence of zinc oxide decomposition was made for the environmentally worst case scenario: all of the zinc oxide from dust fallout from the Sintering Machine into the soil and water environment is decomposed. Two averaged dust fallout from samples collected over six months were used as objects of the study.

For these estimates to be correct additional considerations must be taken into account. The annual dust emission from the smelting plant is 48 Mg, of that

3.36 Mg is emitted by the Sintering Machine. The average annual dust fallout calculated on the basis of 25 measurement points located around the Smelting Plant is 59 g/($m^2 \cdot$ year), of that 4.13 g/($m^2 \cdot$ year) is attributed to the Sintering Machine (Melaniuk-Wolny 2001).

Chemical composition of dusts was determined by means of roentgen microanalyser JCXA 733 by Jeol equipped with energy-dispersive spectrometer ISIS 300 by Oxford Instruments. The focal beam of diameter range equal to 1-2 μm and accelerating voltage equal to 20kV were applied during the analysis. Fine-phase samples were additionally analysed with the use of the focal beam of diameter equal to ca. 50 μm, corresponding to maximum scanned area of 50×50 μm.

The chemical composition of dust was estimated as an average of results obtained from ten measurements of 9 microzones laid out for every sample.

The mobility of Cd and Sb present in zinc oxide was determined using geochemical modelling based on Eh-pH diagrams using HSC Chemistry 9.6 software. These diagrams were plotted for conditions characteristic of the soil and water environment of the Smelting Plant area:

- average precipitation – 700 mm/year,
- average temperature in winter – -5°C,
- maximum temperature in summer – + 25°C.

Studies were performed within the water stability region, within Eh range of -0.8-+1.4V and pH range of 4-8 (pH of soils in areas adjacent to the Smelting Plant is within 4.5-7.5). The diagrams show the stability regions of the forms of occurrence of trace elements contained in zinc oxide at extreme seasonal temperatures, i.e. -5° and +25°C.

To plot the diagrams it was necessary to make assumptions on the concentration of the elements in question in the soil and water environment. These concentrations were assumed to be equal to permissible limits specified in the Ordinance of the Minister of Environment of 24 July 2006 on the conditions of discharging wastewater to waters and soil and on substances particularly harmful to aqueous environment (Dz.U. 2006, No. 137, item 984): 2 mg Zn/dm^3, 0.2 mg Cd/dm^3, 0.3 mg Sb/dm^3. As CO_2 occurs naturally in water, it was also taken into account when plotting the diagrams, and the concentration thereof (20 mg CO_2/dm^3) was also assumed to be as specified in the Ordinance mentioned above.

3. Results

In order to determine the migration of elements into the environment, only two of them were considered, namely Sb and Cd. Discussion of all potential migrating elements would require a much broader study. In addition, these two elements can pose a hazard to the environment due to their toxicity. The content of these elements in zinc oxide grains was 0.1302 wt. % Sb and 0.1460 wt. % Cd (Adamczyk and Nowińska 2015).

Taking the average content of PbO and FeO in zinc oxide grains, the weighted average for Sb and Cd content in the phases of the zinc oxide grains is as follows:

- Cd – 0.1459 wt. % w ZnO, 0.00005 wt. % in PbO and 0.00005 wt. % in FeO,
- Sb – 0.1300 wt. % in ZnO, 0.0001 wt. % in PbO and 0.0001 wt. % in FeO.

The amount of zinc oxide in the dust emitted from the Sintering Machine, under the assumptions made, is 0.1429 Mg, which corresponds to 0.1756 g/($m^2 \cdot$ year) in the dust outfall (Table 1). Along with zinc oxide, trace elements are discharged into the environment, among them Cd and Sb, in amounts of 0.0049 Mg/year and 0.0044 Mg/year, respectively, and 0.0060 g/($m^2 \cdot$ year) Cd and 0.0054 g/($m^2 \cdot$ year) Sb in fallen dust.

The worst case scenario may be that when all of the zinc oxide in fallen dust (0.1756 g/($m^2 \times$year)) undergoes decomposition in the soil and water environment. In such case all trace elements bound into that phase will migrate into that environment. Under such assumptions, the maximum concentration of zinc in ground water may reach 0.20 mg Zn/dm^3 (with annual precipitation equal to 700 mm). Under these conditions, the concentrations of cadmium and antimony in ground water will reach 0.009 mg Cd/dm^3 and 0.008 mg Sb/dm^3, respectively.

The plotted Eh and pH diagrams indicate that in the pH range of 11.6 to 8.0 (ΔpH = 3.6) zinc oxide will decompose in the soil and water environment at -5°C into $Zn_5(OH)_6(CO_3)_2$, and at pH < 8.0 it will decompose into Zn^{2+} and HCO_3^- (Fig. 1). This decomposition will occur irrespective of the Eh value in the environment.

With increasing temperature the stability region of zinc oxide is reduced. At 25°C the pH range is 9.6-7.2 (ΔpH = 2.4), thus Zn^{2+} and HCO_3^- are formed as a result of $Zn_5(OH)_6(CO_3)_2$ decomposition at pH < 7.2. Also in this case the decomposition occurs within the entire range of Eh water stability values. It is worth noting that $Zn_5(OH)_6(CO_3)_2$ is a carbonate mineral, called hydrozincite from zones of zinc and lead ores oxidation (Cabała 2009). Another constituent forming as a result of zinc oxide decomposition may be $ZnCO_3$ (smitsonite), which is one of the products of Zn ores weathering – smithsonite, like hydrozincite. Its presence, however, is in fact largely reduced, as conditions of its formation require specific temperatures (ca. 10°C) and relatively high pH values (11.0-11.5).

Table 1. Content of Zn, Cd and Sb in dust emissions and fallen dust from the stack of the Sintering Machine (E3) with zinc oxide amount taken into account

Emission (Mg/year)	Amount of ZnO in dust emissions from E3	0.1429
	Zn fraction in emissions from E3	0.1146
	Fraction of Cd contained in ZnO in emissions from E3	0.0049
	Fraction of Sb contained in ZnO in emissions from E3	0.0044
Dust fall (g/(m^2 · year))	Amount of ZnO in fallen dust from E3	0.1756
	Fraction of Zn in fallen dust from E3	0.1409
	Fraction of Cd contained in ZnO in fallen dust from E3	0.0060
	Fraction of Sb contained in ZnO in fallen dust from E3	0.0054

The Pourbaix stability diagrams suggest that the conditions prevailing in the soil and water environment of the smelting plant area will favour complete decomposition of ZnO to Zn^{2+} and HCO_3^- ions.

Under such Eh/pH conditions Cd and Sb will be released into the environment during zinc oxide decomposition. These elements will take on the following forms (Figs. 2 and 3):

- Cd – ionic: Cd^{2+}, solid: $CdCO_3$ – ottavite.
- Sb – hydrolytic: $Sb(OH)_6$, $Sb(OH)_3^0(aq)$, HSb_2S_4, solid: Sb_2S_3 – stibnite, Sb_2O_4.

irrespective of seasonal temperature changes (-5...+25°C).

Within the pH range characteristic of the soil and water environment in the area covered by the study (pH = 4.5-7.5), only the following ions will be present: Cd^{2+}, $Sb(OH)_6^-$ and $HSb_2S_4^-$ migrating along with ground waters.

Analysis of Eh-pH diagrams shows that Eh value has a major impact on occurrence forms of Sb in hypergenic environment in the area covered by the study. Forms of antimony in hypergenic environment are stable throughout the pH = 4.5-7.5 range.

Characteristic form of the presence of antimony under reducing conditions (with the limit values Eh_L = -0.05V and -0.02V) is $HSb_2S_4^-$, where Sb is on +3 oxidation degree. Above the Eh limit value, for the corresponding pH values (Fig. 3), $HSb_2S_4^-$ is hydrolyzed according to reaction:

$$HSb^{(+3)}{}_2S_4^- + 3H_2O \rightarrow 2Sb^{(+3)}(OH)_3^0(aq) + 4S^{2-} + H^+ \qquad (1)$$

Under oxidizing conditions (Eh_L = 0,15V and 0.35V) (Fig. 3) at a concentration of antimony 10^{-10}mol/dm^3, Sb (III) is oxidized according to reaction:

$$Sb(+3)(OH)_3^0\ (aq) + 1/2O_2 + 2H_2O \rightarrow Sb^{(+5)}(OH)_6^- + H^+ \tag{2}$$

While at a concentration of antimony 10^{-7} mol/dm^3, with the increase of Eh value, the following reaction will take place:

$$HSb^{(3+)}{}_2S_4^- + H_2O \rightarrow Sb^{(3+)}{}_2S_3 + S^{2-} + H^+ + H_2O$$
$$(Eh_L = -0.015V \text{ and } 0.05V) \tag{3}$$

$$Sb^{(3+)}{}_2S_3 + 6H_2O \rightarrow 2Sb^{(3+)}(OH)_3^0\ (aq) + 3H_2S$$
$$(Eh_L = -0.014V \text{ and } 0.06V) \tag{4}$$

$$2Sb^{(+3)}(OH)_3^0\ (aq) + 1/2\ O_2 \rightarrow Sb^{(3+)}\,Sb^{(5+)}\,O_4 + 3H_2O$$
$$(Eh_L = -0.02V \text{ and } 0.035V) \tag{5}$$

$$Sb^{(3+)}\,Sb^{(5+)}\,O_4 + 1/2O_2 + 8H_2O \rightarrow 2Sb^{(+5)}(OH)_6^- + 2H^+ + H_2O$$
$$(Eh_L = -0.014 \text{ and } 0.06) \tag{6}$$

Among the solid forms in hypergenic environment of the research area Sb will be represented by stibnite and Sb_2O_4. However, the research results show (Krupka and Serne 2002) that stability of Sb ions, and mainly occurrence of stable forms of Sb, depend on concentration of this element in the ground water (Fig. 3). At low concentration of Sb (< 10^{-10} molSb/dm^3) throughout the Eh and pH range antimony occurs only in hydrolytic forms, and its solid forms are not observed.

With increasing concentration of Sb (10^{-9} molSb/dm^3) next to hydrolytic forms, the solid forms of Sb occur, and further increase in the concentration of antimony (10^{-7} molSb/dm^3) causes the increase of the area of its stability fields (Fig. 3).

The attention should be paid to the fact, that under the environmental conditions the maximum concentration of Sb specified for research area (0.0054 g/(m^2 · year) correspond to the value of $6.30 \cdot 10^{-8}$ molSb/dm^3, while according to the Ordinance (Ordinance of the Minister of Environment of 24 July 2006 on the conditions of discharging wastewater to waters and soil and on substances particularly harmful to aqueous environment (Dz.U. 2006, No. 137, item 984)) the maximum concentration of Sb corresponds to the value of $2.47 \cdot 10^{-6}$ mol Sb/dm^3.

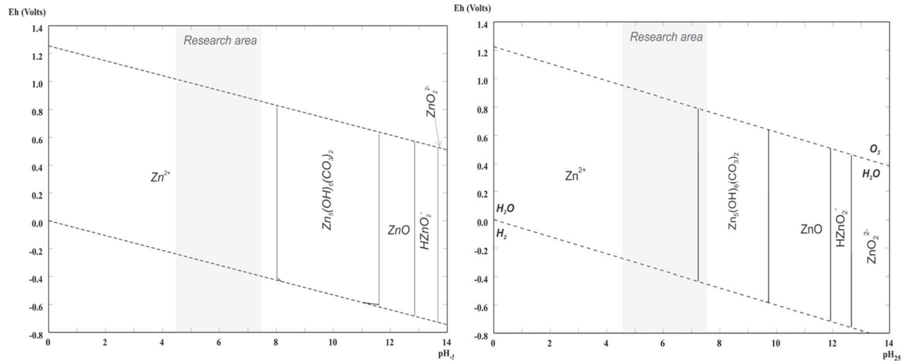

Fig. 1. Mobility of Zn from decomposition of zinc oxide emitted by the Sintering Machine (emission point E3) to the soil and water environment at -5 and 25°C

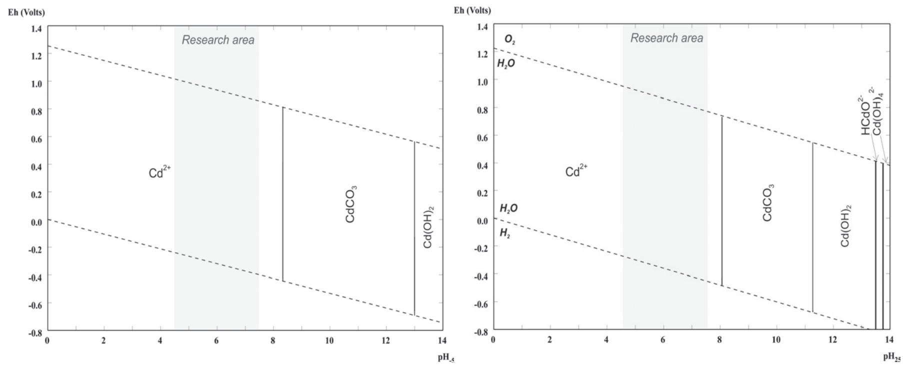

Fig. 2. Mobility of Cd from decomposition of zinc oxide emitted by the Sintering Machine (emission point E3) to the soil and water environment at -5 and 25°C

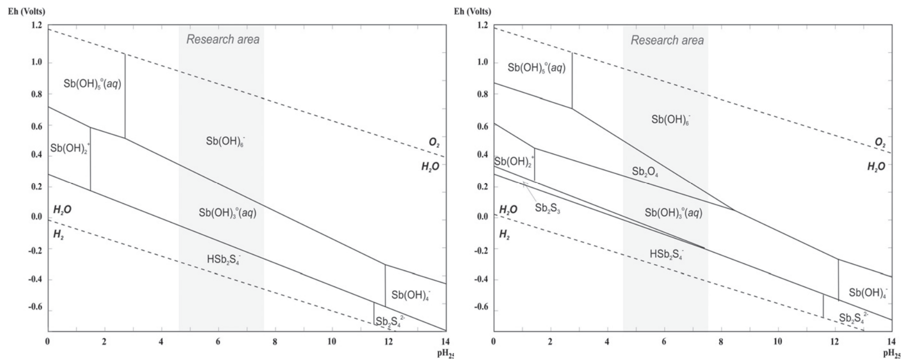

Fig. 3. Mobility of Sb from decomposition of zinc oxide emitted by the Sintering Machine (emission point E3) to the soil and water environment at 25°C

4. Conclusions

Zinc oxide is one of the main phases present in the dust discharged from the stack of the Sintering Machine at the Miasteczko Slaskie Zinc Smelting Plant. Along with zinc oxide, trace elements are discharged into the environment, among them Sb and Cd, in amounts of 0.0148 Mg/year and 0.0049 Mg/year, respectively, and 0.0182 g/($m^2 \cdot$ year) Sb and 0.0076 g/($m^2 \cdot$ year) Cd in fallen dust.

In a hypergenic environment zinc oxide is unstable and will decompose into ionic form Zn^{2+} over the whole pH range, and thereby trace elements Sb and Cd contained in zinc oxide will be released to the environment as a potential pollutant. However, under specific conditions, Zn may form hydrozincite and smithsonite. Hydrozincite is the more environmentally stable form, as its stability region has a wider range of pH and Eh than that of the less stable smithsonite. Smithsonite forms only at temperatures close to 10°C and within a narrow range of relatively high pH values of 11.0 to 11.5.

The plotted Eh and pH diagrams indicate that in the pH range of 4.5 to 7.5, and at temperatures of -5 to +25°C, which is characteristic of the soil and water environment of the area under study, cadmium is only in toxic ion form Cd^{2+} both under reducing and oxidizing conditions. Under reducing conditions antimony is on the third oxidation degree, in the mobile hydrolytic forms $Sb(OH)_6^-$, $Sb(OH)_3^0$(aq), which are characterized by high toxicity. Under strongly oxidizing conditions (pH > 7,5 and Eh > 0.3 V) antimony is on 5 oxidation degree, in mobile form $Sb(OH)_6^-$ characterized by the lower toxicity.

With the increasing concentration of Sb (from 10^{-10} mol/dm^3 to 10^{-7} mol/dm^3, under oxidizing conditions) Sb_2S_3 and Sb_2O_4 are the products of hydrolysis and oxidation reactions, next to the dominant hydrolytic forms of Sb. The area of Sb_2S_3 and Sb_2O_4 stability fields increase with the increase of the Sb concentration.

In the initial period, antimony emitted with zinc oxide from sintering machine is characterized by low concentrations in ground-water environment. It fosters migration of Sb into this environment.

With increasing concentration of antimony concentration, the stable forms of Sb will occur. An important factor which has an impact on the Sb concentration in the ground-water environment, is the rate of decomposition of zinc oxide, which at this stage of research is difficult to determine.

Analysis of the results leads to the conclusion that both cadmium and antimony contained in the zinc oxide from the sintering machine used in the ISP process, due to the predominance of mobile, toxic forms of these elements in the soil and water environment of the smelting plant, pose a potential threat to that environment.

Single-stage extraction tests (Melaniuk-Wolny et al. 2014) also indicate that cadmium emitted with dusts during the oxidizing roasting at the "Miasteczko Śląskie" plant occurs in an exchangeable form, with more than 85% of the metal present in acetate-exchangeable form. The soils around the "Miasteczko Śląskie" plant exhibit poor buffering properties (Kicińska 2011), and hence the consequence of Cd presence in an exchangeable (mobile) form may be the migration of the metal into deeper soil strata and groundwater and the pollution thereof.

The presented results of the studies clearly indicate that, in order to eliminate toxic forms of cadmium and antimony (mainly Sb (III)) the Eh and pH of the soil in the research area should be raised by an appropriate culture of farming and fertilization.

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Abstract

The pyrometallurgical process of production of zinc and lead realized in The Zinc Smelting Plant “Miasteczko Śląskie” S.A. poses a potential threat to the natural environment. Technologies applied in the process produce toxic pollutants, among which one of the most important is dust which contains Pb, Zn, Cd, As, Sb, Tl, etc .

The detailed determination of chemical and mineral compositions of the dust allows to understand its behaviour in the environment and observe migration pathways. The paper presents results of investigations of the migration possibility to the soil and water environment of trace elements cadmium and antimony present in one of the main phases, zinc oxide, emitted with dusts from various operations of pyrometallurgical extraction of Zn and Pb at the Miasteczko Slaskie Zinc Smelting Plant, Poland.

The quantity of elements was estimated on the basis of: (i) dust fall, (ii) zinc oxide content in dust, (iii) element content in zinc oxide, and (iv) mobility of zinc oxide under the hypergenic conditions of the soil and water environment of the Smelting Plant area.

Among the elements considered, cadmium and antimony emitted with zinc oxide contained in dusts from the Sintering Machine will pose a potential hazard for the soil and water environment of the Miasteczko Slaskie Zinc Smelting Plant area.

Keywords:
pyrometallurgy, zinc, lead, zinc oxide, cadmium, antimony, Eh-pH diagrams, ground-water environment

Możliwość migracji kadmu i antymonu z tlenku cynku pochodzącego z maszyny spiekalniczej pyrometalurgicznego otrzymywania Zn i Pb do środowiska

Streszczenie

Proces pirometalurgicznego otrzymywania cynku i ołowiu metodą Imperial Smelting Process (ISP) stwarza potencjalne zagrożenie dla środowiska naturalnego. Proces technologiczny ISP jest źródłem toksycznych zanieczyszczeń, spośród których jednymi z najważniejszych są pyły zawierające w swym składzie między innymi takie pierwiastki jak Pb, Zn, Cd, As, Sb, Tl.

Dokładne poznanie składu chemicznego i mineralnego zanieczyszczeń pyłowych pozwala na określenie ich zachowania się w środowisku, prześledzenie drogi migracji. W pracy przedstawiono wyniki badań możliwości migracji do środowiska gruntowo – wodnego pierwiastków śladowych występujących w jednej z głównych faz – siarczku cynku – emitowanej z pyłami pochodzącymi z różnych odcinków technologicznych pyrometalurgicznego otrzymywania Zn i Pb w Hucie Cynku Miasteczko Śląskie S.A., Polska.

Ilość pierwiastków została oszacowana na podstawie: (i) opadu pyłu, (ii) udziału siarczku cynku w pyle, (iii) zawartości pierwiastka w siarczku cynku oraz (iii) mobilności siarczku cynku w warunkach hipergenicznych środowiska gruntowo-wodnego rejonu huty.

Potencjalne zagrożenie dla środowiska gruntowo-wodnego rejonu Huty Cynku „Miasteczko Śląskie" S.A., spośród rozpatrywanych pierwiastków, będą stanowić kadm oraz antymon emitowane wraz z siarczkiem cynku zawartym w pyłach Maszyny Spiekalniczej

Słowa kluczowe:
pirometalurgia, cynk, ołów, tlenek cynku, kadm, antymon, diagramy Eh-pH, środowisko gruntowo-wodne

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Concentration of Hydrocarbons in Reject Waters During Aerobic Stabilization of Sewage Sludge

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1. Introduction

Along with the construction of new and modernization of existing se wage treatment plants and the application of highly effective methods of treatment, the amount of produced sewage sludge is gradually increasing (GUS 2018). According to the current legislation, it is required to apply sludge treatment processes leading to highly efficient decomposition of organic substances (Dz. U. Nr 134 poz. 1140, 2002). In order to meet these requirements, excluding process of fermentation, especially in smaller wastewater treatment plants, aerobic stabilization is used. In addition to the easily decomposable and biodgradable compounds, both municipal and industrial sewage sludge contains organic and inorganic contaminants classified as non-easily decomposable and toxic (Włodarczyk-Makuła et. al 2003, Lim et. al 2003, Lawal 2017). Among the organic pollutants polycyclic aromatic hydrocarbons (PAHs) are mentioned. Their presence in sewage sludge has been confirmed in literature and pevious ies (Włodarczyk-Makuła et. al 2003, Lawal 2017, Abdel-Shafy 2016). In most publications, PAHs content is determined and converted into a unit of dry matter. The content of these compounds in reject waters was neglected. This problem was taken into account in previous co-authorship studies (Włodarczyk-Makuła 2008, Macherzyński et. al 2014). It has been shown that, despite the fact that a significant number of PAHs present in wastewater is accumulated in sewage sludge, these compounds are also found in reject waters. This is related to the desorption of solid particles, but also to the presence of other organic compounds in wastewater, which increase the solubility of PAHs. Therefore, despite the high affinity and sorption on the surface of solid particles, these compounds are also present in the liquid phase released from the sewage sludge. In addition, they also appear in the film of oils and fats that surround the sewage sludge particles (Dat et. al 2017, Park et. al 2018). The presence of these pollutants in sewage sludge may prevent the use of sewage sludge in agriculture or for natural purposes (Sadecka et.al 2011). In contrast, high concentrations in liquids can enrich the raw sewage stream with an additional amount of these toxic compounds. Although the applicable legal acts do not specify the permissible PAH content in sewage sludge intended for agricultural use, it is proposed to amend Directive 1986/278/EEC. It will determine the permissible content of PAH (acenaphtene, phenanthrene, fluorene, fluoranthene, pyrene, benzo(b)-fluoranthene, benzo(j)-fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene) at the level of 6 mg/kg of dry mass of sludge when using sewage sludge for soil fertilization (1986/278/EEC). Therefore, processes of processing sewage sludge in which these compounds can be effectively removed are an important research issue. The research described in the literature usually focuses on determining the possibility of degradation of these compounds under anaerobic conditions and in municipal sewage sludge (Lim et. al 2003, Dat et. al 2017, Włodarczyk-Makuła 2010, Włodarczyk-Makuła et. al 2018). In the literature one can find information that the loss of PAH under aerobic conditions is faster than under anaerobic conditions and the process of biodegradation occurs with greater efficiency (Lim et. al 2003, Petersen et. al 2003). Other studies prove the superiority of sorption over the PAH biodegradation process in biochemical processes (Lim et. al 2003). Usually, however, the studies were carried out using single hydrocarbons or their mixtures added in a known amount to the samples free of PAH. Research on environmental matrices is conducted much less frequently. Investigation into the possibility of removing these compounds from industrial sewage sludge under aerobic processes is also limited. Also previous studies of co-authors concerned the determination of changes in PAH concentrations in sewage sludge and liquids during methane fermentation, under conditions reducing sulphates or nitrates (Macherzyński et. al 2014, Włodarczyk-Makuła 2011). The transformations of PAHs in municipal wastewater stabilized chemically and in wastewater in the presence of strong chemical oxidants were also studied (Włodarczyk-Makuła 2010b, Kozak et. al 2018, Włodarczyk-Makuła et. al 2016). Initial investigations of co-authors in this field were focused on the determination of PAH levels in stabilized sewage sludge from small wastewater treatment plants and in sewage sludge intended for soil fertilization (Włodarczyk-Makuła 2010, Włodarczyk-Makuła 2010b). The concentrations of low-molecular PAHs in reject water fluids from sewage sludge under aerobic stabilization were also studied (Kozak et. al 2019). The aim of the studies was to follow carcinogenic PAH concentrations in reject water during aerobic stabilization of municipal and industrial sewage sludge.

2. Materials and methods

2.1. Research material

The investigations were conducted using excessive sludge originating from the municipal sewage treatment plant and sewage sludge coming from the coke wastewater treatment plant. Municipal sewage sludge was recycled from secondary settling tanks of the municipal sewage treatment plant of the size exceeding 200,000 PE. In the technological process in the activated sludge bioreactors, denitrification and nitrification are carried out along with the oxidation of organic pollutants. Coking sewage sludge was collected from secondary settling tanks of the biological sewage treatment plant. In the coke wastewater treatment plant PE is not specified, because the installation is not connected to an external network and coking wastewaters are not supplied outside the plant. In this case, activated sludge reactors are applied in which denitrification, nitrification and oxidation of organic compounds are carried out. Characteristics of sewage sludges applied in the experiment is included in Table 1.

Table 1. Physical-chemical properties of sewage sludges

No.	Name	Unit	Sludge-coking wastewater	Sludge of municipal wastewater	Mixed sewage sludge 3/1(v/v)
1	pH	[-]	7.2	7.5	7.9
2	COD	[mg O_2/L]	1200	288	608
3	alkalinity	[mval/L]	-	1.40	2.40
4	moisture	[%]	93.2	97.1	96.1
5	dry mass of sewage sludge	[g/L]	17.54	28.72	34.95

2.2. Technological studies

Oxidation stabilization was carried out under laboratory conditions in open bioreactors with a volume of 14 L. The sewage sludges were continuously aerated (Q = 60 L/h to keep the constant excess of oxygen in bioreactors) using fine-bubble aquarium stones made of quartzite sand for 21 days in ambient conditions 18-22ºC (average temperature 20ºC). The control sample was a municipal sewage sludge, while the second bioreactor was a mixture of municipal sewage sludge and industrial sewage sludge in a 3/1 (v/v). The control of PAH concentration in the reject water samples was carried out before the stabilization process and then three times at 7 day intervals, i.e. after 7, 14 and 21 days of incubation.

2.3. Analytical methodology for PAHs determination

The reject water was separated from the sewage sludge in a laboratory centrifuge at 15,000 rpm for 10 minutes. The preliminary stage of sample preparation for PAH analysis was based on the extraction of organic substances using the liquid-liquid method. This involved adding a mixture of solvents of cyclohexane and dichloromethane in a volume of 5/1 (v/v) into the reject water. Then, samples were shaken on a laboratory shaker for 60 minutes. The separation of the extracts from the samples was carried out using a laboratory separator. The separated extracts were dried using anhydrous aluminum sulphate and purified under vacuum on silica gel. The obtained purified extract was concentrated under a stream of nitrogen to a volume of 2 ml. Subsequently, qualitative and quantitative analysis of PAHs was carried out using a GC-MS gas chromatograph-mass spectrometer. The analysis consists of the injection of 2 μl of the extract on the DB-5 column (length 30 m, diameter 0.25 mm, thickness 0.25 μm). The MS 800 spectrophotometer with 70 eV energy ionization was used for detection and identification. Ion selective monitoring (SIM) m/z was used, selecting three representative ions for each PAH. Helium was the carrier gas. The temperature program was 40°C/min and the final temperature was 280°C for 60 minutes. The following compounds were quantified on the chromatograph at the appropriate retention time: 5-ring: benzo(b)fluoranthene BbF, benzo(k)fluoran-thene BkF, benzo(a)pyrene BaP, dibenzo(ah)anthracene DahA and 6-ring: benzo(ghi)-perylene BghiP, indeno(1,2,3-c,d) pyrene IP. The analyzed hydrocarbons are on the list of priority substances of the US EPA, and according to the results of toxicological tests show a carcinogenic effect on indicator organisms.

3. Results and discussion

The total concentration of hydrocarbons studied in the reject water separated from the sewage sludge placed in the control reactor containing sewage sludge from municipal sewage (C) before the stabilization process was equal to 23 μg/L. Whereas, in the reject water originating from the reactor containing the mixture of sewage sludge (M), the PAH concentration was on the level of 29 μg/L. Concentration of PAHs in rejected water separated from coke wastewater was not determined.

3.1. Changes of concentration of 5-ring PAHs

Figures 1 and 2 present changes in the concentration of 5-ring hydrocarbons in the reject water during aerobic stabilization of sewage sludge.

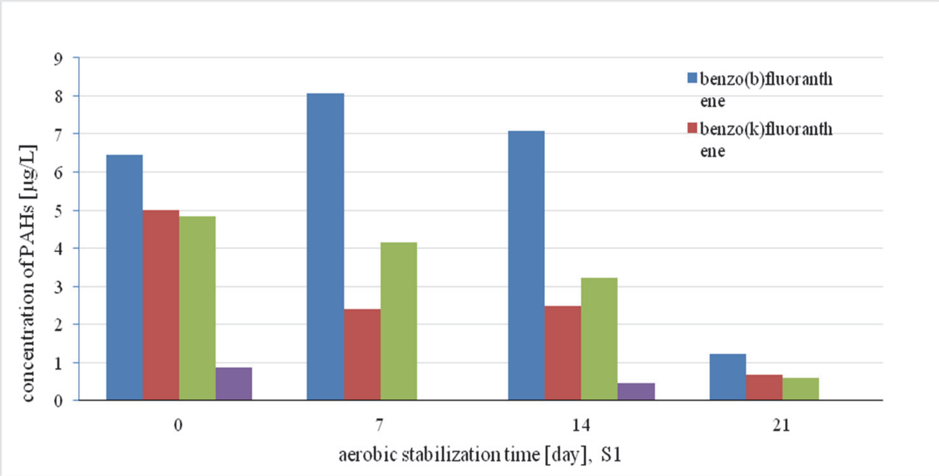

Fig. 1. Concentration of 5-ring PAHs in reject water during aerobic stabilization (C- control sample)

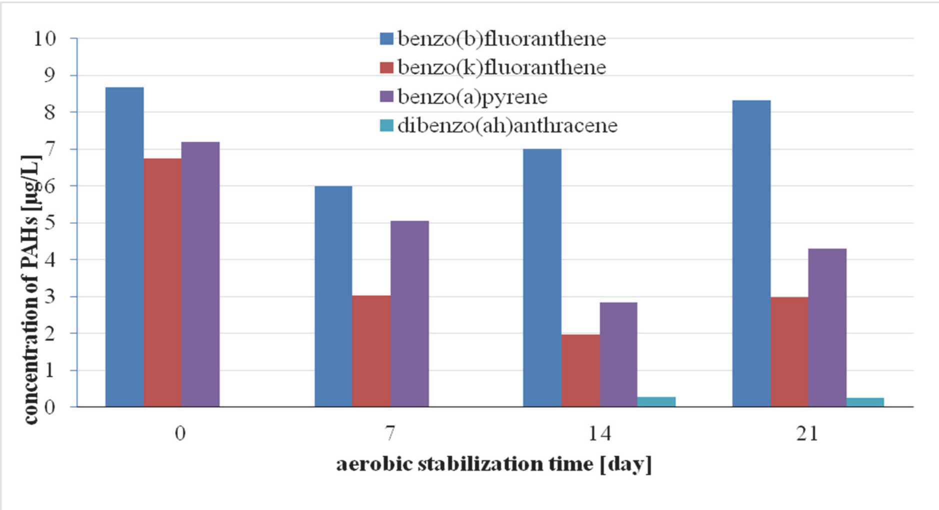

Fig. 2. Concentration of 5-ring PAHs in reject water during aerobic stabilization of mixture sewage sludge (municipal and coke sewage sludge)

The initial concentration of 5-ring hydrocarbons in the reject water coming from the municipal sludge reactor was 17.1 µg/L, and in the reject water taken from the mixed-bed reactor – 22.7 µg/L. Control of the concentration of these compounds during the process showed that PAH concentrations fluctuated, but the final values were lower than the initial ones. The effectiveness of PAH removal in the reject water from the control sludge was at the level of 73%, and in the reject water from the mixed sludge – 31%. Thus, along with the coke oven sludge, some additional PAHs were introduced into the municipal sludge, which inhibited the removal of these compounds during oxygenation. The initial concentration of PAHs in mixed sewage sludge was 33% higher than in control and the final concentration was almost 3 times higher.

3.2. Changes of concentration of 6-ring PAHs

Figures 3 and 4 show the changes in the concentration of 6-ring hydrocarbons, during the stabilization process of the control sewage sludges and mixed sewage sludges. The initial concentration of 6-ring compounds was similar in both liquids and was 5.9 µg/L and 6.4 µg/L respectively from control and from mixed sewage sludges. During 21 days of incubation under aerobic conditions, a gradual decrease in the concentration of these compounds was noted, and the final contents was lower than the initial one by 90 and 64%, respectively in the case of control and mixed sludge. Summarizing the course of changes in PAH concentrations present in reject waters, it can be concluded that the loss of 6-ring compounds was greater than 5-ring ones, although they are more easily sorbed, as evidenced by the octanol/water partition coefficient and their solubility in water is lower.

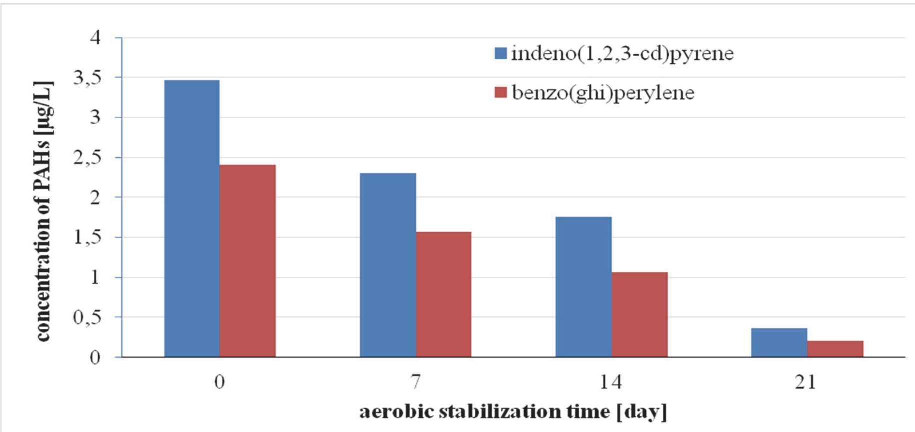

Fig. 3. Concentration of 6-ring PAHs in reject water during aerobic stabilization (C- control sample)

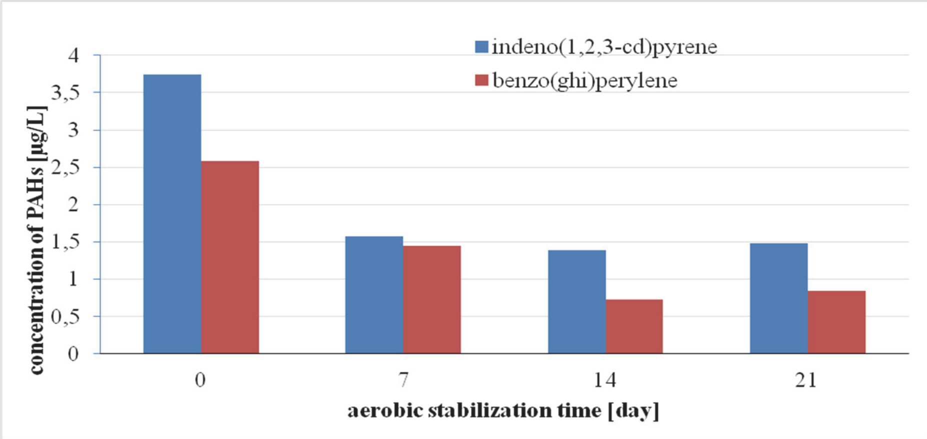

Fig. 4. Concentration of 6-ring of PAHs in reject water during aerobic stabilization of mixture sewage sludge (municipal and coke sewage sludge)

3.3. Summary

The loss of PAHs during aeration of sewage sludge consists of several processes that occur simultaneously. This applies to volatilization, sorption and desorption, reactions with other liquid components as well as biodegradation. Determining the mutual proportions between these processes is not easy and requires further research. Difficulties result from the complexity of processes and ensuring a permanent matrix composition. Sewage sludge is a heterogeneous material with a diverse composition. While compounds with high vapor pressure can escape from the liquid during intensive aeration, heavier hydrocarbons are usually permanently bound to solid particles. They may also occur in the form absorbed by the cells of microorganisms (Traczewska 2003). Literature data indicate that desorption of these compounds from the solid phase and their release into the liquid after the breakdown of cells is possible. Therefore, in monitoring studies involving concentration control, periodic variations in the concentration of PAHs during oxygenation were observed. Such fluctuations were noted in liquids from mixed sewage sludges, which may indicate the presence of microorganisms in industrial sludges containing PAHs inside cells. These sewage sludges were separated from coke wastewater, which contain much higher amounts of PAH than municipal sewage sludge. These wastewater is treated in a sewage treatment plant with activated sludge and it is possible that during this process sorption of PAHs takes place not only on the particles of sludge forming slurries, but also in the cells of microorganisms. Literature and previous studies indicate that microorganisms that were previously exposed to the presence of these compounds are able to decompose them. This ability results from the adaptation of the enzyme apparatus to the metabolization or transformation of co-metabolic PAHs. In the described studies on the aerobic stabilization of coke deposits with municipal sewage, a significant loss of carcinogenic PAHs from the reject water was demonstrated. Similar results were obtained in studies on low-ring hydrocarbons. However, different results were noted in the fermentation process, where it was shown that hydrocarbons can be released into the reject water during sewage sludge incubation under anaerobic conditions. However, confirmation of the intermetallic phenomena of PAHs in sewage sludge undergoing processing requires continued testing under controlled conditions that allow comparison of results.

4. Conclusions

Based on the obtained results, the following conclusions can be formulated in the assumed experimental conditions:

- Control of hydrocarbon concentration during the aerobic stabilization process of sewage sludge showed gradual decrease of the total concentration of these compounds in reject water, which after 21 days of incubation were lower than the initial ones by 78% and 38% in control reject water sample and separated from the sewage sludge mixture, respectively.
- In the reject water originating from municipal sewage sludge, the loss of hydrocarbons grouped by the number of rings in the molecule was in the range of 73-90%, whereas in the reject water separated from the mixture of municipal sludge with coke plants from 31 to 64%.
- In the process of aerobic stabilization of industrial sewage sludge along with municipal sewage sludge, the effective removal of carcinogenic PAH from the reject water takes place.

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Abstract

The article presents the concentrations of selected polycyclic aromatic hydrocarbons (PAHs) in reject water during aerobic stabilization of sewage sludge process. The investigations were carried out in parallel for two samples i.e. for sewage sludge samples coming from a treatment of municipal wastewater treatment plant (control sample) and for mixture of municipal and industrial sludge. The aerobic stabilization process was carried out for 21 days. The concentration of 5-ring and 6-ring PAHs was determined at the beginning of the experiment (day 0) and in seven-day intervals: after 7, 14 and 21 days, respectively. The initial contents of PAHs was equal to 23 μg/L and 29.1 μg/L respectively in reject water from municipal and mixture sludge. During aerobic stabilization process the decrease in the concentration of studied PAHs in reject water was observed. At the end of carrying the aerobic stabilization process the decrease of the total concentration of PAHs achieved 78% in municipal reject water, whereas in coke reject water reached the value of 38%, respectively.

Keywords:
PAHs, reject water, municipal sewage sludge, coking sewage sludge, aerobic stabilization

Stężenie WWA w cieczach nadosadowych w procesie stabilizacji tlenowej osadów ściekowych

Streszczenie

W artykule przedstawiono stężenia wybranych wielopierścieniowych węglowodorów aromatycznych WWA w cieczach nadosadowych w procesie stabilizacji tlenowej osadów ściekowych. Badania prowadzono z wykorzystaniem osadów powstających podczas oczyszczania ścieków komunalnych oraz ścieków koksowniczych. Badania technologiczne prowadzono równolegle dla dwóch próbek, tzn. osadów komunalnych (próbka kontrolna) oraz mieszaniny osadów komunalnych z przemysłowymi. Proces stabilizacji tlenowej był prowadzony przez 21 dób. Stężenie 5- oraz 6- pierścieniowych WWA oznaczano na początku badań, dwukrotnie podczas trwania procesu stabilizacji oraz po upływie 21 dób. Początkowe stężenie WWA wynosiło 23 μg/L i 29,1 μg/L odpowiednio w cieczach nadosadowych z osadów komunalnych i z osadów mieszanych. Podczas stabilizacji tlenowej osadów odnotowano spadek stężenia WWA w cieczach nadosadowych. Po zakończeniu procesu stabilizacji tlenowej osadów spadek sumarycznej ilości badanych WWA był na poziomie 78% w przypadku osadów komunalnych i 38% – w przypadku osadów mieszanych.

Słowa kluczowe:
WWA, ciecze nadosadowe, osady ściekowe komunalne, osady koksownicze, stabilizacja tlenowa

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Normative Problems of the Nitrogen Oxides Concentration Limiting in the Human Residence Environment

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1. Introduction

Internal air is a multiphase mixture of ingredients (gases and vapours and liquid & solid suspended substances) that surrounds the human in enclosed spaces (Miller 1997, Bieniek 2008). It is an extremely dynamic system. Its composition is characterized by high variability in a short period of time, both in terms of chemical compounds and levels of their concentrations (Klepeis et al. 2015). Together with physical factors, the chemical composition forms the quality of the internal air (Hess-Kosa 2011, Daisey & Lioy 1987).

The problem of internal air quality assessment and its impact on human health is now the subject of studies conducted by specialists from different fields of science worldwide. (Capello & Gaddi 2018, Nadadur & Hollingsworth 2015). It is considered that the internal environment is some kind of barrier protecting human beings from the changing and often negative impact of external factors (Woolley 2017, Pluschke & Schleibinger 2018). However, due to the wide variety of presented contaminants, it can cause health problems and even pose a threat to the health and well-being of users of enclosed spaces (Szkarowski & Maliszewska 2018).

The expansion of Poland's gas infrastructure foresees that by 2022, nearly 90% of Polish citizens will be inhabited by municipalities that are gasified (Strategia 2016). Natural gas is a cheap and convenient to use fuel, but you should be aware of the dangers of its use. The combustion of organic fuels is always associated with the emission of harmful substances such as nitrogen oxides (NO_x) and carbon oxides (CO and CO_2).

2. Purpose of work and research methods

Paradoxically, in the legal regulations of many countries, there are no precisely defined rules on the content of harmful substances in rooms with permanent human beings. More often speaking about the working environment, while living residence, where a person spits a similar part of his life is neglected. At the time, even the relatively low levels of harmful substances, with a long exposure period, could pose a serious risk to health.

Risks for carbon monoxide are fairly well identified. Many social campaigns make the public increasingly aware of the risks that CO may pose. Carbon dioxide exhibits poisonous properties only at very high concentrations, in the order of several volume percent. The issue of nitrogen oxides emissions looks much worse.

The only device that emits combustion products directly into the indoor air of living quarters are gas cookers. The purpose of this work is to analyse the normative problems that hinder the control and reduction of the NO_x content emitted during the combustion of natural gas in gas cookers to the internal air of flats.

With such defined work objectives, a combined research method has been used. It is composed in succession with:

- analysis of the normative bases of different countries in terms of reducing the NO_x content in the human environment;
- analysis of the impact of existing ventilation regulations on the NO_x content of the kitchen area;
- experimental verification of the received conclusions.

3. The analysis of the standards concerning NO_x content

3.1. External air

Poland has the same levels of permissible concentrations of pollutants in atmospheric air as other Europe Union countries (Air quality 2018). Table 1 shows the permissible concentration levels for the protection of human health and Table 2 summarised data in terms of plant protection (Rozporządzenie 2012).

Table 1. Permissible levels for nitrogen dioxide in terms of human health

Substance	Averaging period of measurement	Acceptable level, mg/m^3	The permissible frequency of exceeding the acceptable level during the year	Deadline for reaching the acceptable level
Nitrogen dioxide (NO_2)	One hour	0.20	18 times	2010
	One year	0.04	–	2010

Table 2. Permissible levels for nitrogen oxides in terms of plant protection

Substance	Averaging period of measurement	Acceptable level, mg/m^3	Deadline for reaching the acceptable level
Nitrogen oxides (NO_x)[1)]	One year	0.03	2003

[1)] Sum of nitrogen dioxide and nitric oxide, expressed as nitrogen dioxide.
The levels of the substance in air for gaseous pollutants are determined in the conditions: Temperature 293 K, pressure 101.3 kPa.

3.2. Work area

In Poland, the regulations determining the permissible levels of harmful substances in the working area specify 556 substances, including nitrogen oxides (Rozporządzenie 2018). Information on nitrogen oxides is presented in the Table 3.

Table 3. Permissible levels of nitrogen oxides in the working areas

Item No	Substance (CAS number)	Exposure duration	Permissible concentration	
			ppm	mg/m^3
1	Nitrogen monoxide (10102-43-9)	15 min.	-	-
		8 hr	1.33	2.5
2	Nitrogen dioxide (10102-44-0)	15 min.	0.80	1.5
		8 hr	0.37	0.7

3.3. Living quarters

Indoor air that surrounds man in enclosed spaces creates a peculiar microclimate. It is different from the composition of the outer atmosphere often can be much more polluted. The broadly understood internal air quality control is therefore an indispensable element in ensuring the comfort of users of enclosed spaces. The existing rules and recommendations for the permissible levels of NO_2 in residential areas in the selected countries have been analysed.

In **Poland**, according to the authors, mainly for economic reasons, the problem of internal air quality and its impact on users' health has been and remains marginalised. It is shown, among other things, by the smaller attention to quality of construction and finishing materials in comparison, for example, with the Scandinavian countries. In addition, internal air quality issues have in Poland a much lower societal interest compared to the assessment of pollution of other environmental elements such as atmospheric air or surface water. In Poland the rules for human housing define the permissible concentrations only for 35 harmful substances (Zarządzenie 1996). Unfortunately, these rules do not consider nitrogen oxides.

In the **United States**, there are national air quality standards for living quarters. The permissible concentration ranges for NO_2 are shown in Table 4 (Campagna et al. 2017).

Table 4. US permissible NO_2 concentrations in living quarters

Substance (CAS number)	Exposure duration	Permissible concentration	
		ppm	mg/m^3
Nitrogen dioxide (10102-44-0)	30 min.	0.45	0.85
	24 h	0.21	0.39
	One year	0.05	0.09

In **Germany**, the Dangerous Substances Regulation (GefStoffV) sets out two thresholds in the premises for individual substances. The RWI threshold corresponds to the concentration level of the substance in the internal air, for which there is currently no evidence that it has a negative impact on health. Exceeding the RWI value is undesirable for health reasons and requires appropriate action to minimize side effects.

The RWII threshold corresponds to the proven effects of harmfulness, based on the current toxicological and neurological knowledge. Achieving or exceeding this concentration of a substance requires immediate action as it may pose a health hazard, especially for sensitive persons who are living in these areas for a long time. Depending on the exposure time, the threshold II may be defined as short-term (RWII K) or long-term (RWII L).

Table 5 shows the threshold values established by the German IRK/AOLG Working Group (German Committee 2005).

Table 5. German threshold values for NO_2 in living quarters

Substance (CAS number)	Threshold RWI		Threshold RWII		Exposure duration	Year of establish-ment
Nitrogen dioxide (10102-44-0)	ppm	mg/m^3	ppm	mg/m^3		
	0.04	0.08	0.13	0.25	1 h	2018

In **Canada**, the reference concentration (RfC) is used to determine the standards for air quality in residential spaces (RIAQG). This concentration means the content of pollutants in the air below which persons (including sensitive sub-groups) do not suffer adverse health effects. For NO_2, the RfC values are shown in Table 6 (Government 2015).

Table 6. Canadian NO_2 thresholds for living quarters

Substance (CAS number)	Exposure duration	Threshold RfC		Noticeable effects after RfC exceeded
		ppm	mg/m^3	
Nitrogen dioxide |(10102-44-0)	Short-term (1 h)	0.09	0.17	Decreased lung function and increased respiratory response of asthmatics
	Long-term (> 24 h)	0.01	0.02	Higher frequency of days with respiratory symptoms and/or taking medications for children with asthma

4. Health effects of exposures to nitrogen dioxide

The accumulation of nitrogen oxides in poorly ventilated rooms is irritating to the respiratory tract. Much of NO_2 is not absorbed in the upper respiratory tract, but penetrates deep into the lungs, causing toxic effects.

The threshold for perceptibility of smell and irritating effects is similar and ranges from 0.23-0.41 mg/m^3.

Repeated, short-term exposure to NO_2 worsens the existing respiratory tract disease and may induce the development of chronic obstructive disorders, including asthma (Kroczyńska-Bednarek 2008).

Dutch researchers have shown that hourly exposure to NO_2 already at a concentration of 0.21 mg/m^3 causes an increase in bronchial hyperreactivity in patients with asthma.

Exposure to high concentrations (0.56 mg/m^3) results in impaired lung ventilation and a significant increase in airway resistance. On average, an increase in NO_2 concentration of 0,10 mg/m^3 causes a decrease in FVC (Forced Vital Capacity) by 15% (Ackermann-Liebrich et al. 1997).

Sensitive to NO_2 are especially children in whom exposure to this gas for several days, even in low concentrations, can increase the frequency of morning asthma symptoms. Chronic exposure can promote the development of chronic bronchitis and increase susceptibility to respiratory infections (Mortimer et al. 2002).

5. Analysis of standards related to ventilation

The probability of high NO_x concentrations in a residential area (in case of heavier load of gas equipment or malfunctioning ventilation) is quite high (WHO Guidelines 2010).

Nitrogen dioxide in the internal environment is the result of both infiltration of NO_2 from the outside air and produced by combustion sources at home. The impact of NO_x emissions from gas equipment can be minimized when the rooms are well ventilated and exhaust gases are effectively evacuated outside. However, this impact can become significant if the rooms are poorly ventilated.

The requirements concerning residential ventilation differ in particular European countries. Some of them are presented in Table 7 (Indoor air 2015).

In Poland, ventilation of apartments is provided mainly by natural systems. The exhaust is carried by gravity ventilation ducts, and the supply through disordered infiltration and airing. In this case, it is very difficult to achieve the air exchange at the recommended level.

In “Technical conditions to which buildings should correspond” (Regulation 2002), we find contradictions that additionally heighten the scale of the problem.

Table 7. Ventilation requirements for living quarters in selected EU countries

Country, standard and status	Ventilation level for the entire building	Kitchens	Bathroom + WC	WC only
Belgium (NBN D 50-001) Required	3.6 m^3/h per m^2 of area	Open kitchens, min. 75 m^3/h (exhaust)	Min. 50 m^3/h (upper limit 75 m^3/h)	Min. 25 m^3/h
Poland (PN-B-03430:1983/AZ3:2000) Recommended to use	Min. 20 m^3/h per person	30-70 m^3/h (gas cookers)	50 m^3/h	30 m^3/h
UK (Approved Document F) Recommended to use	46.8-104.4 m^3/h (depending on the number of rooms)	46.8-216 m^3/h (exhaust)	28.8-54 m^3/h (exhaust)	21.6 m^3/h (exhaust)
EN 15251 European Standard	1.26-1.76 m^3/h per m^2 of floor surface	50.4-100.8 m^3/h	36 -72 m^3/h	25.2 -50.4 m^3/h

According to §150.9 of the Regulation "*In a room with solid fuel furnaces, liquid or with gas appliances that collect air for combustion from a room and with a gravity exhaust gas duct, the use of mechanical exhaust ventilation is forbidden*".

But according to §176.2 of the same document "*Boilers for gaseous fuels with a total thermal power of up to 30 kW can be installed in rooms not intended for permanent human stay*".

As a result of these regulations, it is possible to install low-power gas boilers both in the bathrooms and in the kitchens. This is space where residents spend a lot of time. If we install gas devices there, then mechanical ventilation in these rooms is forbidden. In this case, the concentration of harmful substances in the room is largely dependent on the varying conditions, such as the correctness of channel selection, outside air temperature, wind power and others. Using a ventilation hood over a gas stove is contrary to the provision of § 150.9 of the Regulation.

The kitchen hood connected to the ventilation duct is undoubtedly the installation of mechanical exhaust ventilation and its simultaneous use with gravity ventilation is forbidden. However, cooker hoods are often assembled by users as specific type of the technical equipment of the building. Only the flat users decide about the purchase and the designers have no influence on its parameters, such as flow, noise and connecting place.

Installing the hood, it is necessary to provide the air supply during its operation. Only under this condition the operation of the main ventilation system will not be disrupted. Unfortunately, for the most part, housing users do not realize the importance of this issue.

A growing problem is also the issue of the proper selection of gravity channels at the stage of the construction design. Ventilation ducts for each flat should be individually calculated by the right selection of their cross sections and the numbers, for the reference conditions, such as outdoor temperature + 12ºC, internal temperature + 20ºC, and wind speed 0 m/s (Polska Norma 2000).

Most often calculations are not made. Then they are usually built in brick technology with a cross section of 140×140 mm or made of ceramic hollow block with a diameter of 150 mm, without considering their height and location in the apartment. As a consequence, the ventilation air flow recommended in Polish standards is practically impossible (Opaliński & Rabczak 2003).

A separate issue is the amount of air delivered to the rooms. In the case of properly operating gravity ventilation, the volume flow rates of the extract air and infiltrating air should be equal. This is usually done through leaks in the window and door openings and airing, rarely through window air grates (Szkolenie 2014).

In heating season the dangerous concentration of hazardous substances in the residential space increases significantly. In this time the amount of airing rooms is limited due to avoid heat loss. The outside air can only get to the rooms through leaks in the windows and door joinery. However, currently used technology of tight joinery has radically changed the issue of air exchange, making leakage infiltration unworkable or dysfunctional. It should be considered that new windows without installed inlets are unable to provide the required amount of inflow air.

Please note that gas cookers are most likely to charge the air necessary for the combustion process directly from the room in which they are installed. In the case when a gas stove is installed in the room, the inflow of fresh air takes on special significance. The necessary amount of fresh air must be supplied for the fuel combustion process.

This amount of air must be additionally supplied, regardless of the air necessary for hygienic and sanitary purposes. If during combustion the natural gas, the amount of air supplied is lower than required, then harmful substances will appear in the combustion products next to carbon dioxide. These substances will be that more, than the imbalance in delivery of air for burning process will be higher.

6. Experimental research

The above analysis shows that gas cookers can be a very important source of NO_x emissions. If the kitchen hoods are absent and ventilation is functioning improperly, nitrogen oxides generated during the work of the cookers, are accumulated in the kitchen first. Then they extend to space of other rooms.

Properly assess the impact of indoor air on human health and well-being can only be based on experimental studies. In the world literature, only a limited number of such studies can be found. An example is research published by Slovak scientists (Šenitkova & Vilčeková 2009). Figure 1 presents the seasonally results of research on the concentration of nitrogen dioxide in the internal environment, depending on the type of room.

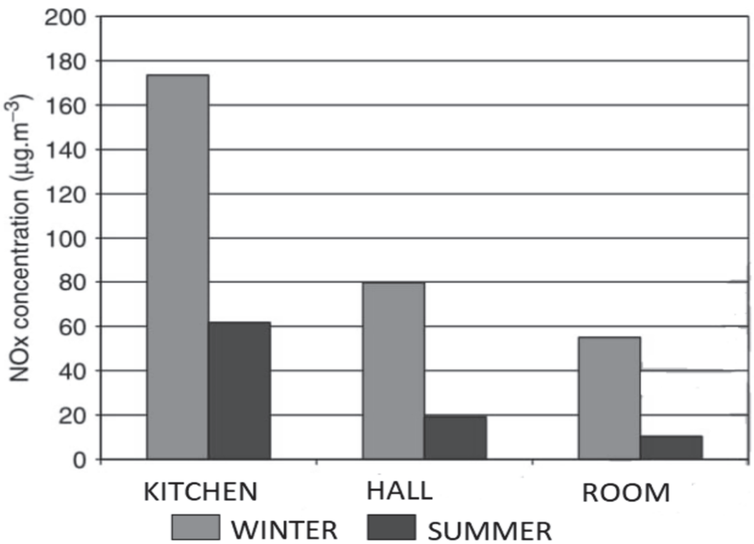

Fig. 1. NO_x concentration in the internal area, depending on the type of room and the season

As can be seen from these data, kitchens are particularly dangerous for human health. In extreme cases, differences recorded between concentrations in the kitchen and in other rooms were up to 300%.

The authors also began their own series of experimental studies. The purpose of these measurements was:

- estimation of the possible concentration of harmful substances arising during the normal use of gas equipment,
- assessment of extent of influence on a human body of harmful substances presented in the internal air;

- the development of technical and organizational measures to protect human health effectively;
- the development of recommendations enabling improvement and optimization of the standards and regulations in the examined area.

The researches of concentrations of nitrogen oxides have normalized standards. However, for the analysis of chemical contaminants generated in the tested room, for the needs of the experiment, the gas analyzer giving the measurement result in real time was used. The measurements were carried out using the certified flue gas analyser Sigma from MRU, meeting the requirements of the PN-EN 482: 2002 standard.

Measuring points were located in three-dimensional grid nodes with a spacing of 10.0 cm, in the height range from 1.50 to 1.80 m, so that the measurements included the breathing zone of an adult person. The measurements were made with closed windows and doors, under stabilized conditions. The stove was working with all the burners switched on except the oven burner. The measurement results averaged in the above-mentioned height range are depicted in Figure 2.

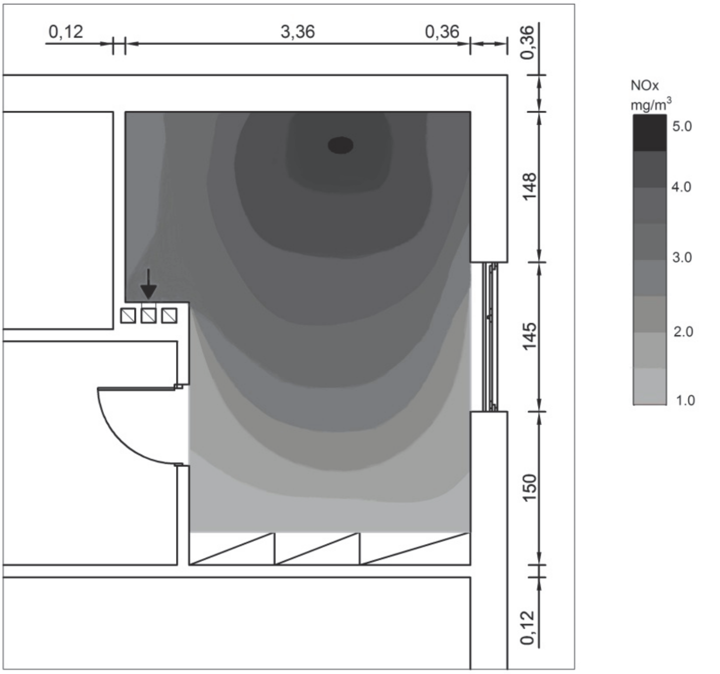

Fig. 2. The maximum concentration of NO_x in the tested room during operation of the gas equipment

Some results of this series have already been published (Szkarowski & Maliszewska 2018). The researches presented in this work were carried out under different conditions in a flat with other gas equipment installed. Room and equipment characteristics are listed in Table 8.

Table 8. Characteristics of the experimental room and equipment

Room	Kitchen			
Location	Three-storey building, first floor			
Area	13.26 m^2			
Height	2.53 m			
Volume	34.24 m^3			
Type of ventilation	Gravity ventilation duct 14x14 cm			
Indoor gas equipment				
Type of device	Four-burner gas stove with oven			
Burner type	Power, kW	Maximum gas flow, dm^3/h	Quantity, PCs.	Maximum gas flow, dm^3/h
Big	3.0	238.9	1	238,9
Normal	1.9	151.3	2	302,6
Auxiliary	1.0	79.6	1	79.6
Gas oven	3.0	238.9	1	238.9
Total	Maximum power, kW		Maximum gas flow, dm^3/h	
	10.8		860.0	

The figure shows the results with the measured maximum NO_x concentration in the tested room. A total of 30 experimental studies have been carried out so far, from February to April, in average operating conditions of gas appliances. The obtained results indicate that in 70% the norms of permissible levels of nitrogen oxides in relation to work rooms were exceeded. Almost every study (98%) has exceeded the NO_2 concentration above the level of 1,0 mg/m^3, which may affect the increase of bronchial hyperreactivity in patients with asthma, additionally promote the development of chronic bronchitis and increase susceptibility to respiratory infections in children.

7. Conclusions

1. Nitrogen oxides are a very dangerous for human health. The gas cookers are the main source of air pollution with nitrogen oxides in flats. Exhaust gases from cookers go directly to the living quarters, and in consequences the average exposure time of nitrogen oxides to inhabitants is several hours.
2. Polish standards, in contrast to other countries, do not specify the permission limits for NO_x in living quarters. The most similar, comparing the time of staying in a polluted atmosphere, are standards for working area.
3. The inconsistency of regulations regarding the ventilation of gas supplied rooms and the high tightness of the currently used window joinery, practically prevent effective ventilation of the rooms and removal of the generated NO_x.
4. The performed part of experimental research confirms the conclusions of the analysis. In a large part of the kitchen room, at the level of breathing, there are concentrations exceeding the standards for the working space and acceptable standards for the external environment.
5. The results of the work prove the need to introduce standards for NO_x content in the living quarters in Poland. In addition, the clarification of building regulations on ventilation would allow the use of solutions for human-friendly air quality at the design stage.

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Abstract

The gas supply of apartments, especially with the use of natural gas, is welcomed by the majority of residents. Jest to komfortowe, łatwe w użyciu i stosunkowo tanie źródło energii. The Polish Gas Development Program foresees that in 2022 to 90% of residents of the country will be provided with gas supply. However, this inevitably involves the emission of exhaust gases from gas equipments into air in apartments. Nitrogen oxides (NO_x) are considered to be the most dangerous components of combustion products for human health. They are created even during complete combustion of fuel and efficiently operating burners.

Air in apartments is a separate type of people's environment compared to the outside atmosphere and the working area. The man spends in this environment a considerable part of his life comparable with the working time. However, in standards of many countries it is not considered. This complicates the analysis and effective solution of human health protection against the effects of NO_x. The sanitary standards of several countries were analysed from this point of view (Tab. 1-6). The Polish norms define the requirements in relation to the air of the apartments, but paradoxically lack nitrogen oxides in them. Therefore, it is currently only possible to orientate on the permissible NO_x concentration in the working environment.

The second important issue is the effectiveness of ventilation, which should ensure the discharge of gases generated during the combustion of natural gas. The standards and building regulations of several countries were analysed from this point of view (Tab. 7). It was found that Polish standards for kitchen ventilation are less stringent in terms of global trends. In addition, national building regulations have contradictions that hinder the use of effective solutions at the design stage.

Additional difficulties arise from the very high tightness of the currently used window joiners. This practically prevents the supply of adequate air to the premises through infiltration, which is assumed in the standards.

In order to verify the obtained conclusions, the literature experimental data in this field were analysed (Fig. 1). The own experimental series was then carried out (Tab. 8, Fig. 2). The average operating conditions of the standard equipment have been tested. It has been proven that the concentration of NO_x in the kitchen air can significantly exceed the Polish permissible compartments for the working environment and global requirements for living quarters.

In order to ensure the protection of human beings against NO_x emitted into the air of gas-supplied housing is requested to introduce urgent changes to national sanitary standards.

The second necessary action is to eliminate inconsistencies in national building regulations in terms of kitchen ventilation. This would allow the use of effective technical solutions already at the design stage.

Keywords:
gas supply, gas equipment, health protection, nitrogen oxides, emissions,
sanitary standards, building regulations, experimental research

Normatywne problemy ograniczenia stężenia tlenków azotu w środowisku przebywania ludzi

Streszczenie

Gazyfikacja mieszkań, szczególnie z użyciem gazu ziemnego, jest mile widziana przez większość mieszkańców. Jest to komfortowe, łatwe w użyciu i stosunkowo tanie źródło energii. Program rozwoju gazownictwa Polski przewiduje, że w roku 2022 do 90% ludności kraju zostanie ogarnięto zaopatrzeniem w gaz. Jednak to nieuchronnie wiąże się z emisją spalin od urządzeń gazowych do powietrza w mieszkaniach. Za najgroźniejsze dla zdrowia ludzi składniki spalin uznaje się tlenki azotu (NO_x). Powstają one nawet przy zupełnym spalaniu paliwa i sprawnie działających palnikach.

Powietrze w mieszkaniach stanowi odrębny rodzaj otoczenia ludzi w porównaniu z atmosferą zewnętrzną i środowiskiem pracy. Człowiek spędza w tym środowisku sporą część swego życia porównywalną z czasem pracy. Jednak w normach wielu krajów tego się nie uwzględnia. Utrudnia to analizę i skuteczne rozwiązanie zagadnienia ochrony zdrowia ludzi przed działaniem NO_x. Przeanalizowano sanitarne normy kilku krajów z tego punktu widzenia (Tab. 1-6). Normy polskie definiują wymagania w stosunku do powietrza mieszkań, jednak paradoksalnie brakuje w nich tlenków azotu. Dlatego orientować się w tej sprawie można obecnie tylko na dopuszczalne stężenie NO_x w środowisku pracy.

Drugą istotną kwestią jest skuteczność wentylacji, która powinna zapewnić odprowadzanie spalin powstających w trakcie spalania gazu ziemnego. Z tego punktu widzenia przeanalizowano normy i przepisy budowlane kilku wybranych krajów (Tab. 7). Ustalono, że normy polskie w zakresie wentylacji kuchni są mniej rygorystyczne względem trendów światowych. Ponad to w krajowych przepisach budowlanych występują sprzeczności utrudniające zastosowanie efektywnych rozwiązań na etapie projektowania.

Dodatkowe utrudnienia sprawia bardzo wysoką szczelność obecnie stosowanej stolarki okiennej. Praktycznie uniemożliwia to doprowadzanie odpowiedniej ilości powietrza do pomieszczeń na drodze infiltracji zakładanej w normach.

W celu weryfikacji uzyskanych wniosków przeanalizowano literaturowe dane doświadczalne (Rys. 1) w tym zakresie. Następnie przeprowadzono własną serie eksperymentalną (Tab. 8, Rys. 2). Przetestowano przeciętne warunki eksploatacji standardowego wyposażenia. Udowodniono, że stężenie NO_x w powietrzu kuchni może znacznie przekraczać polskie dopuszczalne przedziały dla środowiska pracy i światowe wymagania w stosunku do pomieszczeń mieszkalnych.

Żeby zapewnić wymagania ochrony ludzi przed działaniem NO_x emitowanych do powietrza mieszkań zaopatrywanych w gaz wysunięto wniosek o wprowadzeniu pilnych zmian w krajowych normach sanitarnych.

Drugim koniecznym działaniem uznano wyeliminowanie niespójności w krajowych przepisach budowlanych w zakresie wentylacji kuchni. To umożliwiłoby zastosowanie efektywnych rozwiązań technicznych już na etapie projektowania.

Słowa kluczowe:
zaopatrzenie w gaz, kuchenki gazowe, ochrona zdrowia, tlenki azotu, emisja, normy sanitarne, przepisy budowlane, badania doświadczalne.

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Evaluation of the Possibility of Using Post-Production Waste from Zn-Pb Ores as a Material for Natural Land Reclamation

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1. Introduction

In recent years, due to rapid technological development, the global need for natural resources has been growing. Mineral resources are limited, thus environmental protection becomes more and more important and in many countries circular economy is being introduced (EC 2017). The need to provide security in the supply of resources makes the recovery of waste a very important issue. This concerns not only waste formed right now, but also waste deposited in the past in various landfills.

Landfills for industrial waste (e.g. of mining or metallurgical origin) have for many years been a source of mineral resources, e.g. in the form of aggregates or waste containing coal. As we are facing changes to environmental, economic, technological and political conditions, more and more materials are being recovered from landfills of municipal and industrial waste. According to Bass et al. (2010) several aspects have to be solved before land mining: waste composition of landfills, efficiency of materials processing technologies, markets for materials recovered from landfills, and environmental and health risks from excavating landfills. All these aspects have impacted on the economic assessment of landfill mining processes (Kieckhäfer et al. 2017). Factors such as the age and type of the landfill and the country or region where the landfill is located might have an impact on the type of materials stored in the landfill and their valorization potential (Quaghebeur et al. 2013). According to Krook et al. (2012), landfill mining has primarily been seen as a way to solve traditional management issues related to landfills such as lack of landfill space and local pollution concerns, recovery of deposited resources, cover soil, produced waste fuel, recycling efforts have often been largely secondary. Obtaining raw materials from landfills of waste requires technological operations, mainly known from open cast mining, and the application of processing technologies (Matusiak & Kowol 2016, Kudełko & Nitek 2011, Van der Zee et al. 2004). In the literature, the majority of articles are devoted to the land mining of municipal solid waste landfill, with only a few overview articles on the land mining of mineral waste. Non-ferrous and ferrous metals, plastics and combustible fractions (as fuels) are recovered from the landfills of municipal waste, using mobile and stationary plants (Quaghebeur et al. 2013, Svetlov et al. 2015, Rotheut & Quicker 2017, Wanka et al. 2017). Wagner and Raymond (2015) reported the process of mining of municipal solid waste incineration ash landfill. Ash, having been fully processed for ferrous and non-ferrous metals, was then collected and returned to the ash landfill. As a result of landfill mining metal concentrates, construction materials or fuel are obtained; on the other hand often post-processing waste can be formed, which should be utilized.

Mostly mine tailings have been disposed, and according to Edraki et al. (2014) disposal methods include cross valley or hillside dams, raised, embankments/impoundments, dry-stacking of thickened tailings on land or disposal into rivers, lakes and the ocean, but tailings disposal may cause potential environmental problem. However, mine tailings depending on their physical and chemical properties can be reused, recycled and reprocessed. Reuse involves the new use or application of the total mine waste in its original form for a specific purpose directly, without any reprocessing. Recycling extracts new valuable resource ingredients or uses the waste as a feedstock and converts the entire mine waste into a new valuable product or application with some reprocessing. Reprocessing is designed to use the waste material as a feedstock for producing a valuable product, such as recovered minerals and metals (Lottermoser 2011).

Depending on their physical and chemical properties, mine tailings can be used in the construction of buildings and roads, mining, and reclamation, according to the European Waste hierarchy. Argane et al. (2015) proposed the use of mine tailings as aggregates for mortars. Reuse of base-metal tailings generates mortars with good mechanical and durability performance, and the risk that metals release from tailings mortars is minor. Thomas et al. (2013) observed that copper tailing may be used as partial replacement of natural fine aggregates in cement concrete until 60% replacement is achieved. According to (Onuaguluchi & Eren 2016), the best tailings reuse based on corrosion performance and cost efficiency analyses was utilisation of 5% pre-wetted cooper tailings either as a cement replacement or an additive material. Because of grain composition, post-flotation waste cannot be used in underground mines as hydraulic backfill. However, it can be used as a component of suspensions (with binding materials such as fly ash after coal combustion or cement) designed for sealing longwalls with cavingsin underground mines (Kępys 2017). In the case of reclamation works, the waste is used as a material or component of various blends in the technical phase to shape the relief and improve the physical and chemical properties of grounds, and in the biological phase, in the process of soil reconstruction (Śliwka et al. 2017a, b). The application of waste in reclamation depends on fulfilling the requirements defined in legal acts, regarding the geo-mechanical effect of waste on terrestrial and aquatic environment and vegetation. Thus, a certain scope of research must be conducted, including, first of all, an assessment of the amount of chemical pollutants from waste which can get into the environment, and the assessment of the impact of waste on living organisms, especially plants (Baran et al. 2015).

The article presents the results of studies on the possibility of use of post-processing waste in land remediation. This waste was created in the process of re-flotation of old post-flotation waste after the processing of zinc and lead ores. The purpose of re-flotation was to recover metals from storage waste. Because the age of the landfill is several dozen years, the landfill was partly reclaimed, a comprehensive approach to its exploitation is important. Recovery of useful components from deposited waste, such as zinc and lead sulphides used for metal production is important, but the issue of residue management (waste) after the processing, especially after flotation, is important too. In order to avoid the build of a new repository, it is necessary to carry out a series of tests to determine the possibilities of their use. Due to environmental as well as social aspects (society's fear of exploitation of a disused landfill and construction of a new repository), it is necessary to develop methods for using this type of tailings. One of the considered possibilities of using this kind of waste is the use in engineering works. In order to determine the suitability of tested waste to the production of materials used for reclamation, tests of physical and chemical properties were carried out, as well as tests of their phytotoxic properties.

2. Materials and methods

The subject of studies were post-flotation waste, formed in the process of metal recovery from waste deposited in old repositories of a zinc and lead metallurgy plant. To define the possibilities of the utilisation of the examined waste, their physical, chemical and phytotoxic properties were determined.

In the analysis of the physical and chemical properties of waste the following tests were carried out:

- grain composition was marked with the laser diffraction method using the Analysette 22 by Fritsch,
- determination of the natural concentrations of radioactive elements: ^{40}K, ^{226}Ra, and ^{228}Th was carried out with the use of gamma-ray scintillation and semiconductor spectrometry and two coefficients f_1, f_2 to establish whether

building material or waste are, acceptable for use. F_1 and f_2 coefficients were calculated according to (Ordinance of the Council of Ministers of 2 January 2007).

Coefficient f_1 determines the limit of exposure of the body to gamma radiation and is defined as:

$$f_1 = 0.00027S_K + 0.0027S_R + 0.0043S_T \qquad (1)$$

where:
S_K, S_R, S_T – the contents of potassium K-40, radium Ra-226 and thorium Th-232 in a sample in $Bq \cdot kg^{-1}$

Coefficient f_2, which determines the limit of the concentration of radium Ra-226 in a building material and waste with reference to emanation of radon Rn-222 from the walls, ceilings and ground is defined as:

$$f_2 = S_R \qquad (2)$$

- chemical composition analysis, post-flotation waste was digested using a mixture of HNO_3/HCl in a microwave oven. The obtained solution was analysed after dilution by the Inductively Coupled Plasma Spectrometry/Atomic Emission Spectroscopy (ICP-AES) and by the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with the use of the Perkin Elmer Elan 6100 apparatus,
- leachability tests were conducted according to the EN 12457-2 standard. The distilled water, with a liquid-to-solid ratio (L/S) of 10, was used as a leaching solution. The suspension was agitated in a plastic flask for 24 hours, then the mixture was filtered through a 0.45 µm membrane filter. The resulting leachate was analyzed for pH and trace elements using ICP-AES and ICP-MS methods. The amount of chlorides was analysed using the Volhard titration method.

The phytotoxicity of waste of the lower content of metals was examined to define their impact on the germination, growth and condition of plants. The toxicity of waste was defined with regard to two selected test species: white mustard (*Sinapis alba*) and garden cress (*Lepidium sativum*). These are standard procedures used to assess germination and plant growth (e.g. Test No. 208: Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test; PN-EN ISO 11269-2:2013-06; microbiotest Microtox procedure).

The first stage of the study involved a standard toxicity test of the aqueous extract from waste in relation to a test plant (*Lepidium sativum*). The water extract was prepared from the waste (standard procedure), and then a range of solutions was prepared: 12.5, 25, 50, and 100%. 3 ml of the prepared solution was put to Petri dishes, lined with the filtration paper (three repetitions for each concentration); control dishes were also prepared. 10 seeds of *Lepidium sativum* were put to each dish and incubated for 72 hours. Then the number of germination seeds was determined and the length of roots and aerial parts was measured. The impact of wastewater extract on the germination of test plants was defined as the percentage of inhibition and calculated according to the formula:

$$\left(\frac{A-B}{A}\right) \cdot 100\% \tag{3}$$

where:
A – the number of germinated seeds in control object,
B – the number of germinated seeds in experimental object.

The second stage involved pot observations. Both species of test plants were cultivated on a universal medium (peat substrate, pH 5.5) mixed with the examined waste. The same substrate was used in each experimental object. In every pot, 10 seeds of test plants were placed (selected). Experimental groups were differentiated in terms of the waste content in the medium (content: 10, 20, 30, 40 and 50% – of the volume). For comparison reference (control) pots were prepared, without the addition of waste.

All the observations were carried out in four repetitions, for each experimental object. Plant were cultivated in controlled laboratory conditions (humidity, access to light). Observations of germination and early growth of plants continued for seven days (to grow two leaves, standard procedure). Non-parametric Kolmogorov-Smirnov test in Statistica software was used to assess the significance of results.

3. Results

The studied waste has very fine granulation (Fig. 1). Almost 50% of grains are below 100 µm, and the maximum size of grains is 550 µm.

The analysis of the granulometric composition, according to EN ISO 14688-1:2018 and EN ISO 14688-2:2018, showed that the granulation in the studied material corresponds to silty sands (siSa). The values of the coefficient of graining non-uniformity and grain-size distribution curve allow us to classify the analysed waste as grain-uniform material.

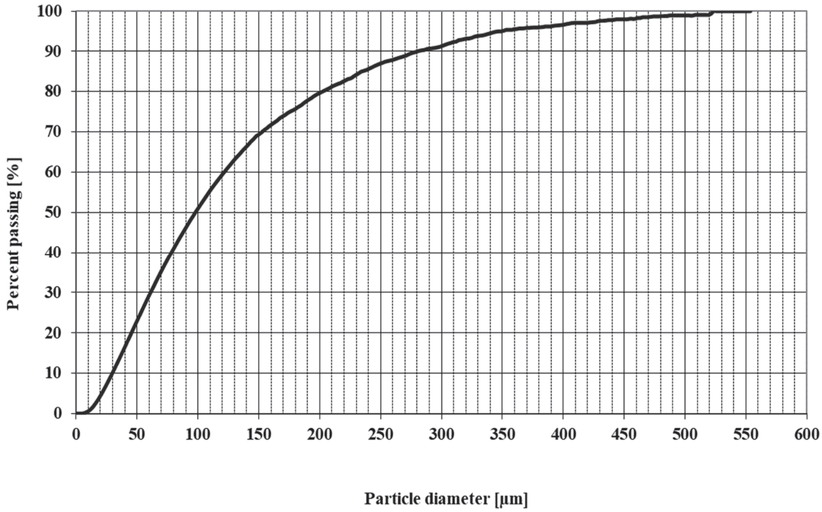


Fig. 1. The curve of the grain composition of the studied waste

In terms of the content of radioactive isotopes, indexes f_1 and f_2 defined for post-flotation waste (Table 1), fulfill the requirements for Poland (Polish legal act: Ordinance of the Council of Ministers of 2 January 2007). According to these regulations, the indexes f_1 and f_2 cannot exceed the values f_1 = 2 and f_2 = 400 Bq·kg^{-1} by more than 20% in the case of waste applied for the levelling of areas allocated for development, and f_1 = 3.5, f_2 = 1000 Bq·kg^{-1} in the case of other areas.

Table 1. The content of natural radioactive isotopes in post-flotation waste

Specification		Post-flotation waste
Specific Reactivity	K-40 [Bq·kg^{-1}]	102±6
	Ra-226 [Bq·kg^{-1}]	27±2
	Th-228 [Bq·kg^{-1}]	9±2
Reactivity Indexes	f_1 [-]	0.17±0.01

Table 2. Chemical composition of post-flotation waste

Chemical composition [% dry mass]											
P_2O_5	Mn_2O_5	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	ZnO	PbO	K_2O	Na_2O	SO_3
0.01	0.78	16.5	9.91	11.57	31.38	19.08	3.12	0.65	0.36	0.05	6.45
Trace element content [$mg \cdot kg^{-1}$]											
As	Cd	Cr	Cu	Co	Mo	Hg	Ni	Sn	Sr	Ti	V
0.711	0.109	25.621	460.499	5.097	0.134	0.027	33.937	0.003	87.056	104.092	59.96

Table 2 shows chemical composition of the studied post-flotation waste. The main elements of the studied waste are CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3, these components also occur naturally in soils.

The results of the studies on the leachability of chemical pollutants from the analysed waste are presented in Table 3. Substances leached out from waste can pollute the soils and ground waters. However, in Poland there is no legal act that clearly defines the load of pollutants that can be introduced into the environment with leachate. Consequently, the results were compared with maximum (accepted by Polish law) contents of pollutants introduced to the ground with the released sewage (Polish legal act: Ordinance of the Minister of Environment of 18 November 2014). Such a comparison results from the assumption that if the permissible amount of pollutant load, which is introduced into the ground with sewage is safe for the environment, then also the same amount of pollutant load introduced into the ground with leachate is safe (Klojzy-Karczmarczyk & Mazurek 2015). The obtained results show that the value of the pH of the aqueous extract and its content of heavy metals is lower than the one acceptable in sewage. Only the value of sulphates exceeds the acceptable one (1,354 mg $SO_4 \cdot dm^{-3}$, while the accepted value is 500 mg $SO_4 \cdot dm^{-3}$).

Table 3. Leachability of chemical pollutants from post-flotation waste

Kind of pollution	Post-flotation waste [mg·dm^{-3}]	Acceptable value according to [23] [mg·dm^{-3}]	Kind of pollution	Post-flotation waste [mg·dm^{-3}]	Acceptable value according to [23] [mg·dm^{-3}]
pH	7.85	6.5-9	Cadmium	0.0214	0.2
Sodium	1.48	800	Selenium	< 0.02	1
Potassium	2.75	80	Antimony	0.00023	0.3
Calcium	499.9	no requirements	Aluminium	0.002	3
Magnesium	33.2	no requirements	Chromium	0.004	0.5
Strontium	0.602	no requirements	Molybdenum	0.015	1
Manganese	2.039	no requirements	Titanium	< 0.002	1
Zinc	0.761	2	Arsenic	0.0012	0.1
Copper	0.0017	0.5	Chlorides	2.1	1,000
Nickel	0.006	0.5	Sulphates	1,354	500
Cobalt	0.0044	1	Cyanides	< 0.01	0.1
Lead	0.0024	0.5	Sulphides	< 0.05	0.2
Mercury	0.0001	0.03	COD	< 100	125

Because the concentration of sulphate ions in the leachate has been exceeded, direct addition of this waste to the ground in the process of biological reclamation is impossible. Therefore, it was checked whether reduction in the concentration of sulphate ions by blending waste with soil is possible. In the blend with soil, waste accounted for 10-50% of the mass; the results of leachability of sulphates are presented in Table 4. For the blend of soil with 10% of waste the concentration of sulphates is within the required limits. Importantly, in soil alone the leachability of sulphates was almost half of the acceptable value – 241 mg·dm^{-3}, the maximum acceptable level is 500 mg·dm^{-3}.

Table 4. The concentration of sulphate ions in the blend with waste with soil [mg·dm^{-3}]

Pollution	Blends of waste with soil					
	100% soil	90% soil + 10% waste	80% soil + 20% waste	70% soil + 30% waste	60% soil + 40% waste	50% soil + 50% waste
Sulphates	241	439	636	782	876	972

Pursuant to the Ordinance of the Minister of Environment of 1st September 2016 on the manner of conducting soil surface pollution assessments (Journal of Laws of 2016, item 1395), the concentration of substances causing particular risk for the soil surface should not be exceeded. For zinc, lead, and copper, the maximum allowed concentrations were exceeded in waste (Table 5). Due to high levels of these metal concentrations, detailed studies of their impact on plant growth were carried out.

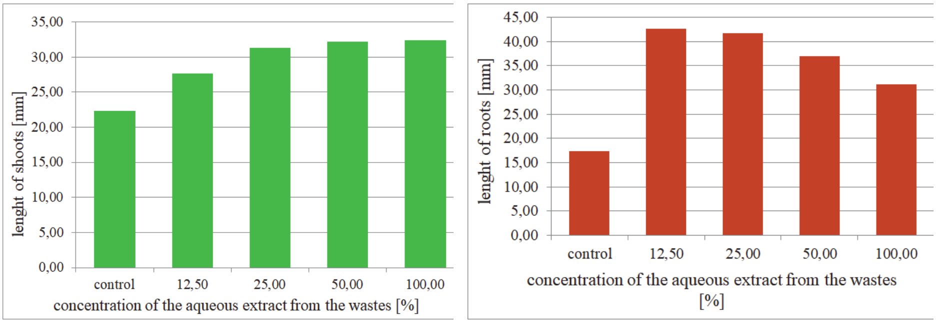
Table 5. Acceptable content of elements in soil (Journal of Laws of 2016 item 1395) and in waste

Substance	Soil – maximum acceptable value [mg·kg^{-1}] (Journal of Laws of 2016, item 1395)						The studied waste [mg·kg^{-1}]
	Group I	Group II-1	Group II-2	Group II-3	Group III	Group IV	
Arsenic (As)	25	10	20	50	50	100	0.711
Barium (Ba)	400	200	400	600	1,000	1,500	237.6
Chromium (Cr)	200	150	300	500	500	1,000	25.6
Tin (Sn)	20	10	20	40	100	350	0.003
Zinc (Zn)	500	300	500	1,000	1,000	2,000	25,084
Cadmium (Cd)	2	2	3	5	10	15	0.109

Table 5. cont.

Substance	Soil – maximum acceptable value [mg·kg^{-1}] (Journal of Laws of 2016, item 1395)						The studied waste [mg·kg^{-1}]
	Group I	Group II-1	Group II-2	Group II-3	Group III	Group IV	
Cobalt (Co)	50	20	30	50	100	200	5.097
Copper (Cu)	200	100	150	300	300	600	460.5
Molybdenum (Mo)	50	10	25	50	100	250	0.134
Nickel (Ni)	150	100	150	300	300	500	33.937
Lead (Pb)	200	100	250	500	500	600	6,064
Mercury (Hg)	5	2	4	5	10	30	0.027

First, the test of the phytotoxicity of aqueous extract of waste towards *Lepidium sativum* was carried out. It did not show any toxic impact on the plants. A stimulation of the development of the aerial parts of plants was observed with an increase in the concentration of aqueous extract in the medium, as compared to control objects (Fig. 2a). In the case of assessment of the rhizosphere, stimulation of the growth of roots was also found. The highest mean growth value was observed in concentration equaling 12.5%. Then a slight decrease of the roots growth with the growth of the concentration of aqueous extract from waste was observed, but the mean values were higher than the mean value in control (Fig. 2b). One should emphasize that the development of roots in all the experimental objects was significantly higher than in control objects without the addition of the aqueous extract (Fig. 2b and 3), and the rhizosphere was more developed.



(a) **(b)**

Fig. 2. Mean growth of *Lepidium sativum* in subsequent experimental objects (various concentrations); (a) aerial parts, (b) roots

In experimental objects in the concentration of aqueous extract equalling 25% or higher, the length of stems was significantly different than in control objects, as 3. presented in Fig. 3.

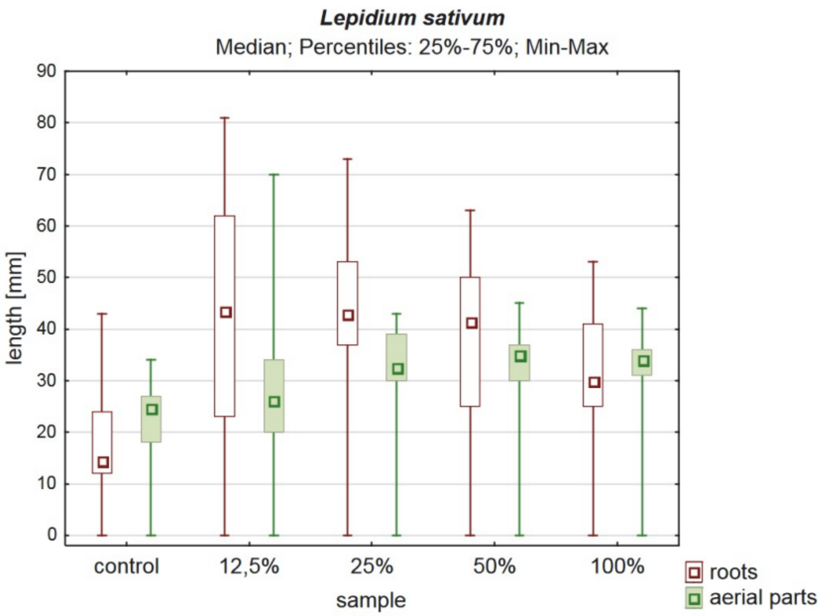


Fig. 3. The growth of *Lepidium sativum* after 72 hours of incubation of subsequent objects (for the studied concentrations)

The mean value and standard deviation for control sample and all dilutions are presented in Fig. 4. The highest values of standard deviation (25.7 for roots and 15.1 for steams) occur in the 12.5% aqueous extract concentration.

Because toxicity assessment should not be based on only one test type, pot tests were also carried out. Assuming that waste would not be a good substrate for plants, we carried out all experiments on different blends of this waste with the soil. Pot experiments revealed that the addition of waste to the medium in an amount of up to 30% caused the stimulation of germination in both species of test plants, while for higher concentrations (above 30%) seed germination in *Sinapis alba* and *Lepidium sativum* was observed to halt (Fig. 5 and Fig. 6).

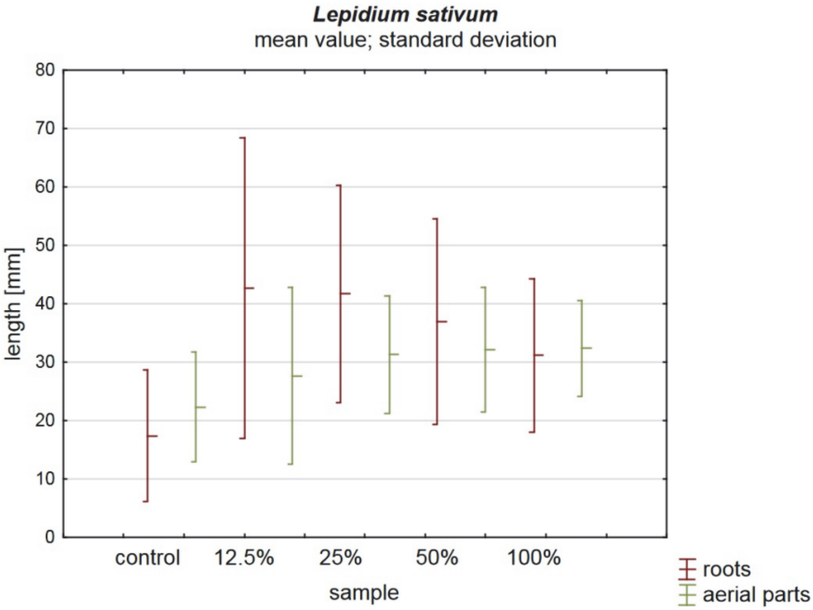


Fig. 4. Standard deviation of the growth of *Lepidium sativum* after 72 hours of incubation of subsequent objects (for the studied concentrations)

The addition of the examined waste to the medium in the amounts of 10, 20 and 30% was significantly beneficial for the development of the aerial parts of *Sinapis alba* compared to control objects cultivated on the universal medium. The limitation of the plant growth was observed for waste concentrations 40-50% in the medium, as was shown in Fig. 7a.

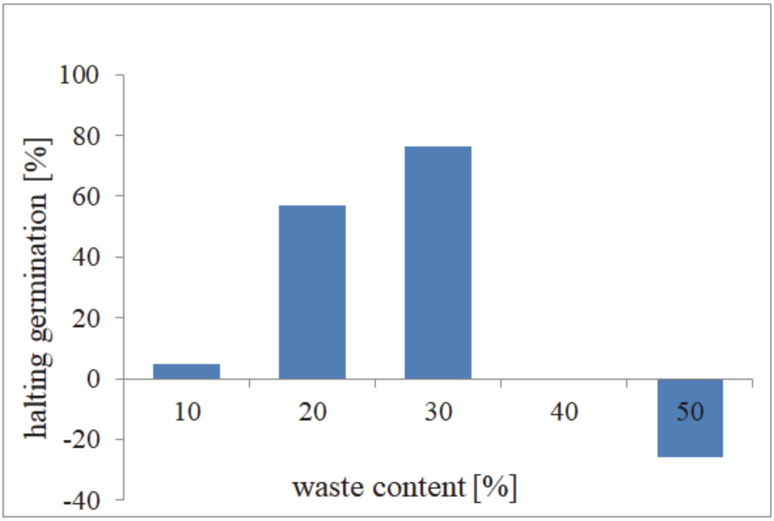


Fig. 5. Halting germination of *Lepidium sativum* in subsequent experimental objects (the percent of inhibition)

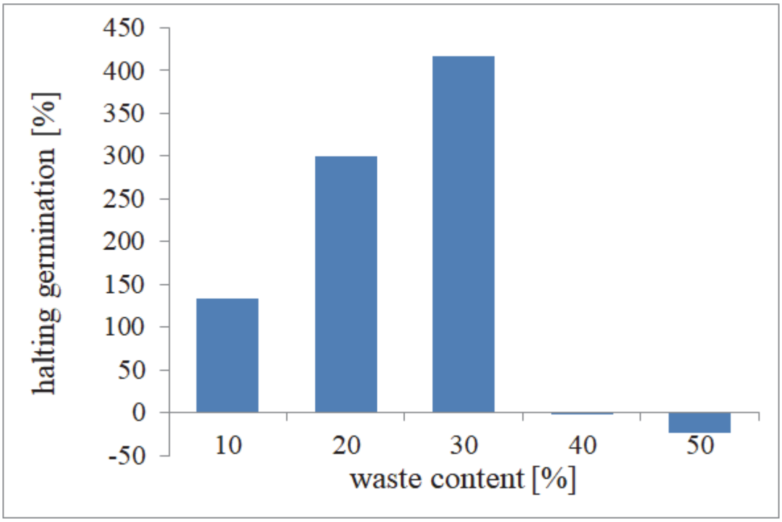


Fig. 6. Halting germination of *Sinapis alba* in subsequent experimental objects (the percent of inhibition)

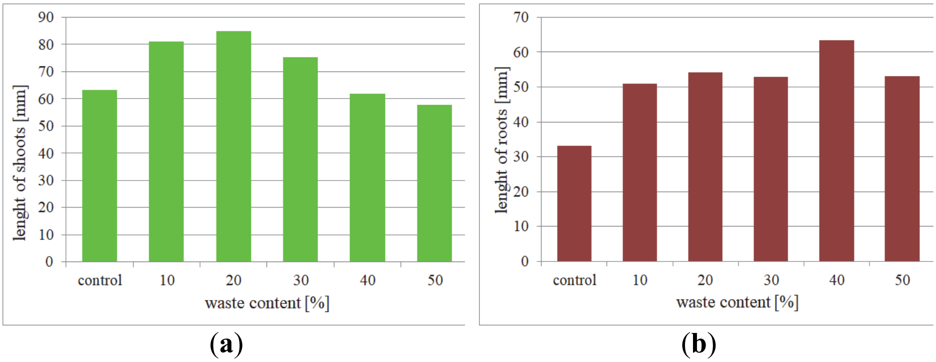


Fig. 7. Mean growth of *Sinapis alba* in subsequent experimental objects: (a) aerial parts; (b) roots

The addition of the examined waste to the medium was also beneficial for the development of the rhizosphere of *Sinapis alba*, the roots of test plants were longer (mean value) and more developed compared to plants from control objects (Fig. 7b). However, the Kolmogorov–Smirnov test did not show any significant differences between control objects and objects with 20% and 30% waste addition (Fig. 8). Significant differences were observed between the control and remaining objects.

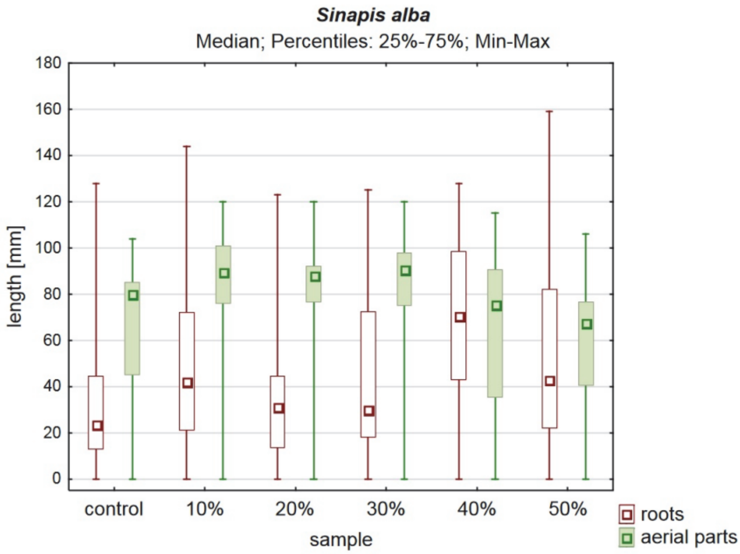


Fig. 8. The growth of roots and stems of *Sinapis alba* on the 7th day of the experiment on the medium with various additions of waste

Mean value and standard deviation for the control sample and all concentrations of waste in the medium are presented in Fig. 9. The highest values of standard deviation (42.5 for roots and 38.0 for steams) occur in concentrations of waste equaling 40% and 30% respectively.

A significant impact of the media containing the addition of waste on the biomass growth was observed (summary length of the aerial parts and roots) in *Sinapis alba* in the amount of up to 40% (Fig. 7 and 8). As already mentioned, the higher content of waste in the medium halted the germination of plants (after three days from sowing), but the growth of plant biomass, also for the concentration of 50%, was comparable with control objects.

In the case of the second test plant, *Lepidium sativum*, a beneficial impact of the content of waste in the medium on the development and growth of plants was found. For the content of 30% of waste in the medium, a significant stimulation of the growth of aerial parts was observed (Fig. 10a and 11), and the development of the rhizosphere was significantly higher in the objects with greater participation of waste (30% and 40%) than in control objects (Fig. 10b and 11).

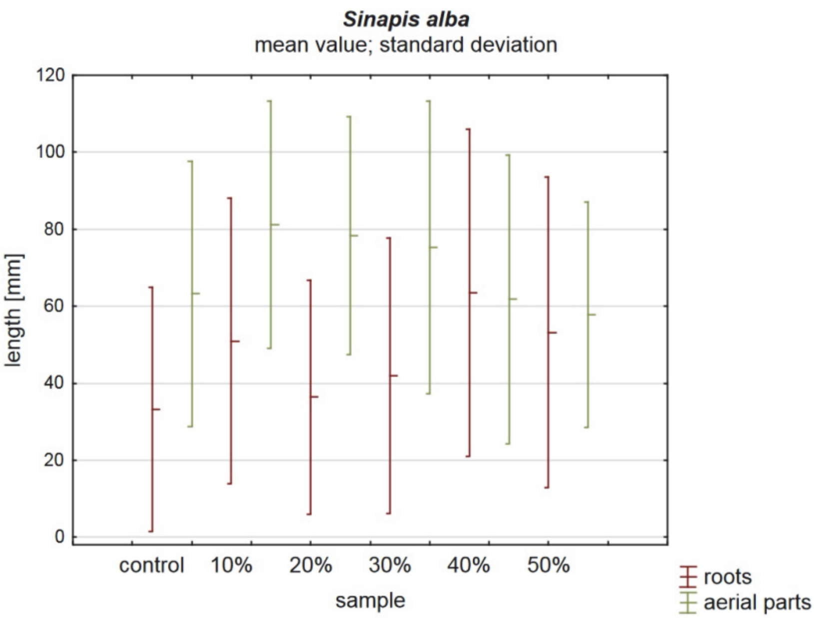


Fig. 9. Standard deviation of the growth of *Sinapis alba* on the 7th day of the experiment on the medium with various additions of waste

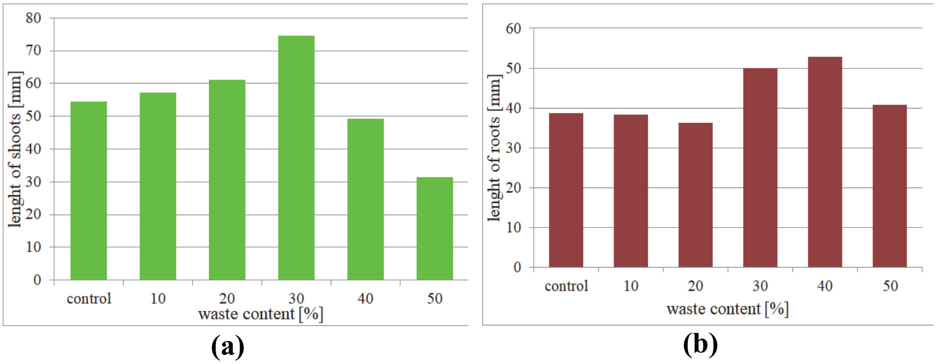


Fig. 10. Mean growth of *Lepidium sativum* in subsequent experimental objects: (a) aerial parts, (b) roots

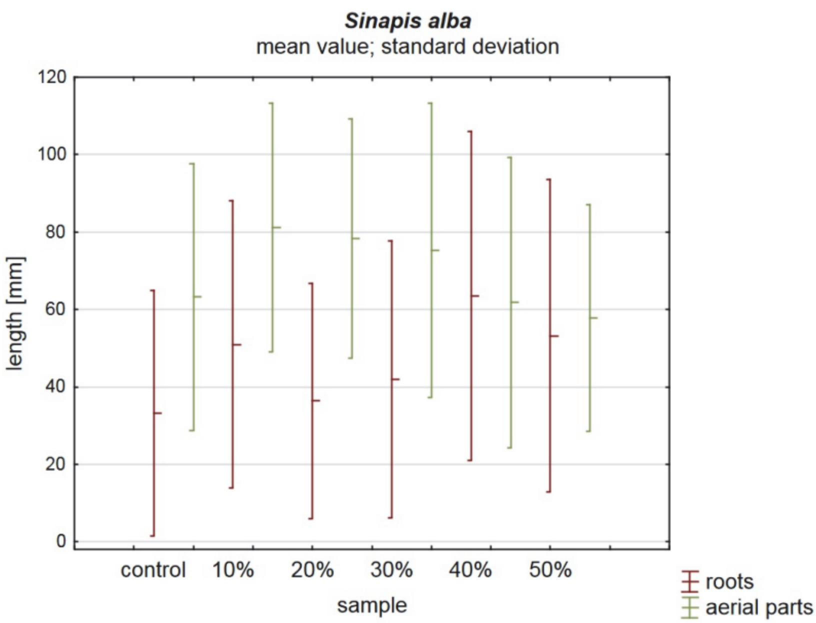


Fig. 11. The growth of roots and stems of *Lepidium sativum* on the 7th day of the experiment on the medium with various additions of waste

The mean value and standard deviation for the control sample and all concentrations of waste in the medium are presented in Fig. 12. The highest values of standard deviation (31.9 for roots and 32.2 for steams) occur in concentrations of waste equaling 40% and 10%, respectively.

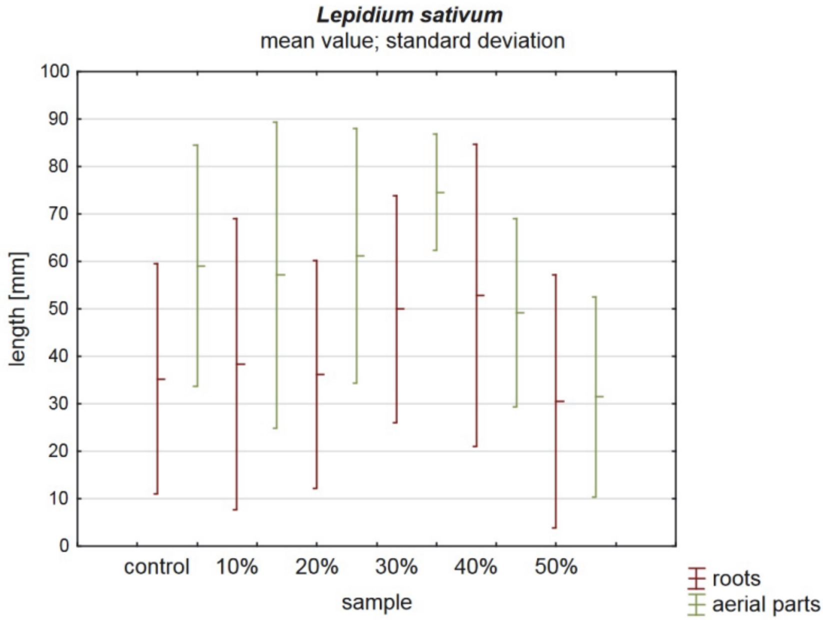


Fig. 12. Standard deviation of the growth of *Lepidium sativum* on the 7th day of the experiment on the medium with various additions of waste

The mean growth of the aerial parts and roots of *Lepidium sativum* was the highest in the group with 30% content of waste in the medium (the Kolmogorov-Smirnov test showed significant differences between this group and the control sample). The addition of 50% waste caused a marked decrease in the plant biomass growth, compared to the control of objects and objects of the lower content of waste.

4. Discussion

The studied waste is a fine-grained material. Its granulation is typical for post-flotation waste. It is the result of grinding of the waste before the flotation process. Considering grain composition, this waste can be used to produce a blend added to the soil during the biological reclamation process. The content of radioactive isotopes is also low and does not exceed the admissible values specified in Polish law for materials used for surface levelling.

When analyzing the results of ion concentrations in the leachate, it was found that only concentration of sulphates exceeded the acceptable values (1,354 mg $SO_4 \cdot dm^{-3}$, while the accepted value is 500 mg $SO_4 \cdot dm^{-3}$) according to Polish law. Other parameters were within the range of permissible standards.

However, due to the concentration of sulphates, the direct addition of this waste to the ground is impossible. So this waste cannot be used as the final product in a reclamation process. Its application will depend on whether it can be blended with other materials to lower the leachability of pollutants, which is practiced in engineering works and usually means mixing waste in proper quantities with the subsoil and other ingredients. It should be stressed that the level of sulphate ion concentration in the blend also depends on the concentration of these ions in the subsoil. Therefore, one should carry out studies with the ground, which will be applied in engineering works, to select a proper proportion of the blend. If such a blend meets all the quality requirements, it can become a product that will be used in reclamation. In our case, for the blend of soil with 10% of waste, the concentration of sulphates in the leachate was within the required limits. It may seem that a 10% waste addition is low, but it should be mentioned that in soil alone the leachability of sulphates was almost half of the acceptable value – 241 $mg \cdot dm^{-3}$. The concentration of metals in the leachate was within acceptable limits also, despite the high content of these metals in the waste. It should be noted that the studied waste had a high pH value, which can inhibit metals from being discharged into aqueous solutions. Excessively high metal concentrations in the analysed waste (according to Polish law) are also the reason why this waste (without dilution) cannot serve as the final product in the reclamation process - it may be toxic for the environment, including plants.

The phytotoxicity test with *Lepidium sativum* did not show any toxic impact of the waste aqueous extract on plants. Stimulation effects were observed in all samples with the addition of aqueous extract, as compared to control objects. In experimental objects, where the concentration of aqueous extract was 25% or higher, the lengths of roots and stems were significantly different from those in control objects. The highest mean value of root lengths was recorded for concentration 12.5%, while the highest mean value of stem lengths was recorded for concentration 100%. Pot experiments with *Sinapis alba* and *Lepidium sativum* showed that a small addition (up to 30%) of waste to the medium caused stimulation of seed germination, but higher concentrations (above 30%) halted germination. Similarly, in the case of early plant growth, beneficial effects were observed when the concentration of waste in the substrate did not exceed 30%. In experimental objects with higher waste concentrations, the shoots were shorter than in the control objects. Based on the toxicity tests carried out, we can assume that the waste addition to the subsoil in the amount of up to 30% will be beneficial for plant growth.

5. Conclusions

The assessment of the properties of the examined flotation waste of lower content of metals was to identify the possibility of applying this waste for engineering purposes, including especially its ecological utilization, e.g. in production a material (subsoil) for natural land reclamation. The obtained results were referred to the requirements defined in the legislation connected with the proposed direction of the utilization of this waste.

The conclusions from conducted research are as follows:

1. The analysis of the granulometric composition showed that the examined material of granulation corresponds to silty sands. In terms of the content of radioactive isotopes, this waste can be used in area levelling for development.
2. When comparing waste leachability with legal requirements for wastewater released to the soil, the excess of the load of sulphate ions was found. However, selecting a proper participation of waste in the blend with the ground, the required level of content could be obtained. In a similar way the decrease in the concentration of zinc, lead and copper can be obtained in the blend of waste with the ground.
3. The phytotoxicity test of aqueous extract with waste towards the test plants showed the stimulation of their growth compared to control objects. One should notice, however, that at the concentration of aqueous extract with waste of the values of 50% and higher, the development of the plant rhizosphere was slightly limited, compared to lower concentrations.
4. As a result of the pot experiments, it was found that the content of waste in the amount of 10-30% in the medium stimulated the germination of plants, as compared to the control objects, while the higher participation of waste in the blend caused the halting of the plant germination. Similar reactions were observed in the case of both species of test plants.
5. Observations of early growth revealed the stimulation of the growth of the aerial parts in test plants in experimental objects up to the content of 30% of waste in the medium. In the case of the rhizosphere, no halting effect was observed in roots.
6. Despite a relatively high level of the concentration of metals in the waste and a high leachability of sulphate ions, it is possible to select such a dose of waste for release to the ground, which will stimulate plant development.
7. The waste tested can be used in production of material (subsoil) for natural land reclamation.

Test plant species used in the experiments are species recommended for the tests of the phytotoxicity assessment (Traczewska 2011). It is reasonable to continue vegetation experiments based on plant species applied in biological reclamation (with the exception of agricultural remediation), biological lining of engineering objects or native species accustomed to local habitat conditions.

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Abstract

Rapid technological development in the second half of the 20th century has led to the production of large amounts of waste, which have been collected for years in landfills. The municipal solid waste deposited in landfills and waste from the mining and metallurgical industries constitutes a major environmental problem, but on the other hand these types of waste serve as a reservoir of raw materials, therefore, they are becoming more and more popular as a source of raw materials. Obtaining raw materials from landfills of waste requires technological operations, mainly known from open cast mining, and the application of processing technologies. As a result of landfill mining metal concentrates, construction materials or fuel are obtained; on the other hand often post-processing waste can be formed, which should be utilized, to reduce their nuisance to the environment.

Depending on their physicochemical properties, they can be used, e.g. in construction, road engineering, mining or land reclamation.

This paper presents research on the possibilities of using post-flotation waste from zinc and lead ores, deposited in old repositories, for land reclamation after waste reflotation. For this purpose, the physical and chemical properties of waste were examined, such as: grain composition, chemical composition, content of radioactive isotopes and leaching. To determine the ecotoxicity of the investigated wastes, vegetative experiments were carried out. These studies allowed the assessment of the impact of the tested wastes on selected test plant species. Among other things, the impact of waste on such physiological processes as germination of seeds and the growth of plants (roots and above-ground parts) were investigated. Despite relatively high metal concentration levels in waste and a high leachability of sulphate ions, a small dose of waste, which will be added to soil will stimulate plant growth. It was found, that the addition of waste to the substrate in quantities of 10-30% have accelerated germination of plants compared to control objects. In the case of higher waste content (over 30%) germination inhibition was observed. Similar reactions were observed for both test plant species. It was found that it is possible to select such a dose of waste for release to the ground, which will stimulate plant development. So, there is a possibility of using the tested waste to produce material (substrate) for natural land reclamation. The natural use of industrial waste can substantially contribute to solving the problem of the negative impact of deposited waste on natural environment.

Keywords:
ore processing waste, post-flotation waste, reclamation, raw material recovery, phytotoxicity, waste utilisation

Ocena możliwości wykorzystania odpadów poflotacyjnych z rud Zn-Pb jako materiału do naturalnej rekultywacji gruntów

Streszczenie

Szybki rozwój technologiczny, który nastąpił w drugiej połowie XX wieku, doprowadził do powstania dużych ilości odpadów, które gromadzone były przez lata na składowiskach. Stałe odpady komunalne, odpady z przemysłu wydobywczego i metalurgicznego zdeponowane na składowiskach stanowią poważny problem środowiskowy, ale jednocześnie są także istotnym rezerwuarem surowców i cieszą się coraz większym zainteresowaniem. Pozyskanie surowców ze składowisk wymaga stosowania operacji technologicznych z zakresu górnictwa odkrywkowego, a także zastosowania procesów przeróbczych. W efekcie tych procesów otrzymywane są koncentraty metali, materiały budowlane lub paliwo. Niestety, w procesach tych mogą także powstawać odpady przeróbcze, które należy w odpowiedni sposób zagospodarować, tak, żeby zmniejszyć ich uciążliwość dla środowiska. W zależności od właściwości fizykochemicznych odpadów wydobywczych i przeróbczych, można je stosować, np. w budownictwie, drogownictwie, górnictwie lub rekultywacji gruntów.

W pracy przedstawione zostały wyniki badań związanych z oceną możliwości przyrodniczego wykorzystania odpadów poflotacyjnych z rud cynku i ołowiu, zdeponowanych na starych składowiskach, po poddaniu ich przeróbce w celu odzysku z nich metali. Zbadano właściwości fizyczne i chemiczne odpadów, takie jak: skład ziarnowy, skład chemiczny w tym zawartość izotopów promieniotwórczych oraz wymywalność. W celu określenia ekotoksyczności badanych odpadów przeprowadzono doświadczenia wegetacyjne, które pozwoliły na ocenę wpływu badanych odpadów na wybrane gatunki roślin testowych. Badano między innymi wpływ odpadów na takie procesy fizjologiczne jak kiełkowanie nasion oraz wzrost roślin (korzeni i części nadziemnych). Wyniki przeprowadzonych doświadczeń wykazały, że pomimo stosunkowo wysokich poziomów stężenia metali w odpadach oraz wysokiej wymywalności jonów siarczanowych, niewielki dodatek odpadów do podłoża, na którym uprawiane były rośliny, miał korzystny wpływ na kiełkowanie roślin i przyrost ich biomasy. Stwierdzono, między innymi, że dodatek do podłoża odpadów w ilości 10-30% stymulował kiełkowanie roślin w porównaniu z obiektami kontrolnymi. W przypadku większej zawartości odpadów zaobserwowano zahamowanie kiełkowania. Podobne reakcje obserwowano w przypadku obu gatunków roślin testowych. Stwierdzono, że możliwe, jest dobranie takiej dawki odpadów w podłożu, która nie spowoduje wprowadzenia do gleby nadmiernych ilości zanieczyszczeń, natomiast korzystnie wpłynie na rozwój roślin. Istnieje więc możliwość wykorzystania badanych odpadów do produkcji materiału (podłoża) do naturalnej rekultywacji gruntów. Naturalne wykorzystanie odpadów przemysłowych może znacząco przyczynić się do rozwiązania problemu negatywnego wpływu składowanych odpadów przemysłowych, po przeróbce rud metali, na środowisko.

Słowa kluczowe:
odpady z przeróbki rud metali; odpady poflotacyjne, rekultywacja,
odzyskiwanie surowców; fitotoksyczność; utylizacja odpadów

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Biological Control as an Alternative Method of Protecting Crops Against Fungal Pathogens

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1. Introduction

The intensive development of agriculture in the 20th century has led to a significant increase in food production through the cultivation of efficient crop varieties and the widespread use of fertilizers and chemical plant protection products. Intensive agricultural production has contributed significantly to environmental degradation and pollution. The great challenge for modern societies is to increase plant production in a sustainable, environmentally friendly way, assuming that global food production must keep pace with an increasingly urbanized and growing population. Another problem is the adverse effects of climate change. In order to feed the world, the existing approach to agriculture should be re-examined, which includes the use of artificial fertilizers, herbicides, fungicides and insecticides (Morrissey et al., 2004). Meeting the global challenges of climate change and population growth, and better understanding and control of soil processes will be one of the most important challenges of science in the next decade (McNear Jr. 2013). An increasing number of scientists dealing with increasing the efficiency of agricultural production can see the potential hidden in the roots and adjacent soil included the richness of microorganisms, called the rhizosphere. It is even believed that the roots and rhizosphere are the key to the further development of agriculture (Gewin 2010). In the rhizosphere there are many interactions between different groups of microorganisms and between microorganisms and plants. They are both positive and negative (Whipps 2001). Positive interactions between microorganisms and plants can be symbiotic or non-symbiotic and contribute to the stimulation of plant growth (Glick 2012, Kalitkiewicz & Kępczyńska 2008), whereas between microorganisms they can rely on the mutual use of metabolism products (Kołwzan et al. 2006). Negative interactions between microorganisms and plants are caused by plant pathogens and they lead to disruption of basic physiological functions of plants, causing diseases and thus a decrease in productivity in agricultural production. Negative interactions between microorganisms can be used to biological control of plant pathogens. Importantly, the use of microorganisms to inhibit the development of plant diseases is an environmentally friendly solution (Bolwerk & Lugtenberg 2005, Lugtenberg & Kamilova 2009). Bacteria can limit the development of pathogens, including through competition for space on the root, reducing iron availability to pathogens by chelation to siderophores, synthesis of antifungal and antibacterial metabolites, including antibiotics and production of enzymes lysing fungal cell walls (Glick, 2012). Rhizobacteria that produce siderophores may limit the occurrence of certain diseases by hindering phytopathogens to obtain enough iron, thus limiting their ability to develop properly. They achieve this mainly due to the fact that the siderophores have a much greater affinity for iron binding compared to fungal pathogens (Dowling et al. 1996). Many bacteria also produce peptide antibiotics. These are oligopeptides that inhibit the synthesis of cell walls of pathogens (Maksimov et al 2011), including 2,4 - diacetylphloroglucinol (2,4-DAPG), hydrogen cyanide, oomycin A, phenazine, tensin and cyclic lipopeptides produced by bacteria from the genus *Pseudomonads*, as well as oligomycin A, zwittermycin and xantobacin produced by *Bacillus*, *Streptomyces* and *Stenotrophomonas* spp. (Compant et al. 2005). Extremely important is the ability of bacteria to produce enzymes lysing the cell walls of the fungal pathogens and thereby limit their spreading on the soil. These enzymes include chitinases, cellulases, β-1,3 glucanases, proteases and lipases. Chitinases and glucanases are key enzymes responsible for the hydrolysis of chitin and glucan, the main components of fungal cell walls (Kisiel & Kępczyńska 2017). It has been proven the effectiveness of antifungal activity of bacteria, including to *Streptomyces*, *Bacillus*, *Pseudomonas* or *Serratia* against such plant pathogens as *Fusarium*, *Botrytis*, *Rhizoctonia* and many others (Kisiel & Kępczyńska 2017).

The aim of this study was to determine the effectiveness of bacteria isolated from alfalfa (*Medicago sativa*) rhizosphere to reduce the growth of fungal pathogens, as well as to check the possible mechanisms used for this purpose by these bacteria.

2. Material and methods

A total of 16 strains of bacteria were isolated from the soil collected from the alfalfa (*Medicago sativa*) rhizosphere cultivated near Stargard (Zachodniopomorskie). Isolates were subjected to molecular identification based on the 16S rRNA gene fragment (Kisiel & Kępczyńska 2016). The present study used the following strains: from the family *Bacillaceae* (*Bacillus niacini* KK 1b, *B. megaterium* KK 11, *Lysinibacillus fusiformis* KK 2 i *L. fusiformis* KK 3, *Paenibacillus* *odorifer* KK 1a, *P. borealis* KK 4, *P. amylolyticus* KK 9a), family *Pseudomonadaceae* (*Pseudomonas brassicacearum* KK 5, *P. corrugata* KK 7 and *P. corrugata* KK 12), family *Xantomonadaceae* (*Stenotrophomonas maltophilia* KK 8b and *S. maltophilia* KK 9b), family *Enterobacteriaceae* (*Citrobacter muliniae* KK 10, *Leclercia adecarboxylata* KK 6 and *Raoultella planticola* KK 8a) and family *Rhizobiaceae* (*Sinorhizobium meliloti* KK 13).

Fungal pathogens used in this study *Phoma medicaginis* Malbr. strain Ph 33 and *Fusarium culmorum* strain Cul-3 were made available from the collection of the Institute of Plant Genetics, PAS in Poznań. A sporulating mycelium was used to make an inoculum. Using a hemocytometer (Bürker chamber), the density of the spore suspension was determined using the formula:

$$Ld = a \times b \times 2500 \times 1000$$

where:
Ld – number of spores in 1 ml,
a – average number of spores,
b – dilution used.

The studies used a suspension with a density of 10^6 spores per 1 ml of inoculum.

The effect of bacteria on fungal growth evaluated on solid and liquid media. In the first method, 7-day *Fusarium culmorum* or *Phoma medicaginis* culture and bacterial colonies were placed on opposite poles of the dish with PDA medium. After 7 days, the diameter of the mycelium was measured. To assess the growth of the fungus in liquid cultures, bacteria grown in liquid medium Czapek DOX were used. The culture supernatant was aseptically filtered through 0.45 μm sterile membrane filters. For the falcon tubes containing the Czapek DOX medium, in combination with the 5% bacterial culture filtrate, 100 μl of the inoculum was added. After 5 days, the cultures were placed on filter paper and dried, and weighed to determine the dry weight. The inhibition rate of fungal growth in both cases was expressed in relation to the control being pure fungal cultures.

The activity of β-1,3-glucanase in bacterial cells was determined by spectrophotometric method for Lim et al. (1991). Bacteria were grown in M9 or DF media with the addition of 0.02% laminarin (from *Laminaria digitata*). Measurements were made in a plate spectrophotometer at 540 nm. The calculations were made after determining the standard curve for glucose in the range of 0 - 10 mM. The unit of β-1,3-glucanase activity was defined as 1 μmol of released glucose/mg protein/min.

Chitinase activity was determined based on the ability of the strains to hydrolyze chitin in the medium. The medium was supplemented with a suspension of colloidal chitin, prepared according to the procedure described by Rodriguez-Kabana et al. (1983). The medium for determining the chitinase activity consisted of (g/l) $(NH_4)_2SO_4$ – 1.0; KH_2PO_4 – 1.34; yeast extract – 5.0; bacteriological agar – 20.0; 0.01 M Tris-HCl topped to 1L and 1% colloidal chitin. Bacterial colonies were applied to the plates and incubated at 28°C for 14 days. After this time the clearing zones around the colony were measured.

The production of siderophores was determined using CAS-Agar medium and assessing clearing zones around the bacterial colonies. The Chrome azurol S (CAS) culture medium was prepared according to the procedure according to Alexander and Zuberer (1991). HDTMA, a cationic detergent that stabilizes Fe-CAS and gives a blue color, which turns orange in the presence of siderophores, was added to the medium. Bacteria were inoculated into this prepared medium and incubated in a thermostat at 28°C for 5 days. After this time, the ability to produce siderophores was estimated based on the diameter of the orange zones visible after iron binding by the siderophores. To evaluate the effects of siderophores and chitinases used the 5-grade scale: „-" – 0-0,5 mm; „+/-" – 0,5-1 mm; „+" – 1-2 mm; „++" – 2- 3 mm; „+++" - > 3 mm.

3. Results and discussion

The pathogens that most often attack alfalfa crop (*Fusarium culmorum* Cul-3 oraz *Phoma medicaginis* Ph-33) was used to evaluate the potential use of bacteria for biological control against fungal pathogens. It was found that all bacterial strains inhibit the growth of *F. culmorum* Cul-3 on both solid and liquid media (Fig. 1A). The most inhibitory effect on this fungus on solid medium, as much as 42.2% showed *Raoultella planticola* KK 8a strain. A significant inhibition of fungal growth was also caused by *Pseudomonas corrugata* KK 12 strain (39.3%) and both strains *Stenotrophomonas maltophilia* KK 8b (36.4%) and KK 9b (31.1%). A higher degree of fungal growth inhibition was observed on the liquid medium in the presence of bacterial filtrates. Similarly to the solid medium, the most effective strains were *Raoultella planticola* KK 8a (64.5%) and *Pseudomonas corrugata* KK 12 (46.5%). Previously, antifungal activity of bacteria of the genus *Pseudomonas* and *Bacillus* has been demonstrated against pathogens such as *Fusarium oxysporum* and *Rhizoctonia solani* or *Sclerotinum rolfsii* (Wahyudi et al. 2011a and b). The strains of the genus *Pseudomonas* (Khan et al. 2006) and *Bacillus*, as well as *Stenotrophomonas* (Kamil et al. 2007) proved effective against *Fusarium culmorum*.

All isolated strains also inhibited the growth of *P. medicaginis* (`. 1B). The highest inhibition of this fungus on solid media was found for *Pseudomonas brassicacearum* KK 5, it was 35.5%. Two strains from the *Bacillaceae* family, *Lysinibacillus fusiformis* KK 3 and *Bacillus megaterium* KK 11 also significantly limited the growth of this fungus by 25.1% and 22.6%, respectively. In liquid cultures of *P. medicaginis*, as in the case of *Fusarium*, most strains showed a higher ability to inhibit fungal growth compared to cultures on solid media. *Pseudomonas corrugata* KK 7 and *Leclercia adecarboxylata* KK 6 inhibited the growth of fungal pathogen in 46%, while strains from the *Enterobacteriaceae* family, *Raoultella planticola* KK 8a and *Citrobacter murliniae* KK 10, respectively in 35.9% and 33.5%. Efficacy of bacteria in limiting the development of *Phoma medicaginis*, one of the most dangerous fungal pathogens of alfalfa, has been previously observed for bacteria of the genus *Pseudomonas* (Guevara & Lukezic 2000), *Sinorhizobium* (Mrabet et al. 2011) or *Bacillus* (Slimene et al. 2015).

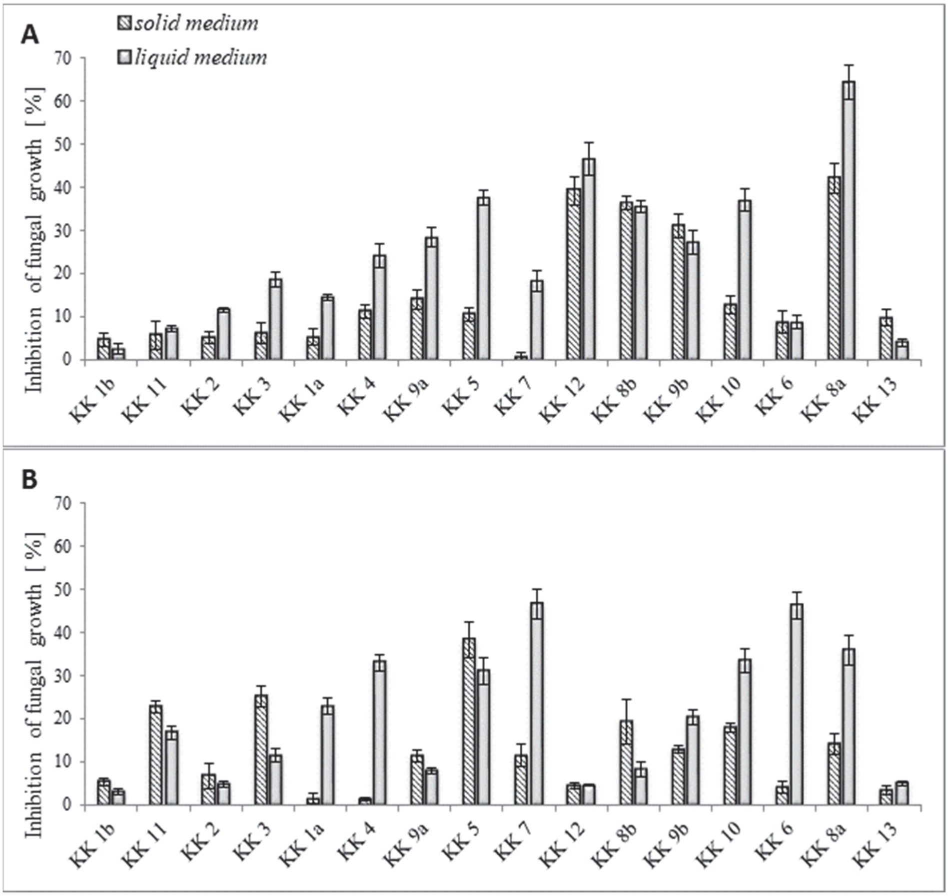

Fig. 1. Inhibition of growth *Fusarium culmorum* Cul-3 (A) and *Phoma medicaginis* Ph-33 (B) by bacteria

Various mechanisms were found as the core of the antifungal activity of rhizobacteria: the ability to produce antibiotics and metabolites (HCN, siderophores, 2,4-DAPG) and cell wall lysing enzymes (glucanases and chitinases) (Beneduzi et al. 2012). After confirming that all strains of isolated bacteria were more or less able to inhibit the growth of both fungal pathogens *F. culmorum* Cul-3 and *P. medicaginis* Ph-33, it was necessary to check whether this could be due to the production of enzymes that hydrolyse the fungal cell wall or in the case of *Pseudomonas* strains, the ability to produce the 2,4-DAPG antibiotic (Table 1).

Table 1. Bacterial features affecting antifungal activity

Strain of bacteria	β-1,3-glucanase activity (μM glucose/mg protein/min)	chitinase activity	siderophore production
KK 1b	62,7 ± 5,1	+	-
KK 11	13,3 ± 7,7	-	+++
KK 2	70 ± 0,2	-	-
KK 3	60 ± 6,8	-	+
KK 1a	51,7 ± 9,1	++	-
KK 4	72,5 ± 5,9	+	+
KK 9a	37,3 ± 11	-	+++
KK 5	12,8 ± 5,1	-	+++
KK 7	2,3 ± 0,1	-	+++
KK12	13,2 ± 7,7	-	++
KK 8b	9,2 ± 4,7	+++	+++
KK 9b	43,5 ± 11,9	+	++
KK 10	6 ± 2,4	-	++
KK 6	16,3 ± 3,3	-	+++
KK 8a	2,4 ± 0,2	-	+
KK 13	2,2 ± 0,4	-	+

All the bacterial strains isolated from *M. sativa* rhizosphere showed β-1,3-glucanase activity in the range of 2.3 to 72.5 μmol glucose/mg protein/min. The highest activity of this enzyme was found in strains belonging to the family *Bacilliaceae*, and in particular in *Paenibacillus borealis* KK 4 (72.5 μM), both strains belonging to *Lysinibacillus fusiformis* KK 2 (70 μM) and KK 3 (60 μM) and *Bacillus niacini* KK 1b (62.7). Of the other strains, fairly high activity of this enzyme was found in *S. maltophilia* KK 9b (43.5). The lowest activity (2.2) was observed for the *Sinorhizobium meliloti* KK 13. Of all the isolated bacterial strains, only five showed chitinolytic activity. The highest activity of chitinases was characterized by a strain of *Stenotrophomonas maltophilia* KK 8b, the slightly lower *Paenibacillus odorifer* KK 1a, the lowest *Bacillus niacini* KK 1b, *Paenibacillus borealis* KK 4 and *S. maltophilia* KK 9b. In addition, thirteen out of the 16 analyzed strains of rhizobacteria were decomposing the colored complex present in the CAS medium (CAS-Fe(III)), was evidence of the production of iron chelating compounds. The most efficient siderophore producers were the following 6 strains: *Bacillus megaterium* KK 11, *Paenibacillus amylolyticus* KK 9a, *Pseudomonas brassicacearum* KK 5, *P. corrugata* KK 7, *Stenotrophomonas maltophilia* KK 8b, *Leclercia adecarboxylata* KK 6. Due to the ability to produce chelating compounds, whose primary function is to chelate the ferric iron, bacterial make it available for plant thereby while limiting the availability of the element for pathogens (Glick 2012). In earlier studies siderophores has been detected among others in bacteria of the genus *Pseudomonas* (Luján et al. 2015), *Bacillus* (Wahyudi et al. 2011b) or *Stenotrophomonas* (Kumar & Audipudi 2015).

Ahmad et al. (2008) showed a close relationship between the anti-fungal effect of bacteria and the production of HCN and siderophores. Similarly, as in the case of these studies, in other studies the production of bacterial chitinases did not correlated with the fungal growth inhibition (Wahyudi et al 2011a). In turn, Slimene et al. (2015) showed that in *Bacillus licheniformis* S213 rhizobacteria, the activity of chitinolytic enzymes can be increased by cultivating them on the medium with the addition of colloidal chitin, which provided high activity this bacteria in inhibiting the growth of fungi, such as *F culmorum* or *P. medicaginis*. The same bacteria cultured on medium without colloidal chitin limited the growth of these fungal pathogens to little or none at all. This may be due to the fact that bacterial chitinases activate with a significant delay, which is related with the long time needed for the degradation of high molecular weight chitin that is found in the cell walls of fungi. In addition, the production of chitinases by bacteria is closely related to the concentration of colloidal chitin, incubation time and nutrient composition or pH (Gomaa 2012).

It is known that not only fungal cell wall hydrolysing enzymes, i.e. glucanases and chitinases, are involved in inhibiting the growth of fungal pathogens, but also antibiotics and secondary metabolites produced by bacteria. This group of antimicrobial compounds includes the broad-spectrum antibiotic, 2,4-diacethylphloroglucinol (2,4-DAPG). *Pseudomonas* bacteria can produce this metabolite (Raaijmakers et al. 1997). Of all three isolates from the Pseudomonadaceae family analyzed in this work in *P. brassicacearum* KK 5 and *P. corrugata* KK 12, the presence of the *phlD* gene, responsible for the synthesis of monoacetylglucinol, the precursor 2,4-DAPG, was previously confirmed (Kisiel & Kępczyńska 2016). This gene has been detected in many strains belonging to *Pseudomonas*, including *P. brassicacearum* (Kwak & Weller 2013).

The observed inhibition of the growth of both pathogens *Medicago* spp. (*Phoma medicaginis* and *Fusarium culmorum*) by *P. brassicacearum* KK 5 and

P. corrugata KK 12 may be probably the resultant production of the metabolite 2,4-DAPG and β-glucanase activity. Participation in this process does not take endocitinase, in three *Pseudomonas* species no activity of these enzymes has been detected. It is difficult to determine which mechanisms are crucial for antifungal activity. The most effective bacteria that inhibit fungal growth included both, which at the same time were capable of high production of siderophores and were found to have chitinases and glucanases activity, such as *Stenotrophomonas maltophilia* KK 8b and those in which the production of siderophores was at a low level, as was the activity of enzymes that hydrolyzed fungal cell walls, such as *Stenotrophomonas maltophilia* KK 8a.

4. Conclusions

Biological control can be an alternative to chemical plant protection products like pesticides and help reduce them and the same contribute to protect the environment. This study confirms the potential of bacteria isolated from the rhizosphere to control the dangerous biological fungal pathogens that limit crops.

1. The results presented here confirm that bacteria isolated from the Medicago sativa rhizosphere were able to biological control of fungal pathogens such as Fusarium culmorum and Phoma medicaginis in vitro.
2. The observed inhibition of growth of these pathogens by the tested bacteria may be related to the production of enzymes that hydrolyse fungal cell walls, i.e. chitinases and glucanases, and in the case of bacteria of the *Pseudomonas* genus, the production of the secondary metabolite like 2,4-DAPG.
3. Potentially, in limiting the development of fungal pathogens may also be the useful ability of bacteria to produce siderophores that bind iron and thus prevent the fungus from taking this element.

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Abstract

Progressive degradation of the environment caused, among others, by the excessive use of chemical pesticides forces us to look for alternative methods of protecting crops against pathogens. Definitely beneficial for the environment, but also, as confirmed by numerous studies, the use of biological control mechanisms can be an effective solution. The bacteria can inhibit the growth of fungi through the production of enzymes that lyse their cell walls, such as chitinases and glucanases, but also by limiting the availability of microelements important to growth, such as iron, by chelating them to siderophores, and finally producing antibiotics and secondary metabolites, like 2,4-DAPG.

The present study examined 16 strains of bacteria isolated from *Medicago sativa* rhizosphere for their suitability for the control of fungal pathogens such as *Fusarium culmorum* and *Phoma medicaginis*. Among of bacteria were strains belonging to the family *Bacillaceae* (genus *Bacillus*, *Lysinibacillus* and *Paenibacillus*), the family *Pseudomonadaceae* (genus *Pseudomonas*), the family *Xantomonadaceae* (genus *Stenotrophomonas*) of the *Enterobacteriaceae* family (genus *Citrobacter*, *Leclercia* and *Raoultella*) and of the family *Rhizobiaceae* (genus *Sinorhizobium*).

In vitro, both on solid and liquid media, all bacterial strains were able to limit the growth of *Fusarium culmorum* and *Phoma medicaginis*. The effective inhibitors of *Fusarium culmorum* Cul-3 were *Roultella planticola* KK 8a, *Pseudomonas corrugata* KK

12, and both strains belonging to *Stenotrophomonas maltophilia* KK 8b and KK 9b. Limiting the development of the second *Medicago* pathogen, *Phoma medicaginis*, was the most effective after the use of *Pseudomonas corrugata* KK 7, *Leclercia adecarboxylata* KK 6 and *Pseudomonas brassicacearum* KK 5.

By studying the mechanisms that may be potential for bacteria to inhibit the growth of fungi was tested production of lytic enzymes the cell walls, and siderophores. All bacterial strains showed β-1,3-glucanase activity in the range of 2.3 to 72.5 μmol glucose /mg protein/min. Five strains showed chitinolytic activity, with *Stenotrophomonas maltophilia* KK 8b being the most active. Thirteen of the 16 analyzed strains of rhizobacteria were able to produce iron chelating compounds, siderophores. In addition, the presence of the *phlD* gene was confirmed in *Pseudomonas brassicacearum* KK 5 and *P. corrugata* KK 12, which may indicate the production of 2,4-DAPG.

The results obtained indicate that the bacteria isolated from the rhizosphere have the potential for biological control of fungal pathogens, which limit the plant cultivation, using various mechanisms. The use of rhizobacteria as biopesticides is an environmentally friendly alternative to chemical plant protection products.

Keywords:
fungal pathogens, biological control, rhizobacteria

Zwalczanie biologiczne jako alternatywna metoda ochrony upraw przed patogenami grzybowymi

Streszczenie

Postępująca degradacja środowiska spowodowana między innymi nadmiernym wykorzystywaniem chemicznych środków ochrony roślin zmusza nas do poszukiwania alternatywnych metod zabezpieczania upraw przed patogenami. Zdecydowanie korzystnym dla środowiska ale również, jak potwierdzają liczne badania, skutecznym rozwiązaniem może być wykorzystanie mechanizmów zwalczania biologicznego. Bakterie mogą ograniczyć rozwój patogenów grzybowych poprzez produkcję enzymów lizujących ich ściany komórkowe, takich jak chitynazy i glukanazy ale także poprzez ograniczenie dostępności ważnych dla ich wzrostu mikroelementów, jak żelazo, chelatując je do sideroforów, czy wreszcie produkując grzybobójcze antybiotyki i metabolity wtórne, jak 2,4-DAPG.

W niniejszych badaniach przeanalizowano 16 szczepów bakterii wyizolowanych z ryzosfery *Medicago sativa* pod kątem ich przydatności do zwalczania patogenów grzybowych takich jak *Fusarium culmorum* i *Phoma medicaginis*. Wśród bakterii były szczepy należące do rodziny *Bacillaceae* (rodzaju *Bacillus*, *Lysinibacillus* i *Paenibacillus*), z rodziny *Pseudomonadaceae* (rodzaju *Pseudomonas*), z rodziny *Xantomonadaceae* (rodzaju *Stenotrophomonas*), z rodziny *Enterobacteriaceae* (rodzaju *Citrobacter*, *Leclercia* i *Raoultella*) oraz z rodziny *Rhizobiaceae* (rodzaju *Sinorhizobium*).

W warunkach *in vitro* zarówno na pożywkach stałych jak i płynnych wszystkie analizowane szczepy bakterii były zdolne do ograniczenia wzrostu *Fusarium culmorum* oraz *Phoma medicaginis.* Do skutecznych inhibitorów rozwoju *Fusarium culmorum* Cul-

3 należy zaliczyć szczepy *Roultella planticola* KK 8a, *Pseudomonas corrugata* KK 12, oraz oba szczepy należące do *Stenotrophomonas maltophilia* KK 8b i KK 9b. Ograniczenie rozwoju drugiego patogena *Medicago*, tj. grzyba *Phoma medicaginis* było najskuteczniejsze po zastosowaniu szczepów *Pseudomonas corrugata* KK 7, *Leclercia adecarboxylata* KK 6 i *Pseudomonas brassicacearum* KK 5.

Badając mechanizmy, które mogą stać za potencjałem bakterii do hamowania wzrostu grzybów sprawdzono produkcję enzymów lizujących ściany komórkowe oraz sideroforów. Wszystkie szczepy bakterii wykazywały aktywność β-1,3-glukanazy w zakresie od 2,3 do 72,5 µmol glukozy/mg białka/min. Pięć szczepów wykazało aktywność chitynolityczną, największą aktywnością charakteryzował się szczep *Stenotrophomonas maltophilia* KK 8b. Trzynaście z 16 analizowanych szczepów ryzobakterii było zdolnych do produkcji związków chelatujących żelazo, sideroforów. Ponadto u *Pseudomonas brassicacearum* KK 5 i *P. corrugata* KK 12 potwierdzono obecnośc genu *phlD*, co może świadczyć o produkcji 2,4-DAPG.

Jak wynika z przeprowadzonych badań bakterie izolowane z ryzosfery posiadają potencjał do zwalczania patogenów grzybowych ograniczających uprawy, wykorzystując do tego szereg mechanizmów. Zastosowanie ryzobakterii jako biopestycydy jest przyjazną dla środowiska alternatywą dla chemicznych środków ochrony roślin.

Słowa kluczowe:
patogeny grzybowe, zwalczanie biologiczne, ryzobakterie

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Impact of Changes of the Permissible Railway Noise Levels on Possibilities of Spatial Management in Urban Areas

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1. Introduction

Topic of spatial harmony and life quality are very important in areas located close to railway or situated on post-railway grounds. It was especially important after changes in Law of spatial planning and management, which enable new developments in closed areas of railway transport. Issues of spatial management of railway and post-railway areas are significant for companies, local administration and inhabitants. Evidence of such a situation was conference entitled Spatial planning in post-railway areas, held by Ministry of Infrastructure and Development in October 13th 2015. Lecturers from Polish State Railways, government, local administration, transport experts, designers and scientists discussed how to use railway and discard areas in proper way to create valuable areas for further settlement and investments. It was mentioned, that spatial, economic and demographic development of big cities caused changes like localisation of train lanes inside city centres and housing districts. In the same time, post-railway areas became potential reserve for new functions and are under strong pressure of investing. In the present time this type of landscape in terms of aesthetics and management is different than in surrounding parts of the city (Ryś 2015).

Proper planning of surfaces localised near railway should take into account their real pressure on the environment. Noise is perceived as most important and strongest impact of railway on environment (Makosz 2015). Based on the reports of EU countries, which are collected by European Environmental Agency in the year 2010 the railway noise was a problem for about 12 millions of inhabitants during day time (>55 dB (A)) and for about 9 millions of people during night time (>50 dB(A)) (Clausen 2012).

Taking this into account localisation of new settlements and services near train lanes should be preceded by acoustic analyses. But in the literature related to this issue there are more elaborations touching problem of sound level along roads (Popławski et al. 2012, Profaska 2012, Podawca 2014) or even caused by domestic appliances (Zagubień & Wolniewicz 2017) rather than railways (Deja & Kopeć 2016). Railway noise is perceived as a factor decreasing life quality of citizens and was surveyed in countries like Latvia, Turkey, Korea, Japan and EU (Lim et al. 2006, Paozalyte et al. 2011, Clausen 2012, Demir et al. 2016).

2. Aim and scope analysis

Aim of studies was to evaluate consequences of the law changes in October 1st, 2012 related to increase of permissible noise levels from train lanes for different functions of particular city areas.

To describe this problem actual courses of equal-loudness contours were presented using acoustic maps of Warsaw for the 2017 prepared as digital maps in PUWG 200 system by BMTcom, SVANTEK and PVO companies for President of Warsaw. Following threshold contours were used:

- LN50(2007) equal-loudness contours 50 dB presenting permissible long term average sound level A evaluated for all night times in years 2007-2012,
- LN59(2012) equal-loudness contours 59 dB presenting permissible long term average sound level A after October 1st, 2012,
- LDWN55(2007) equal-loudness contours 55 dB presenting permissible long term average sound level A evaluated for day time (8:00 – 18:00), evening time (18:00-22:00) and night time (22:00-6:00) obligatory in years 2007-2012,
- LDWN60(2007) equal-loudness contours 60 dB presenting permissible long term average sound level A evaluated for day time (8:00 – 18:00), evening time (18:00-22:00) and night time (22:00-6:00) obligatory in years 2007-2012,
- LDWN64(2012) – equal-loudness contour 64 dB showing permissible long term average sound level A evaluated for all days from the year, taking into account day time (8:00-18:00), evening time (18:00-22:00) and night time (22:00-6:00) obligatory after October 1st 2012;
- LDWN68(2012) - equal-loudness contour 68 dB representing permissible long term average sound level A evaluated for all days from the year, taking into account day time (8:00-18:00), evening time (18:00-22:00) and night time (22:00-6:00) obligatory after October 1st 2012.

The course of border of equal-loudness contours LN and LDWN 2007 were taken directly from acoustic maps and contours of LN and LDWN 2012 were estimated by means of interpolation and using of Interpolation and

Reclassify tool from the Arcgis program as acoustic maps became very popular tool in landscape planning.

In this paper the main task was not exact depiction of sound levels. The idea was to describe the belts located in studied area where land development was restricted according to the law from year 2007 and possible since the year 2012. These belts of noise were presented as certain area (Fig. 1, Fig. 2) and also using area-noise coefficients showing the rate of studied terrain, which is not treated as a noise sensitive area according to actual normative.

Due to the characteristics of studied issue and accepted methodology presented paper is a case study. Case studies are increasingly used method in architecture and city planning. The single case study used in the article is based on a detailed analysis of a particular object, through the identification of features and qualitative elements of a certain urban area (Niezabitowska 2014).

Criteria used in selection of areas for studies were:

- direct neighbourhood of railway and housing-trading areas,
- presence of obligatory spatial management plan,
- presence of investments in housing and trading,
- presence of objects under cultural heritage protection (on the base of the list of municipal record of heritage items for Warsaw, July 11th, 2018),
- localisation inside Warsaw administrative borders.

Area selected for further studies was located in Włochy district of Warsaw. It is situated in areas 2-08-10 and 2-08-11 and is crossed by railway line 447. This line is very busy and connect Warsaw West with Grodzisk Mazowiecki and historically it was line connecting Warsaw and Vienna. Lines of long-distance tram are also crossing studied area.

3. Method of analysis

3.1. Normatives regulating the impact of railway and management of real estates

There are several legal documents, which partially regulate way of the real estate management in areas located close to railway. Act on train transport, chapter 9, article 53 define the distance of buildings from the border of railway area as not smaller than 10 meters and distance from lane not smaller than 20 metres. Simultaneously, these distances should be increased to maintain permissible noise level in case of houses, hospitals, kindergartens and schools [Journal of Laws 2003, No. 85, pos. 789].

Table 1. Permissible noise levels in environment caused by railway (based Dz.U. Nr 120 z dnia 5 lipca 2007 r., poz. 826 and Dz.U. 2012, poz. 1109)

Type of area	Permissible noise level A [dB] for railway							
	2007				2012			
	$L_{Aeq\,D}$	$L_{Aeq\,N}$	L_{DWN}	L_N	$L_{Aeq\,D}$	$L_{Aeq\,N}$	L_{DWN}	L_N
a/ protected zone A – health resorts b/ hospitals outside cities	50	45	50	45	50	45	50	45
a/ housing areas b/ areas with long or short term stay of kids and youths c/ areas of social welfare d/ hospitals in cities	55	50	55	50	61	56	64	59
a/ housing development areas, residential districts b/ croft buildings c/ recreation areas d/ housing and servicing areas	60	50	60	50	65	56	68	59
Downtowns of cities > 100,000 inhabitants	65	55	65	55	68	60	70	65

In case of railways the permissible noise levels are depending on function, which is assigned to certain area and type of index. Indices LAegD and LAeqN can be used for setting and controlling of environment usage according to the one day during daytime and night. LDWN index means longterm average noise level A evaluated during all days in the year taking into account day time (8:00–18:00), evening time (18:00-22:00) and night time (22:00-6:00). LN index means long term average noise evaluated for night time during whole year. These indices have application in longterm policy in protection against noise.

Duties in the protection of areas and objects against noise have a background in:

- art. 5 of Construction law stated, that building item as a whole, its parts, building devices need to be designed and constructed concordantly with future time span of usage, standard technical knowledge and maintaining needs defined in attachment I to the directive of European Parliament and European Council No. 205/2011, March 9th, 2011 harmonising conditions of introduction building products to market and cancelling of directive EU 89/106/EWG (protection against noise among others),

- section IX of directive of Ministry of Infrastructure (April 12th, 2002) describing terms of technical conditions for building and their localisation. Houses, housing districts and public buildings should be situated in places with negligible presence of noise and vibrations. If they are present and their values exceeded permissible thresholds the effective protection is necessary like proper distance from source of problem, use of elements decreasing rate of vibrations, screening elements, rational displacement of rooms and isolation inside external construction items (Ministry of Infrastructure April 12th, 2002),
- sections III and IV of Environmental Protection Law stated, that in Study of Conditions and Directions of Spatial Management (SCDSM) and in local plans of spatial management the necessary conditions for nature balance and rational management of environmental resources (among others by protection against noise and emissions from railway) cannot cause any decline of environmental quality outside the railway real estate borders,
- general provisions of the Act on spatial planning and development, including SCDSM is taking into account conditions of life quality of inhabitants including health protection, which should be in agreement with local plan of spatial management (Spatial Planning and Land Development Act of 27 March 2003).

In particular, the requirements of the last two legal acts are consistent with the fundamental principles of sustainable development, which is considered as a socio-economic development where the process of integrating political, economic and social activities takes place. In the same time, maintaining of the natural balance and durability of basic natural processes, in order to guarantee the possibility of satisfying the basic needs of present and future generations are necessary (Environmental Protection Act of 27 April 2001).

3.2. Pressure of railway noise in studied areas

To show the rate of railway noise conditions in studied areas several features were selected for further evaluation. Particular features were representing different indices potentially applicable in long term policy in protection against noise and thus in spatial planning. As many as 22 features were presented in Table 2:

- area between railway and equal-sound contour 50 dB at night, P_{50dBLN},
- area between railway and equal-sound contour 59 dB at night, P_{59dBLN},
- area between railway and equal-sound contour 55 dB at day-evening-night time, $P_{55dBLDWN}$,
- area between railway and equal-sound contour 60 dB at day-evening-night time, $P_{60dBLDWN}$,

- area between railway and equal-sound contour 64 dB at day-evening-night time, $P_{64dBLDWN}$,
- area between railway and equal-sound contour 68 dB at day-evening-night time, $P_{68dBLDWN}$,
- number of buildings vulnerable to noise exceeding standards for night time according to law of 2007, LB_{50dBLN} and law of 2012, LB_{59dBLN},
- number of buildings vulnerable to noise exceeding standards for day-evening-night according to law of 2007, $LB_{55dBLDWN}$, $LB_{60dBLDWN}$ and law of 2012, $LB_{64dBLWN}$, $LB_{68dBLDWN}$,
- number of buildings under conservational protection vulnerable to noise exceeding standards at night time according to law of 2007, LBK_{50dBLN} and law 2012, LBK_{59dBLN},
- number of buildings under conservational protection vulnerable to noise exceeding standards from the year 2007 $LBK_{55dBLDWN}$, $LBK_{60dBLDWN}$ and from the year 2012, $LBK_{64dBLDWN}$, $LBK_{68dBLDWN}$,
- distance from closest housing developments to the railway, LMW-GK,
- distance from closest housing developments to the far lane, LMW-OT,
- distance from closest housing areas to the railway, LMN-GK,
- distance from closest housing areas to the far lane, LMN-OT.

Table 2. Features of vulnerability to noise inside borders of studied area (own elaboration)

No.	Sign	Unit	Value	No.	Sign	Unit	Value
1.	P_{50dBLN}	m^2	113765	12.	$LB_{68dBLDWN}$	pcs.	4
2.	P_{59dBLN}	m^2	28906	13.	LBK_{50dBLN}	pcs.	11
3.	$P_{55dBLDWN}$	m^2	162979	14.	LBK_{59dBLN}	pcs.	0
4.	$P_{60dBLDWN}$	m^2	77466	15.	$LBK_{55dBLDWN}$	pcs.	7
5.	$P_{64dBLDWN}$	m^2	38550	16.	$LBK_{60dBLDWN}$	pcs.	5
6.	$P_{68dBLDWN}$	m^2	21734	17.	$LBK_{64dBLDWN}$	pcs.	2
7.	LB_{50dBLN}	szt.	52	18.	$LBK_{68dBLDWN}$	pcs.	0
8.	LB_{59dBLN}	szt.	10	19.	$L_{MW\text{-}GK}$	m	24
9.	$LB_{55dBLDWN}$	szt.	30	20.	$L_{MW\text{-}OT}$	m	28
10.	$LB_{60dBLDWN}$	szt.	21	21.	$L_{MN\text{-}GK}$	m	31 (6)
11.	$LB_{64dBLDWN}$	szt.	9	22.	$L_{MN\text{-}OT}$	m	39 (11)

4. Results of the analyses

4.1. Indices of railway noise effect

Increase of the risk of noise in studied area due to mitigation of permissible noise level s in the year 2012 was showed using indices of acoustic release, that is to say presentation areas, which were under protection of train noise according to law from the year 2007 and not protected after law changes in the year 2012. Studied indices were as follows:

- acoustic release indices for night time expressed as $W_{uaLN}=(P_{50dBLN}-P_{59dBLN})/P_{50dBLN}$, (Fig. 2),
- acoustic release indices for day-evening-night expressed as $W1_{uaLDWN}=(P_{55dBLDWN}-P_{64dBLDWN})/P_{55dBLDWN}$, (Fig. 1),
- acoustic release indices at night expressed as $W2_{uaLDW}N=(P_{60dBLN}-P_{68dBLDWN})/P_{60dBLDWN}$ (Fig. 1).

In the paper impact of law changes on particular buildings was showed according to their category of protection against noise.

Such analysis was executed using building-acoustic indices, as like:

- building-acoustic overall index for night time expressed as $W_{baLN} = (LB_{50dBLN}- LB_{59dbLN}) / LB_{50dBLN})$,
- building-acoustic overall index for day-evening-night expressed as $W1_{baLDWN}=(LB_{55dBLWN}- LB_{64dbLDWN})/LB_{55dBLDWN})$ and $W2_{baLDWN} = (LB_{60dBLWN}- LB_{68dbLDWN}) / LB_{60dBLDWN})$,
- building-acoustic cultural area index for day-evening-night expressed as $W3_{baLDWN}=(LBK_{55dBLDWN}-LBK_{64dBLDWN})/LBK_{55dBLDWN}$ and $W4_{baLDWN}= (LBK_{60dBLDWN}-LBK_{68dBLDWN})/LBK_{60dBLDWN}$.

Table 3. Acoustic indices of studied area (own elaboration)

Index	Sign	Unit	Value
Night release indices			
Night time	W_{uaLN}	-	0.746
Day-evening-night (55-64 dB)	$W1_{uaLDWN}$	-	0.763
Day-evening-night (60-68 dB)	$W2_{uaLDWN}$	-	0.719
Building-acoustic indices			
Night overall	W_{baLN}	-	0.808
Overall, day-evening-night (55-64 dB)	$W1_{baLDWN}$	-	0.700
Overall, day-evening-night (60-68 dB)	$W2_{baLDWN}$	-	0.809
Cultural areas, day-evening-night (55-64 dB)	$W3_{baLDW}$	-	0.714
Cultural areas, day-evening-night (60-68 dB)	$W4_{baLDWN}$	-	1.000

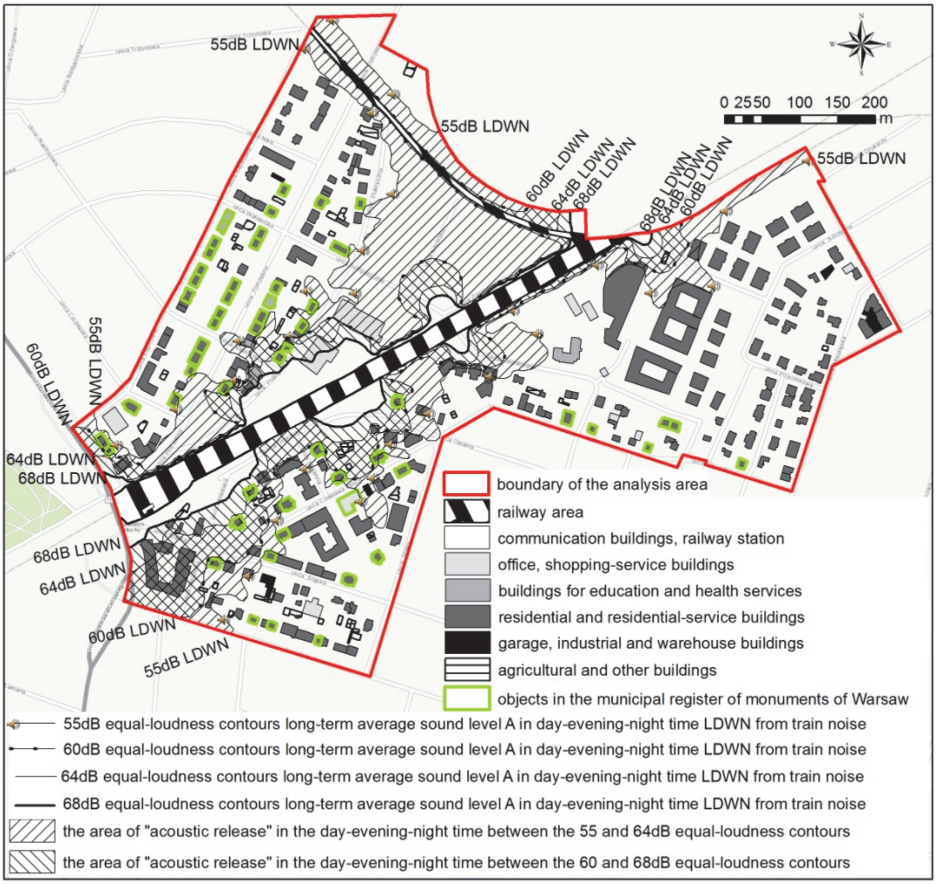

Fig. 1. The area of "acoustic release" when changing the permissible sound levels in the day-evening-night time (own elaboration)

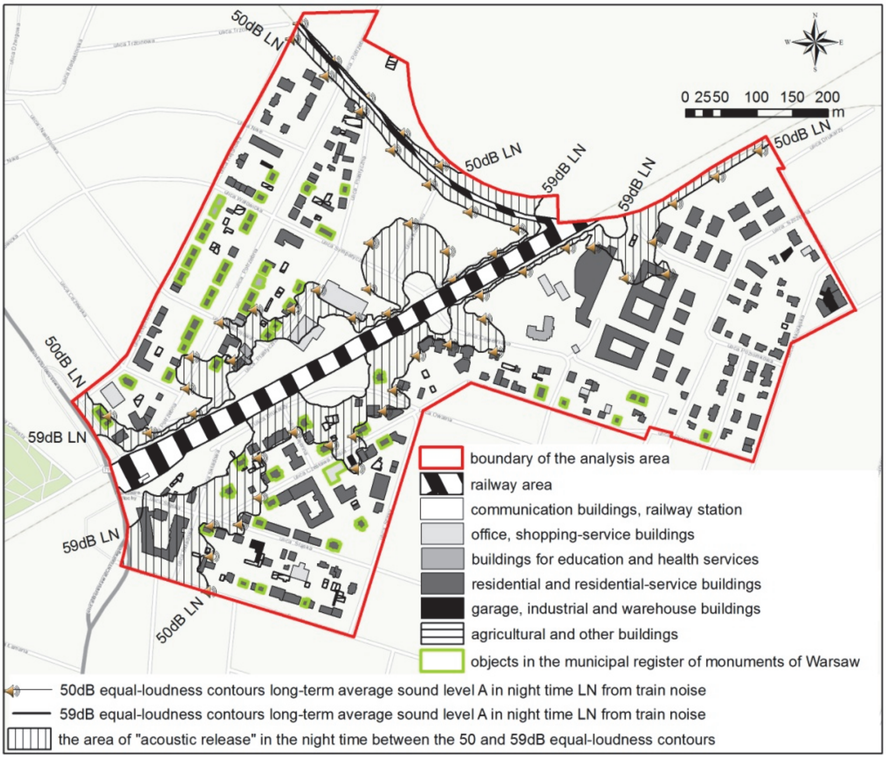

Fig. 2. The area of "acoustic release" when changing the permissible sound levels in the night time (own elaboration)

4.2. Railway noise and spatial planning

For part of studied area the local plan of spatial management is known (Stare Włochy, Stawy street area, law No. XXXVII/1119/2008, Warsaw City Council, July 10th, 2008). Unfortunately it is difficult to find there any information about noise problem, although such a danger is present. Only notation, which could minimise impact of railway is mentioned in §5 where rules of protection and shaping of spatial planning and needs of development of public areas using acoustic barriers were set.

It is worthy to emphasize, that in proposed directions of development of studied area listed in Study of Conditions and Directions of Spatial Management (SCDSM) for Warsaw, there is no decision about areas located between railway and housing developments. In most of the terrain houses should be higher than 12 meters but in some parts height of buildings can reach even 20 meters in height. Some protection can give note, that on the southern part of railway 40 to 60% of biologically active area should be left in case of surrounding individual houses (Fig. 3).

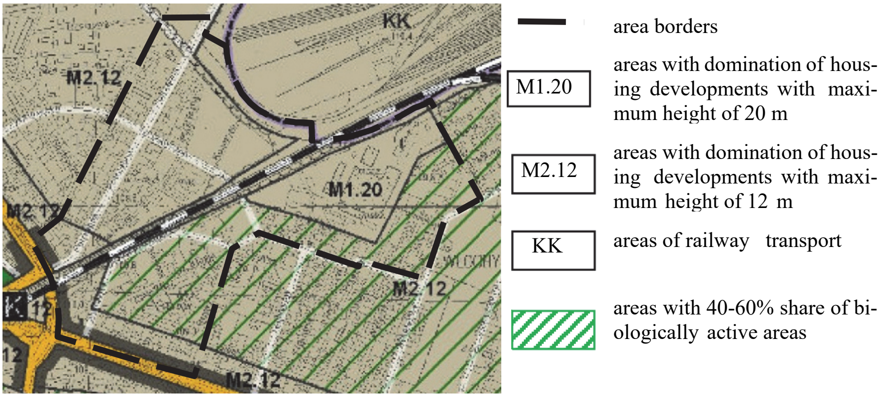

Fig. 3. Planned functions of spatial planning in studied area based on SCDSP for Warsaw

As it was presented on analysed example topic of noise is often marginalized by local groups of experts preparing planning documents. This situation was found in many towns and cities and means, that chapter 14 of Law of environment protection are not realised. This is causing problems in proper categorisation of areas due to their actual state of protection against noise (Kowalczyk 2011).

5. Summary and conclusions

Spatial analyses showed precisely how important is impact of spatial management on the increase of permissible levels of noise for so called fragile functions. Using accepted parameters it can be stated, that:

- the noise present during night time the area treated as fragile was minimised for 75% and rate of buildings vulnerable for noise decreased for 80%, from 52 buildings (including 11 with conservational protection) according to law in year 2007 and 10 after changing law in the year 2012 (with no building encompassed by conservational protection),
- according to day-evening-night noise in areas of private housing, areas connected with stay of kids and youths, social welfare and hospitals change of permissible sound level from 55 to 64 dB caused decrease of fragile territory for 76% and the same time from 30 different buildings mentioned above only 9 were still under protection,

- in case of the noise (day-evening-night time) in residential district, building developments, housing-servicing and recreational areas change from 60 to 68 dB limited fragile surface for 72%, thus only 4 buildings left from initial number equal to 21,
- in the context of acoustic protection of landmarket buildings it should be mentioned, that according to LDWN index there are no buildings in areas with noise above 68 dB, two of them above 64 dB, 5 buildings in area with noise level above 60 dB and 7 in case of 55 dB,
- there are not protected buildings above the 59 dB threshold, while formerly with noise level equal to 50 dB as many as 11 objects were present.

Taking into account presented data it is visible, that investors have greater possibilities to develop areas situated near railway without additional acoustic barriers. Unfortunately, inhabitants will be exposed for negative pressure of noise. Law changes caused fast development of housing areas in the studied part of Warsaw and good example are residential areas 73/6 an 73/4 (Fig. 4).

Of course possibility of development of degraded surfaces near railway is positive aspect of studied issue. Actually only few cases of proper usage of such areas, with regard to actual or future inhabitants and creation of landscape structure avoiding spatial conflicts are known (Makosz 2015).

Knowing above arguments it can be mentioned, that positive aspects of spatial management in areas near railway are location of different services between lanes and housing developments.

But still negative points are predominating, like:

- short distance between railway and houses (real estate no. 67),
- discrete line of acoustic barriers near housing areas (Fig. 5).

Acoustic barriers are perceived as economic and effective way to reduce noise impact on surrounding areas and is recommended in some countries together with additional alternative routes inside and outside of cities, which can increase distance between lanes and housing districts (Demir et al. 2016). Studies of other authors showed, that noise pollution related to transport is sometimes very annoying for inhabitants and as a consequence the number of grievances would be send to local administration, especially in countries like Korea and Japan (Lim et al. 2006). In some cases screens of 2 or 4 metres height and optimal design of housing district are enough to prevent significant part of noise pollution ranged from 2 to 15 dBA (Demir et al. 2016).

In summary, it should be emphasize that near railway areas always generates some conflicts. For instance, after settling of certain areas new residents complain despite being conscious about existing train lanes before start of the construction project. Nowadays, some grievances will have no any legal bases due to change of permissible sound levels. In areas where noise is higher, than new thresholds it is necessary to form local spatial structure in considered way.

Fig. 4. New residential development near the railway area [autor's photo]

Fig. 5. The discontinuity of acoustic barriers [autor's photo]

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Abstract

In this paper problem of noise caused by railway in cities was studied. This aspect was often marginalised in spatial planning process. Using example of areas located in Włochy district (Warsaw, Poland) the function of area and the new permissible sound levels were shown. Analyses based on data obtained from Warsaw acoustic maps generated in the year 2017, spatial management plans and current state of development and investments inside borders of real estate 2-08-10 and 2-08-11.

Based on 22 superficial and quantitative features related to 50 and 59 dB limit sound levels at night and 55, 60, 64 and 68 dB at day-evening-night time, changes in the spatial development possibilities in the analysed area were shown. On the base of area indices and using ArcGis software positive and negative aspects of studied area were presented. The analysis clearly showed that the increase in sound levels by 9 dB at night and 8-9 dB during daylight-night-time resulted in the reduction of areas considered to be susceptible to noise before 2012 by 71.9-76.3%, and decrease of the number of buildings exposed to noise by 70-80%. However, the analysis of the local spatial development plans and the Study of Conditions and Directions of Spatial Development showed that the problem of noise is minimized in documents and planning studies. The effect of law changes is possibility of the implementation of housing projects in the near vicinity of the railway area and the approval of the discontinuity of acoustic barriers along the railway tracks.

Keywords:
spatial planning, railway noise, permissible noise levels, sustainable development

Wpływ zmian dopuszczalnych poziomów hałasu kolejowego na możliwości zagospodarowania przestrzennego terenów miejskich

Streszczenie

W artykule poruszono problem zagrożenia hałasem kolejowym w miastach. Aspekt ten jest często marginalizowany w procesie planowania przestrzennego. Na wybranym przykładzie obszaru położonego w dzielnicy Włochy w Warszawie ukazano lokalizację funkcji terenu na tle zmian dopuszczalnych poziomów hałasu. Analiza została oparta o dane z map akustycznych dla Warszawy opracowanych w 2017 r., opracowań planistycznych oraz obecnego stanu zagospodarowania i realizowane inwestycje w granicach obrębu 2-08-10 i 2-08-11.

Na podstawie 22 cech powierzchniowych i ilościowych odniesionych do granicznych poziomów dźwięku 50 i 59 dB w nocy oraz 55, 60, 64 i 68 dB w porze dzienno-wieczorowo-nocnej ukazano zmiany w możliwościach zagospodarowania przestrzennego na analizowanym obszarze. Na podstawie wskaźników powierzchniowych opracowanych z wykorzystaniem oprogramowania ArcGis, ukazano mocne i słabe strony badanego terenu. Wykonana analiza jasno pokazała, że zwiększenie dopuszczalnych poziomów dźwięku o 9dB w nocy i 8-9dB w porze dzienno-wieczorowo-nocnej spowodowała zmniejszenie terenów uznawanych za wrażliwe na hałas przed 2012 r. o 71,9-76,3%, oraz zniwelowanie liczby budynków narażonych na hałas o 70-80%. Natomiast analiza zapisów miejscowych planów zagospodarowania przestrzennego oraz Studium Uwarunkowań i Kierunków Zagospodarowania Przestrzennego pokazała, że problem hałasu jest minimalizowany w dokumentach i opracowaniach planistycznych. Efektem tego jest dopuszczanie realizacji inwestycji mieszkaniowych w bliskiej odległości obszaru kolejowego oraz zgoda na nieciągłość ekranów akustycznych wzdłuż torów kolejowych.

Słowa kluczowe:
planowanie przestrzenne, hałas kolejowy, dopuszczalne poziomy hałasu, zrównoważony rozwój

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Economic and Environmental Efficiency of the Chemical Industry in Europe in 2010-2016

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1. Introduction

The EU is currently conducting an extremely ambitious policy to reduce climate change by limiting greenhouse gas (GHG) emissions. Work on the introduction of GHG emission reduction policy instruments began in the early 1990s. During this period, two types of solutions were considered: an emissions trading system (ETS) and carbon tax. The EC proposed introducing a carbon tax because the ETS was something new and unproven in a wider context. However, the idea was strongly opposed by both entrepreneurs and some member states that did not want to give the EU authority to introduce direct taxation (Calel, 2013).

Many years of work led to the launch of the EU ETS in 2003 (European Union, 2003). Enterprises operating in the sectors subject to these regulations receive emission allowances free of charge or have to purchase them. Only 10% of the most effective entities are entitled to obtain free allowances, with efficiency determined using special benchmarks. For the chemical industry, 17 benchmarks were determined (European Commission, 2015, p. 49). Meanwhile, purchase of allowances is associated with high costs. Considering the increasingly ambitious plans related to the EU's environmental and climatic policy (reducing the emissions of greenhouse gases by 80-95% by 2050 as compared to 1990) (European Commission, 2011), the issue of economic and environmental efficiency is becoming essential as regards both the states that set reduction objectives and enterprises whose economic results are determined by these issues. That is why it is necessary to combine the economic results of using production factors with carrying out pro-environmental tasks.

The main objective of the study is to determine the economic and environmental efficiency of the chemical industry in the EU (the fifth largest EU industry (Cefic, 2017)). In this article, chemical industry sectors in individual EU countries were adopted as objects for comparison.

The article raises the following research questions:

- Which countries in the EU have a chemical industry with the highest economic and environmental efficiency?
- Are changes occurring in the economic and environmental efficiency of the chemical industry in individual EU countries?
- What is the reason for the improvement in productivity, if such a trend is found?

2. Research basis

2.1. Chemical industry in Europe

The chemical industry is very sensitive to the current economic situation so does other elements of domestic economy (Varjan et al., 2019) it is important for economic growth and society development. In Europe, nearly 70% of sales go to other sectors of the economy, while the rest is marketed directly to consumers – this industry is considered to a linchpin of the entire economy (Centre for Industry Education Collaboration, 2018). The importance of the sector is also demonstrated by the fact that chemical products are used both by large industrial plants and individual customers in the production of everyday consumer goods, in agriculture, production and service activities producing such materials as fuels, plastics, cosmetics, fertilizers and crop protection.

Chemical production in the EU covers three product areas: base chemicals, specialty chemicals and consumer chemicals. In 2016 (latest data of Cefic, 2017), base chemicals constituted 59.2% of the total sales of chemicals in the EU. Specialty chemicals, including paints and inks, crop protection, dyes and pigments, amounted to 27.2% of the total sales of chemical industry products in the EU in 2016. Consumer chemicals accounted for 13.6% of the total sales of chemical products in the EU in 2016 (Cefic, 2017).

In 2016, the two largest producers of chemical industry products in Europe were Germany (28.7% share in total EU chemical sales) and France (13.9%). Italy (10.0%) and Netherlands (9.1%) are the next in line. Sales of chemical products in these countries accounted for 61.7% of the EU market (€ 313 billions). The share increases to 82.6% (€ 419 billions), if the Spain, the United Kingdom and Belgium are listed together with the aforementioned countries. Sales value of the remaining EU countries amounted to € 88 billions in 2016, which constituted 17.4% of the total value of sales. Among the remaining EU countries, Poland and Austria exhibited the largest sales of chemical industry products (Cefic, 2017).

2.2. Environmental economics

The production of such huge amounts of chemical products requires a correspondingly wide variety of types of input, including energy, which depletes non-renewable energy resources. On the other hand, the industry emits GHG during production processes, thus contributing adversely to climate change. Both energy consumption and greenhouse gas emissions constitute a direct burden on the environment and cause a deterioration in the environment for future generations. Therefore, there is a need for effective use of limited resources and minimization of environmental burdens, which is currently the subject of constant research.

This issue is addressed by environmental economics, defined as the field of economic theory (Perman et al., 2003), which studies static and dynamic conditions of optimal use of natural environment resources (Fiedor, 2002). From the point of view of this paper, the most important elements of this theory are the issues related to limiting externalities, such as greenhouse gas emissions, and the proper rate of use of non-renewable resources.

3. Materials and methods

3.1. Sources for materials

The research was based on materials and secondary data from EUROSTAT. In order to determine the efficiency of the chemical industry in European countries in 2016 (the latest available data) the DEA method was used, while the Malmquist Productivity Index was used to determine changes in chemical industry productivity in 2010-2016.

3.2. Data envelopment analysis

The Data Envelopment Analysis (DEA) method is considered one of the non-parametric methods for testing the efficiency of objects. In 1978, the authors of the DEA method (Charnes et al., 1978), using as their base the concept of productivity formulated by Debreu and Farelland defining the measure of productivity as a quotient of a single output and single input, applied it to a multidimensional situation, i.e. one that has more than one output and more than one input (Charnes et al., 1978). Mathematically, the DEA model can be represented as follows (the presented models refer to the model known in literature as CCR and oriented towards minimizing types of input) (Charnes et. al., 1994):
Objective function:

$$\max_{u,v} \frac{\sum_{r=1}^{s} \mu_r y_{ro}}{\sum_{i=1}^{m} v_i x_{io}}, \tag{1}$$

with the following constraints:

$$\frac{\sum_{r=1}^{s} \mu_r y_{rj}}{\sum_{i=1}^{m} v_i x_{ij}} \leq 1 \quad (j = 0, 1, ..., n), \qquad \mu_r, v_i \geq 0, \tag{2}$$

$$\frac{\mu_r}{\sum_{i=1}^{m} v_i x_{io}} \geq \varepsilon \quad \text{for} \quad r = 0, 1, ..., s, \tag{3}$$

$$\frac{v_i}{\sum_{i=1}^{m} v_i x_{io}} \geq \varepsilon \quad \text{for} \quad i = 0, 1, ..., m. \tag{4}$$

where: s – number of outputs, m – number of inputs, μ_r – weights determining the importance of individual outputs, v_i– weightsdetermining the importance of individual inputs, y_{rj} – size of an r-type output (r = 1, ..., R) in object j, x_{ij} – size of an i-type input (n = 1, ..., N) in object j, (j = 1, ..., J).

The DEA method makes it possible to study the relationship between the level of many types of input and many types of output. In the DEA model, m inputs and s various outputs are reduced to individual "synthetic" input and "synthetic" output values, which are then used in the calculation of the object's efficiency index (Roll and Hayuth, 1993). In linear programming, this indicator is the objective function. In the DEA method, two variants of the objective function can be distinguished: maximization of outputs at given inputs or minimization of inputs at set outputs (Cooper et al., 2007). The optimized variables are coefficients μ_r and v_i, which act as weights for the amount of inputs and outputs, while the values for outputs and inputs constitute empirical data (Cooper et al., 2007). The constraint assumes that the quotient of synthetic output and synthetic input is to be less than or equal to one (without such a limitation the task would have infinitely many solutions). Input and output weights are determined in such a way that they maximize the above-mentioned relation of outputs to inputs, and their sizes can be equal to or greater than zero.

The solution of the objective function by means of linear programming makes it possible to determine the efficiency curve on which all of the most effective units of the studied group are located. Graphical presentation of the efficiency curve is possible for the following models: 1 input and 1 output, 2 inputs and 1 output or 1 input and 2 outputs. For multidimensional models, the equivalent of the curve is several interconnected fragments of different hyperplanes. Objects are considered to be technically effective, if they are on the efficiency curve (their efficiency index is 1, which in a model focused on minimizing inputs means that there is no more favorable combination of inputs that allows the enterprise (sector/country) to achieve the same outputs). Meanwhile, if they are outside the efficiency curve, they are technically ineffective (their efficiency index is less than 1, which means that there is a more effective combination of inputs that allows the same outputs to be achieved). The efficiency of an object is measured in relation to other objects from the studied group and takes values from the interval (0, 1). In the DEA method, analysis objects are so-called Decision-Making Units (DMU), which may be enterprises, sectors and/or countries (Charnes et. al., 1994). The subject of the analysis is the efficiency with which a given DMU transforms its inputs into outputs.

3.3. Malmquist Productivity Index

In turn, the structure of the Malmquist Productivity Index (MPI) is based on the principle of comparing the relation of several inputs to several results of a given object at different moments in time (Baran and Wysokiński, 2016). The MPI for a given object is the product of the index of changes in technical efficiency (*EFCH*, the technical efficiency is defined as the relation of the outputs obtained from given inputs against the possible maximum outputs obtained with given inputs) and the index of technological progress (*TECH*, the technological progress is defined as changes in manufacturing technology in the considered period) according to the following formula (Färe et al., 1994):

$$M(y_{t+1}, x_{t+1}, y_t, x_t) = \underbrace{\frac{D^t(y_{t+1}, x_{t+1})}{D^t(y_t, x_t)}}_{EFCH^{t+1}} \cdot \underbrace{\left[\frac{D^t(y_{t+1}, x_{t+1})}{D^{t+1}(y_{t+1}, x_{t+1})} \cdot \frac{D^t(y_t, x_t)}{D^{t+1}(y_t, x_t)}\right]^{\frac{1}{2}}}_{TECH^{t+1}} \quad (5)$$

where: $D^t(y_{t+1}, x_{t+1})$ means efficiency using the technology of year t for data from the year $t+1$, $D^t(y_t, x_t)$ is the unit's efficiency in period t using the technology available at that time and data from the period t, $D^{t+1}(y_{t+1}, x_{t+1})$ shows the unit's efficiency for the period $t+1$, and $D^{t+1}(y_t, x_t)$ means efficiency using the technology of year $t+1$ for data from the year t.

For a MPI value greater than 1, it is assumed that in the audited period, from t to t+1, there was an increase in productivity. Meanwhile, when the value of the MPI is lower than 1, it indicates a decrease in productivity, with a value equal to 1 indicating that efficiency is maintained at the same level. A similar interpretation of the indicators is applied to *EFCH* and *TECH* (Coelli et al., 2005).

The decomposition of this index can be specified as follows (Cooper et al., 2007):

$$EFCH(P) = \frac{\frac{BD}{BP_2}}{\frac{AC}{AP_1}}, TECH = \sqrt{\frac{AC}{AE} \cdot \frac{BF}{BD}}, \text{ so } MPI = \frac{AP_1}{BP_2}\sqrt{\frac{BF}{AC} \cdot \frac{BD}{AE}}, \tag{6}$$

4. Results and discussion

In order to determine the economic and environmental efficiency and changes in productivity over time in the chemical industry sector in individual European countries, the DEA method and the MPI, with a focus on minimising inputs, were used. Based on subject literature, a set of variables was defined for these models. The production size is usually assumed as its volume, i.e. a set of manufactured products, expressed either in physical units or in constant prices. In this study, the production value of the chemical industry was assumed as the production volume (output). The variables explaining the production volume, according to economic theory, are three production factors: labour, objectified work (capital) and land. In reference to the above, the present research assumed the number of employees as the measure of the labour factor (input 1). In non-agricultural enterprises, the land factor generally does not play a significant role. Therefore, it is often omitted or replaced by the consumption of materials and energy – in the research the consumption of energy was assumed as the input (input 2). CO_2 emissions were assumed as the environmental input (input 3).

The following variables were adopted for the calculated models:

- output y_1 – production value (one thousand Euro),
- input x_1 – number of employees (number of persons employed),
- input x_2 – energy consumption (one thousand tonnes of oil equivalent),
- input x_3 – CO_2 emissions (tonnes).

In the first stage of the study, the DEA method was calculated. The average economic and environmental efficiency of the chemical industry in Europe was quite high, with the efficiency index at 0.70 in 2016. Out of 27 analysed sectors of the chemical industry in individual European countries, 10 were considered fully efficient (the DEA efficiency ratio was 1). Countries with a chemical industry characterised as fully efficient include Belgium, Denmark, Germany, Estonia, Ireland, France, Italy, Malta, Netherlands, and Austria. The chemical industry in Romania and Bulgaria proved to be the least economically and environmentally efficient (see Figure 1).

In the second stage of studies, an analysis of changes in the productivity of the chemical industry in individual European countries in the years 2010-2016 was performed. As part of this stage, answers were also sought to the question of what had a greater impact on the change in productivity – improvement in technical efficiency in the industry or technological progress?

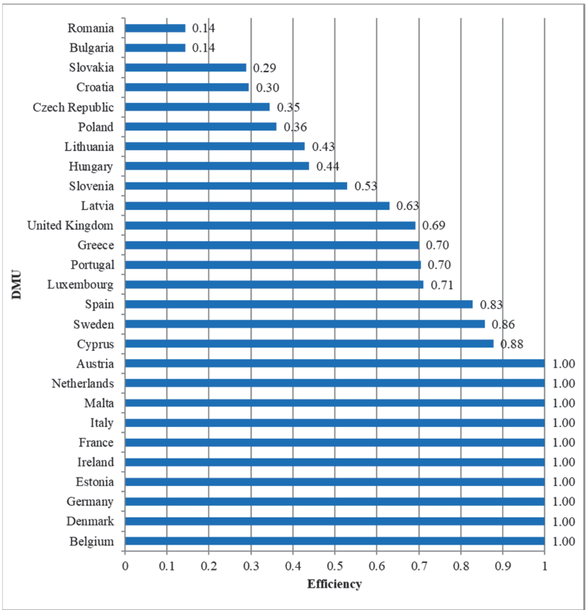

Fig. 1. Technical and environmental efficiency of the chemical industry in EU countries in 2016

In the analysed period, the chemical industry in Europe improved its annual productivity by 5% (see Table 1, row MPI and column Average). It is worth noting, however, that the improvement was still decreasing in the analysed period: from 16% in 2010/2011 to -2% in 2015/2016 (see Table 1). The conducted analyses make it possible to state that, in the period 2010/2011-2012/2013, technological progress had a greater impact on improving the chemical industry's productivity. The average annual *TECH* index was 1.32. In turn, the rate of efficiency change in the same period was below 1, which indicates that in the given period the chemical industry in Europe reported a deterioration in efficiency, and an improvement in this area was only noted from 2013/2014 to 2014/2015. The average annual *EFCH* index was 1.58 in the period, so technical efficiency had a greater impact on improving the chemical industry's productivity in the given period. The decline in productivity in 2015/2016 was due to a decline in both indices.

Table 1. Average annual values of the MPI, changes in technical efficiency (*EFCH*) and technological progress (*TECH*) in the chemical industry as a whole in Europe in the period 2010-2016

Index	2010/ 2011	2011/ 2012	2012/ 2013	2013/ 2014	2014/ 2015	2015/ 2016	Average
EFCH	0.97	0.79	0.81	1.06	2.07	0.99	1.11
TECH	1.20	1.50	1.26	0.99	0.59	0.99	1.09
MPI	1.16	1.14	1.01	1.04	1.00	0.98	1.05

However, the situation of the chemical industry varies depending on the country. Research results indicate that in 2010-2016 the chemical industry improved its productivity in 20 European countries (see Table 2). Countries that experienced deterioration in the chemical industry's productivity are France, Cyprus, Lithuania, Slovakia, and United Kingdom. In Germany and Luxembourg, on the other hand, neither improvement, nor deterioration in the productivity of the chemical industry has been observed. Technological progress (*TECH*), in all countries (except Cyprus) was at a level 1 or above 1.However, this average annual improvement was approx. 9%, while improvement in technical efficiency (*EFCH)* was 11%, although the index was lower than 1 in Spain, France, Cyprus, and United Kingdom.

5. Conclusion

As of 1st January 2013, the third stage of EU ETS came into force (European Union, 2009) which covered the chemical industry. As a result, operating costs increased significantly. The operating principles of this system mean that the issues of energy and emission efficiency (related to setting benchmarks for particular branches of the economy and granting free emission rights) are beginning to play a major role in the economic calculation. The European chemical industry, bearing the costs of the fight for climate stability, is becoming increasingly less competitive with non-EU producers not subject to similar regulations. As the presented research has shown, enterprises are trying to adapt to the emerging situation and improve theirefficiency and productivity. This is particularly evident in the EU countries that are the leadingproducers in the chemical industry, i.e. Germany, France, Italy, and the Netherlands. Under the conducted analysis, these countries achieved the highest economic and environmental efficiency ratios.

Table 2. Average annual valuesof the Malmquist index, changes in technical efficiency and technological progress in the chemical industry in individual European countries in the period 2010-2016

Country	EFCH	TECH	MPI
Belgium	1.00	1.03	1.03
Bulgaria	1.18	1.10	1.04
Czech Republic	1.15	1.16	1.01
Denmark	1.49	1.19	1.06
Germany	1.00	1.00	1.00
Estonia	1.38	1.10	1.18
Ireland	1.17	1.18	1.27
Greece	1.13	1.24	1.16
Spain	0.99	1.02	1.01
France	0.97	1.00	0.97
Croatia	1.12	1.11	1.01
Italy	1.02	1.02	1.04
Cyprus	0.90	0.94	0.83
Latvia	1.15	1.07	1.08
Lithuania	1.07	1.10	0.98
Luxembourg	1.11	1.02	1.00
Hungary	1.14	1.14	1.01
Malta	1.12	1.00	1.11
Netherlands	1.01	1.02	1.03
Austria	1.05	1.04	1.01
Poland	1.06	1.04	1.05
Portugal	1.15	1.16	1.04
Romania	1.28	1.10	1.08
Slovenia	1.17	1.12	1.02
Slovakia	1.04	1.11	0.96
Sweden	1.26	1.23	1.03
United Kingdom	0.97	1.02	0.99
Average	1.11	1.09	1.05
Max	1.49	1.24	1.67
Min	0.90	0.94	0.83

Note: a greyed field indicates an improvement of the given indicator

Considering the tightening EU climate policy, it seems that the best approach to monitoring efficiency is a comprehensive approach to both economic and environmental aspects. The conducted studies present such an approach and make it possible to indicate countries with the highest economic and environmental efficiency of the chemical industry (Belgium, Denmark, Germany, Estonia, Ireland, France,Italy, Malta,the Netherlands, and Austria), as well as thosethat have most improved their productivity in the analysed period (Ireland, Estonia, Greece, Malta). Technological progress was the source of improvement in productivity of the chemicalindustry in the period 2010/2011-2012/2013. But technicalefficiencyhad agreaterimpact on improving the chemicalindustry'sproductivityin the period 2013/2014-2014/2015. The conducted studies and adopted research methods made it possible to accomplish the research goal and to obtain answers to the research questions posed.

The obtained results provide the foundation for further in-depth studies, in which it is necessary to identify the main factors that have had an impact on the economic and environmental efficiency of the chemical industry in individual EU countries which could be realised with methods of prediction market (Czwajda et al., 2019). In future research, the identification might be realised with design thinking methodology (Kostrzewski, 2018).

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Abstract

Based on the Data Envelopment Analysis method and the Malmquist Productivity Index, the article specifies the economic and environmental efficiency and its changes in the chemical industry in individual EU countries from 2010 to 2016. The following have been adopted as variables in the model: 1 output (production value) and 3 types of input (number of employees, energy consumption, CO_2 emissions). The countries where the chemical sector obtained the highest economic and environmental efficiency were: Belgium, Denmark, Germany, Estonia, Ireland, France, Italy, Malta, the Netherlands, and Austria. The chemical industry in Romania and Bulgaria proved to be the least economically and environmentally efficient. As part of the research, it was indicated that both technological progress and the change in technical efficiency had impact on the improvement in productivity in the chemical industry in EU. In the analysed period, the chemical industry in Europe improved its annual productivity by 5%. It is worth noting that the improvement was still decreasing in the analysed period: from 16% in 2010/2011 to -2% in 2015/2016. The conducted analyses make it possible to state that, in the period 2010/2011-2012/2013, technological progress had a greater impact on improving the chemical industry's productivity. In turn, the technical efficiency had a greater impact on improving the chemical industry's productivity in the period 2013/2014-2014/2015. The decline in productivity in 2015/2016 was due to a decline in both indicators. However, the situation of the chemical industry varies depending on the country. Research results indicate that in 2010-2016 the chemical industry improved its productivity in 20 European countries. Countries that experienced slowdown in the chemical industry's productivity are France, Cyprus, Lithuania, Slovakia, and United Kingdom. In Germany and Luxembourg, on the other hand, neither improvement, nor deterioration in the productivity of the chemical industry has been observed.

Keywords:
efficiency, environment, chemical industry, Europe

Efektywność ekonomiczno-środowiskowa przemysłu chemicznego w Europie w latach 2010-2016

Streszczenie

W artykule bazując na metodzie Data Envelopment Analysis i Malmquist Productivity Index określono efektywność ekonomiczno-środowiskową i jej zmiany w przemyśle chemicznym w poszczególnych krajach UE w latach 2010-2016. Do modelu przyjęto jako zmienne: 1 efekt (wartość produkcji), 3 nakłady (liczba zatrudnionych, zużycie energii, emisja CO_2). Krajami, gdzie sektor chemiczny odnotował najwyższą efektywność ekonomiczno-środowiskową były Belgia, Dania, Niemcy, Estonia, Irlandia, Francja, Włochy, Malta, Holandia i Austria. Najmniej efektywny pod względem ekonomiczno-środowiskowym okazał się przemysł chemiczny w Rumunii i Bułgarii. W ramach badań wskazano, że zarówno postęp technologiczny, jak i zmiana wydajności technicznej miały wpływ na poprawę wydajności w przemyśle chemicznym w UE. Przemysł chemiczny w EU w badanym okresie poprawiał swoją produktywność średniorocznie na poziomie 5%. Warto jednak zauważyć, że poprawa uległa zmniejszeniu w analizowanym okresie z 16% w 2010/2011 do -2% w 2015/2016. Przeprowadzone analizy pozwalają stwierdzić, że w okresie 2010/2011-2012/2013 postęp technologiczny miał większy wpływ na poprawę produktywności przemysłu chemicznego z kolei na wydajność techniczną w okresie 2013/2014-2014/2015. Ograniczenie produktywności w latach 2015/2016 było spowodowane spadkiem obu wskaźników. Sytuacja przemysłu chemicznego jest jednak zróżnicowana w zależności od kraju. Wyniki badań wskazują, że w latach 2010-2016 w 20 krajach Europy przemysł chemiczny poprawił swoją produktywność. Kraje, które odnotowały pogorszenie produktywności przemysłu chemicznego to Francja, Cypr, Litwa, Słowacja i Wielka Brytania. Z kolei w Niemczech i Luksemburgu nie odnotowano ani poprawy, ani pogorszenia produktywności przemysłu chemicznego.

Słowa kluczowe:
efektywność, środowisko, przemysł chemiczny, Europa

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Shear Capacity and Residual Strengths of Steel Fibre Reinforced Waste Sand Concrete (SFRWSC)

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1. Introduction

Concrete is the most commonly used structural material today and concrete construction has been developing dynamically throughout the world in recent years (Neville 2000, Czarnecki & Kurdowski 2005, Piekarski et al. 2008, Jasiczak et al. 2008) Generally available and relatively inexpensive to produce, concrete is widely used in both industrial and residential construction. However, modern constructions pose a serious challenge to engineers who must meet requirements regarding limit states under extremely varied conditions of static and dynamic interactions. Unfortunately, concrete is a brittle and hardly deformable material, which means it is vulnerable to cracking. Its low tensile strength and vulnerability to crack propagation are a major reason why new types of concrete, whose physico-mechanical parameters would meet the current requirements, are constantly developed. The addition of steel fibres is one way to improve the properties of brittle concrete. Concretes reinforced with steel fibres, generally referred to as fibre-reinforced composites, are becoming increasingly popular. In some cases, they are used as an alternative to ordinary concrete. The addition of e.g. steel (most commonly used) fibres increases the plasticity and cracking resistance of these materials (Leung 2004). Fibre-reinforced concrete originated in the 19^{th} century when A. Bernard first patented concrete reinforced with steel fibres in 1874. Since that year, attempts have been made to assess both the influence of fibres on concrete's properties and fibre distribution within fibre-reinforced concrete. Consequently, fibre-reinforced concrete has become an alternative to ordinary concrete. The most important advantages of fibre-reinforced concrete are: higher compressive strength at early stages of concrete hardening in comparison to ordinary concrete (Ding & Kusterle 2000), higher tensile strength (Yazici et al. 2007, Głodkowska & Kobaka 2010) and flexural tensile strength (Leung

2004), higher splitting tensile strength (Głodkowska & Kobaka 2010), high dynamic resistance (Tso-Liang 2008, Zhi-Liang 2008), limited crack propagation in construction elements (Uygunoğlu 2008), better behaviour at failure (Wang et al. 2010) (failure does not occur abruptly), possible reduction of conventional reinforcement, resistance to high temperatures (Sukontasukkul 2010). Fibre-reinforced composites are also characterized by higher abrasion resistance and better durability compared with ordinary concrete. On the negative side, steel fibres worsen the workability of the mix and the cost of steel fibres is relatively high – a composite with the volume content of steel fibres equal to 1% constitutes 90% of the price for C25/30 ordinary concrete. However, this cost can be reduced by roughly 30% if expensive gravel is replaced with waste sand.

The field of application for fibre-reinforced concretes in construction is varied. Some examples (Bank 2009, Shakya 2012, Zollo 1997, Salehian & Barros 2015, Arnau & Molins 2011, Schimmelpfennig & Borgerhoff 1995) include: beams, slabs, elements of thin shells, industrial floors, elements of bridges and tunnels, elements reinforcing excavation sites and constructions exposed to seismic hazard (Sevil et al. 2011), elements of nuclear power plants when a high level of safety must be ensured e.g. during a terrorist attack or an earthquake. They are used particularly in elements subjected to significant dynamic loads (Borgerhoff 1995).

Flexural/shear design play an important role in the production of structural elements made from fibre-reinforced composites. The issue of shearing concrete elements reinforced with steel fibres has been an object of research and theoretical analyses for years (Kaushik et al. 1987, Roberts et al. 1983, Swamy et al. 1985, Narayanan & Darwish 1987). For more than a quarter-century, experimental studies have been conducted to investigate the shear behaviour of fibre-reinforced concrete beams with changes of parameters having a major influence on the transmission of transverse forces. It has been confirmed that steel fibres not only increase shear capacity by transmitting tensile stresses but also prevent crack propagation in the same way stirrups and bent up bars do. In spite of extensive research confirming steel fibres' beneficial influence on the properties of concrete, no comprehensive and reliable method for calculating shear capacity has been found.

In Europe, the methods for calculating shear capacity of fibre-reinforced concrete elements are presented in RILEM TC 162-TDF and fib ModelCode 2010 provisions. They are based on the knowledge of residual strengths, which serve as basic values for classifying SFRWSC. Knowing the values of residual strengths, one can determine ultimate moment capacity as well as shear capacity of an element made from a fibre-reinforced composite. It should be pointed out that calculation methods using residual strengths are based on the currently valid standard Eurocode 2 for designing concrete structures.

2. Aim and significance of research

In the Pomerania region of Poland, aggregate deposits occur as a mix of fine and coarse aggregates. Huge demand for coarse aggregates has contributed to the development of hydroclassification (an extraction technology involving washing out aggregates from deposits). A by-product of hydroclassification are piles of sand without coarse fractions (Fig. 1).

Fig. 1. View of heaps of waste sands in Pomerania (Poland)

Excavation sites thus created should become an object of costly reclamation. However, the use of waste sand as a structural material can offer an alternative to reclamation. Partially replacing ordinary concrete with SFRWSC may considerably limit environmental degradation. It will also contribute to the gradual reduction of sand piles and make exploitation of regional aggregates possible.

Partially replacing ordinary concrete with materials which exhibit the same or even better properties is an excellent solution for the regions where natural deposits of coarse aggregate are scarce e.g. the region of Pomerania in Poland (where only 4% of total Polish coarse aggregates occur), the Middle East and North Africa.

This article presents physico-mechanical properties of SFRWSC as an alternative to ordinary concrete. It also contains research results concerning residual strengths (a basic feature in designing structural elements) of fine-grained composites with varying steel fibre content. The next task was to calculate shear capacities of beams made from SFRWSC in accordance with RILEM TC 162-TDF and fibModelCode 2010. It has been demonstrated that SFRWSC, whose properties are similar or better than those of ordinary concrete, can be used to produce structural elements as regards shear capacity.

3. Materials and test specimens

In order to produce test specimens with determined residual strengths, portland cement CEM II/A-V 42,5R (420 kg/m^3), silica fume (21 kg/m^3), superplasticizer (16.8 kg/m^3) and municipal water (160 kg/m^3) were used. Considerable homogeneity of grading as well as smooth grading curve characterised the aggregate (Fig. 2). The waste sand used, as demonstrated by the analysis of the test results [3], meets the requirements for mineral aggregates for regular concrete. Reinforcement is steel hooked-end fibres with the aspect ratio $\lambda = l/d = 62.5$ ($l = 50$ mm, $d = 0.8$ mm). The matrix of the composite was designed using an analytical-experimental method. The composition of the matrix was modified by adding superplasticizer and silica fume, which enabled a w/c = 0.38 ratio to be obtained. Steel fibre content was adopted as the member variable – steel fibres were dosed in 0.5% increments, in relation to the volume of the composite, up to the content of 2.5%. The composite mix was characterised by random distribution of steel fibres.

The research showed that the fine-grained composite reinforced with steel fibres (Table 1) can provide an alternative to ordinary concrete as regards structural design. Partially replacing ordinary concrete with a fibre-reinforced composite which exhibits the same or even better properties is an excellent solution for the regions where natural deposits of coarse aggregate are scarce e.g. the region of Pomerania in Poland (where only 4% of total Polish coarse aggregates occur), the Middle East and North Africa. The detailed characteristics of the fibre-reinforced composite used in the research are presented in the paper (Głodkowska & Kobaka 2010, Głodkowska & Laskowska-Bury 2015).

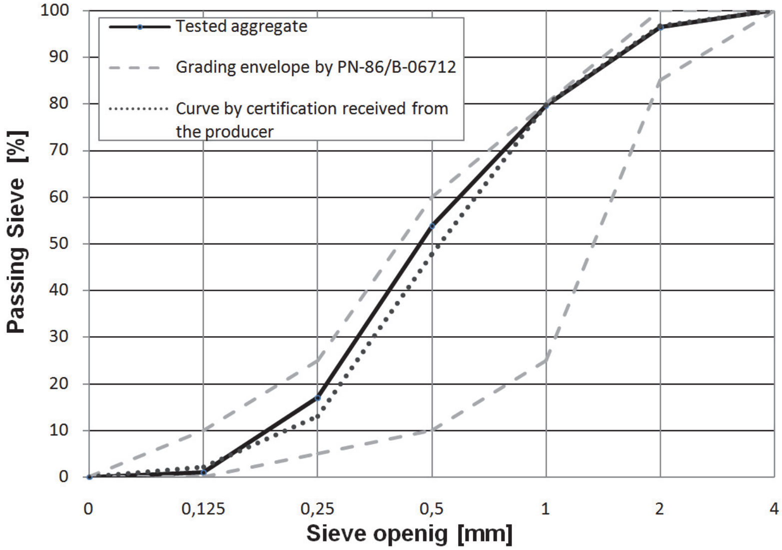

Fig. 2. Smooth grading curve of the aggregate used in the research

Table 1. Basic properties of SFRWSC and ordinary concrete (Głodkowska & Kobaka 2010, Głodkowska & Laskowska-Bury 2015)

Properties of fiber composite	Fibre volume fraction, V_f [%]							regression function / correlation coefficient	properties of ordinary concrete
	0.0	0.5	1.0	1.2	1.5	2.0	2.5		
Apparent density [g/cm^3]	2.1	2.2	2.3	2.3	2.3	2.3	2.3	$\rho = 2.352 - 0.216e^{-0.938V_f}$, $r = 0.97$	2.0-2.6 (PN-EN 12390-7)
compressive strength $f_{c,cyl}$ [N/mm^2]	44	51.8	61.4	64.4	61.6	61.3	61.9	$f_c = 62.77 - 19.22e^{-1.61V_f}$, $r = 0.90$	1-50 (PN-EN 1992-1-1)
compressive strength $f_{c,cube}$ [N-mm^2]	44.5	51.8	61.4	67.6	61.6	61.3	61.9	$f_{c,cube} = 62.77 - 19.22e^{-1.61Vf}$ $r = 0.90$	15-60 (PN-EN 1992-1-1)
split tensile strength $f_{t,spl}$ [N/mm^2]	3.3	5.5	7.7	7.3	8.3	8.8	9.2	$f_{t,spl} = 9.75 - 6.52e^{-0.99Vf}$ $r = 0.97$	3.0-3.7 (PN-EN 12390-6)
static modulus of elasticity E_{cm} [GPa]	32.9	33.3	34.5	36.7	34.7	34.0	33.9	$E_c = 32.7 + 2.35V_f - 0.76V_f^2$ $r = 0.88$	29-37 (PN-EN 12390-13)
dynamic modulus of elasticity E_d [GPa]	41.5	43.7	45.8	45.9	46.3	46	45.5	$E_d = 41.44 + 5.7V_f - 1.65V_f^2$, $= 0.9$	$E_{cm} = 0.83\ E_d$ (wg Neville A.M. 2000)
shrinkage ε_{cs} [‰]	0.91	0.89	0.85	0.88	0.84	0.78	0.75	$\varepsilon_s = 0.898\left(1 - e^{-0.2t^{0,6}}\right) - 0.048V_f, r = 0.93$	0.2-0.6 (ITB 194/98)
Workability Ve-Be test [s]	4.2	6.4	9.5	12	14.3	21.5	32.2	$K = 4.24e^{0.8V_f}$, $r = 0.87$	3-31 (PN-EN 12350-3:2009)
Abrasion resistance A [cm^3/50cm^2]	5.32	6.90	8.17	9.0	8.20	8.16	8.24	$A = 0.04{f_{cyl}}^{1.28}$ $r = 0.99$	1.,5-22 (PN-EN13892-3)
Dynamic modulus of rigidity G_d [GPa]	17.8	18.54	18.33	-	18.81	18.60	18.23	$G_d = 17.83 + 1.146V_f - 0.391V_f^2$ $r = 0.79$	-

The composite's residual strengths serving to calculate shear capacity were determined on fourty-seven 150×150×700 mm prisms. Six prisms were not reinforced with steel fibres whereas other prisms contained steel fibres in the following amounts $V_f = 0.5\%$ (8 prisms) and $V_f = 0.9\%$ (8 prisms). The research presented in the paper (Głodkowska & Kobaka 2010, Głodkowska & Laskowska-Bury 2015) showed that the optimal (exceeding the properties of ordinary concrete), maximum fibre content in SFRWSC is equal to 1.2%. For this fibre content, residual strengths were determined on 31 prisms. Before being tested, the prisms were stored for 28 days at a temperature of 20±2°C and at a relative air humidity of about 100%. Next, they were stored for 24 hours under laboratory conditions (temp. 20±2°C, relative humidity 50±5%).The specimens were tested after 29 days of curing.

4. Test methodology

A research on SFRWSC residual strengths was conducted in accordance with PN-EN 14651. Fig. 3 shows a test set-up where cracking resistance in bending was determined in the form of the so-called residual strengths.

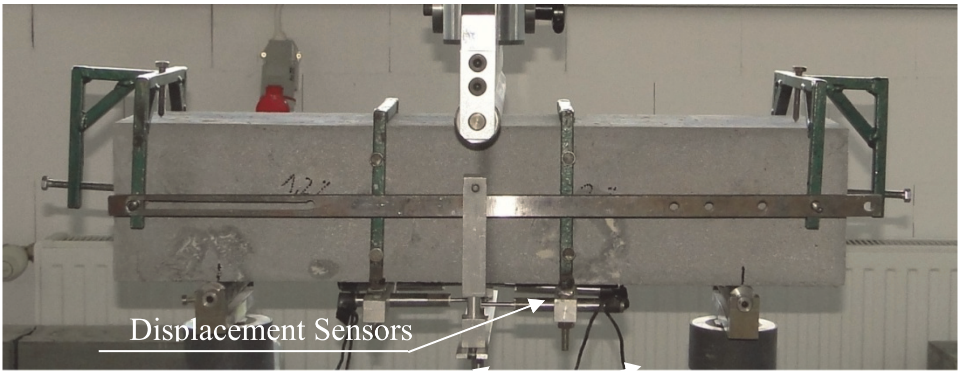

Fig. 3. View on the prisms' set-up, load application and displacement sensors location in the residual strength test

In order to test residual strengths, constant static load was applied to the prisms. Load increase values were set depending on crack mouth opening displacement (*CMOD*). In the case of prisms without steel fibres, the test was terminated when the specimen underwent flexural failure. In the case of fibre-reinforced prisms, the test ended when the specimen's deflection was equal to 5 mm. Ultimate deflection of the prisms was set in accordance with PN-EN 14651 standard in order to achieve all *CMOD* values and to determine residual strengths ($f_{R,j}$)

for the corresponding value $CMOD_j$, in which j = 1,2,3,4. The quantities $f_{R,1}$, $f_{R,2}$, $f_{R,3}$, $f_{R,4}$ correspond to the tensile stresses associated to the force at a given *CMOD*, which were equal to 0.5, 1.5, 2.5, 3.5 mm respectively.

Residual strength can be determined by following expression:

$$f_{R,j} = \frac{3 \cdot F_j \cdot l}{2 \cdot b \cdot h_{sp}^2} \tag{1}$$

where:

$f_{R,j}$ – residual strength [N/mm^2],

F_j – load value [N],

l – lenght of test specimen [mm],

b – width of test specimen [mm],

h_{sp} – distance between tip of the notch and top of cross section [mm].

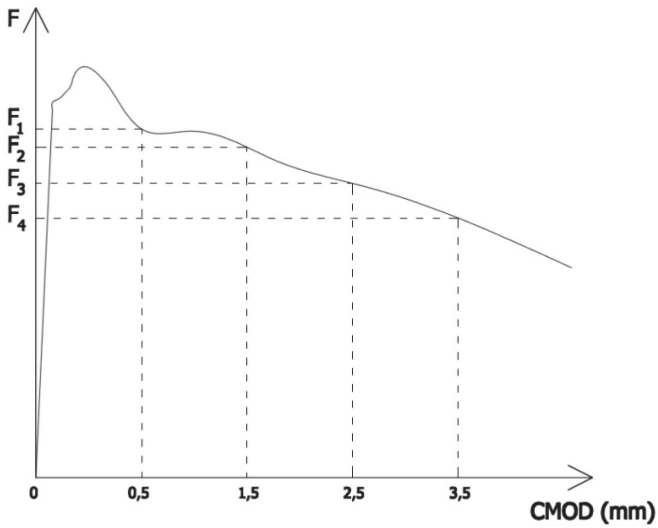

Fig. 4. Graphical interpretation of F_1 – F_4 determination

An important parameter enabling a fibre-reinforced composite to be classified is the chart shape "load-*CMOD*" from the point of attaining limit of proportionality until ultimate deflection. Two shapes of the chart can be defined: the first shape is characterised by a decrease in load and an increase in *CMOD* value following the appearance of the first crack (*post-crack softening – pcs*), the second shape is defined by an increase in both load and *CMOD* value (*post-crack hardening – pch).*

5. Residual strengths – research results and their analysis

Fig. 5-8 present crack width – load relation. In order to facilitate interpretation of the research results in Fig. 6-8, envelopes of the charts (solid lines) as well as average load-*CMOD* relation (broken line) were shown. The prisms without fibres failed when concrete attained tensile strength. It must be emphasized that a three-point bending test according to PN-EN 14651 does not include specimens without fibres and applies only to fibre-reinforced materials. Specimens without fibres were tested to highlight the considerable influence of steel fibres on tensile stresses. An analysis of the test results reveals that the material, even at 0.5% steel fibre content in volume, significantly changes its properties under the action of load. The major observation is that a test specimen made from fibre-reinforced composite did not fail as abruptly as a specimen made from concrete without fibres did. In the case of fibre-reinforced prisms, a crack appeared and increased its width until the ultimate deflection, which ended the testing. This illustrates the considerable influence of steel fibre content on residual strengths. Comparing the chart shapes in Fig. 6-8, one can observe that the prisms with 0.9% and 1.2% fibre content are characterised by *pcs* which stands for a slow decrease in load and an increase in *CMOD* value following the appearance of the first crack. However, the prisms reinforced with fibres in the amount of $V_f = 0.5\%$ are characterised by an intermediate behaviour between *pcs* and *pch* – the load remained constant while *CMOD* value increased. Furthermore, one observed that fibre content influences crack width (an evident relation: the higher the fibre content V_f, the smaller the crack width). For prisms with varying fibre content (V_f), attaining the same *CMOD* values means applying different loads. In other words, higher fibre content in the prisms requires higher load to reach a given *CMOD* value.

The limit of proportionality and residual strength values for the test composite with varying fibre content V_f are presented in Fig. 9.

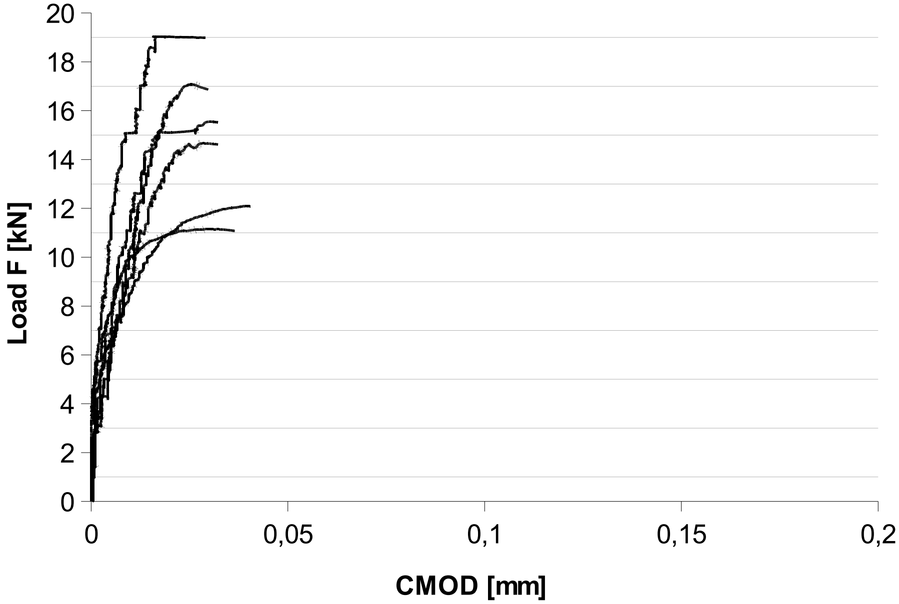

Fig. 5. Load-CMOD relation for $V_f = 0\%$

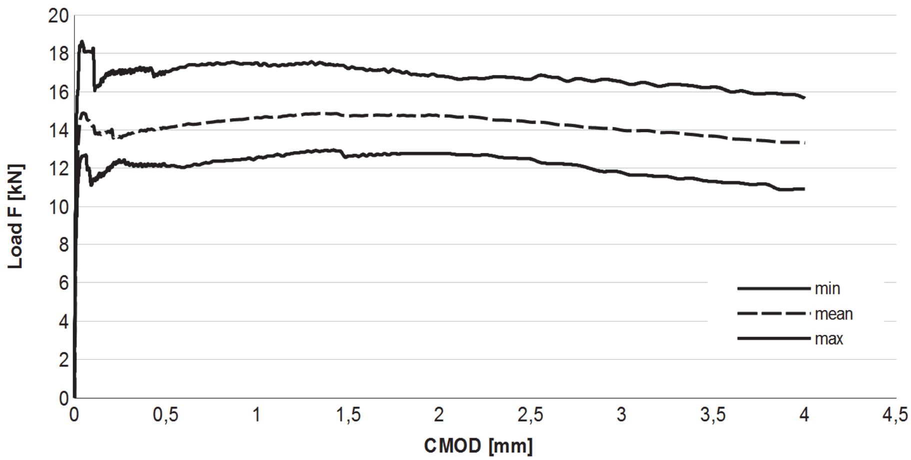

Fig. 6. Load-CMOD relation for $V_f = 0.5\%$

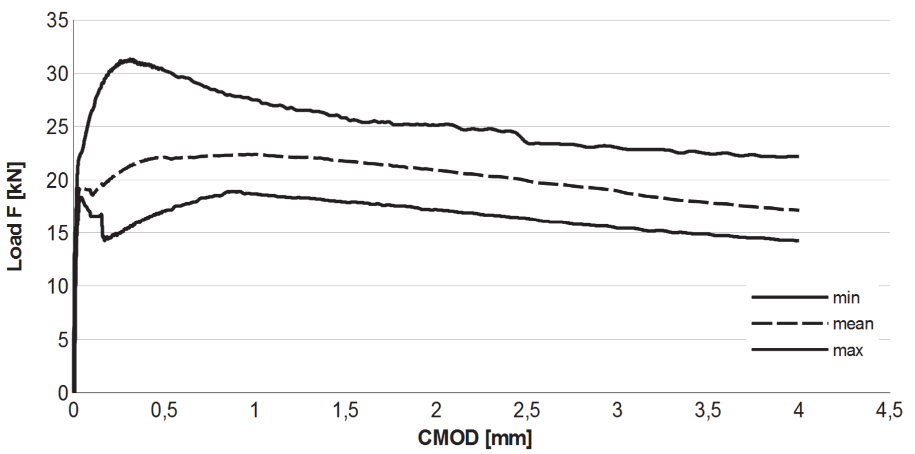

Fig. 7. Load-CMOD relation for $V_f = 0.9\%$

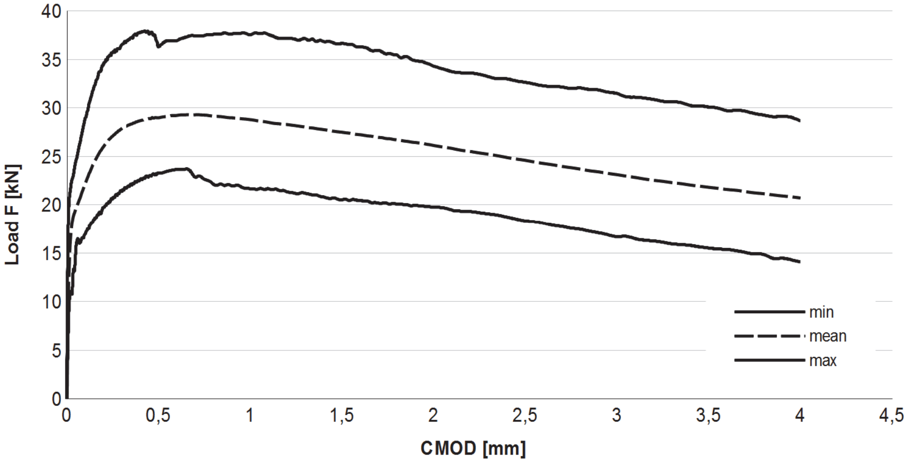

Fig. 8. Load-CMOD relation for $V_f = 1.2\%$

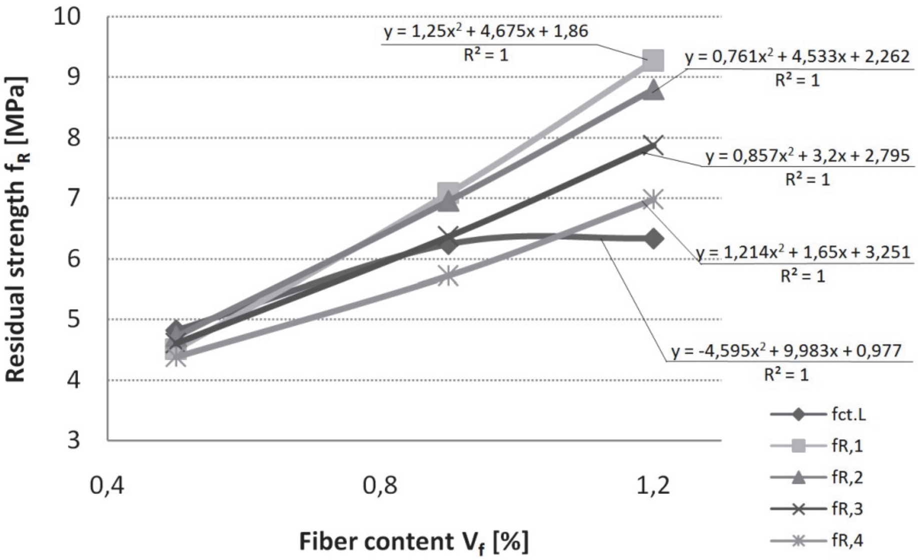

Fig. 9. Residual strength-fibre content V_f relation

Having analysed the presented data, one may conclude that residual strengths increase along with fibre content in the composite mixture. However, it must be pointed out that limit of proportionality was more or less the same in the case of fibre content (V_f) being equal to 0.9% and 1.2%. In view of the fact that the fibre content of 1.2% was optimal (Głodkowska & Laskowska-Bury 2015) for the test composite, characteristic values (Table 3) were determined to calculate shear capacities.

Table 3. Parameters for statistical analysis of residual strengths for the composite with $V_f = 1{,}2\%$

Property symbol	Characteristic value [MPa]	standard deviation s [MPa]	coefficient of variation υ [%]	homogeneity index k [-]	confidence interval [MPa]	material classification by fib Model Code
$f^{f}_{ct,L,k}$	5.24	0.67	11	0.78	6.09-6.60	7b
$f_{R,1,k}$	7.30	1.20	13	0.80	8.82-9.74	
$f_{R,2,k}$	6.68	1.29	15	0.74	8.30-9.28	
$f_{R,3,k}$	5.82	1.25	15	0.74	7.39-8.34	
$f_{R,4,k}$	5.07	1.16	17	0.71	6.53-7.42	

The classification 7b in accordance with [24], defines the test material as a composite with a very high f_{R1} value (ranging from 1 to 8). The letter 'b' indicates that the test composite is characterised by *pcs,* which was determined by means of the ratio f_{R3}/f_{R1} (according to (Model Code 2010) 'a' and 'b' – *pcs*, 'd' and 'e' – *psh*). The strength values presented in the table may be used to design flexural/shear structural elements made from SFRWSC.

Measuring crack widths while testing residual strengths may be problematic. For that reason, the standard (PN-EN 14651, 2005) allows the possibility of calculating *CMOD* value using the prism's deflection value δ according to the formula:

$$\delta = 0{,}85 \cdot CMOD + 0{,}04 \tag{2}$$

Since both crack width *CMOD* and deflection δ were measured in the test, Figures 10-12 present the relation between these two values against the backdrop of a theoretical relation in accordance with PN-EN (PN-EN 14651, 2005).

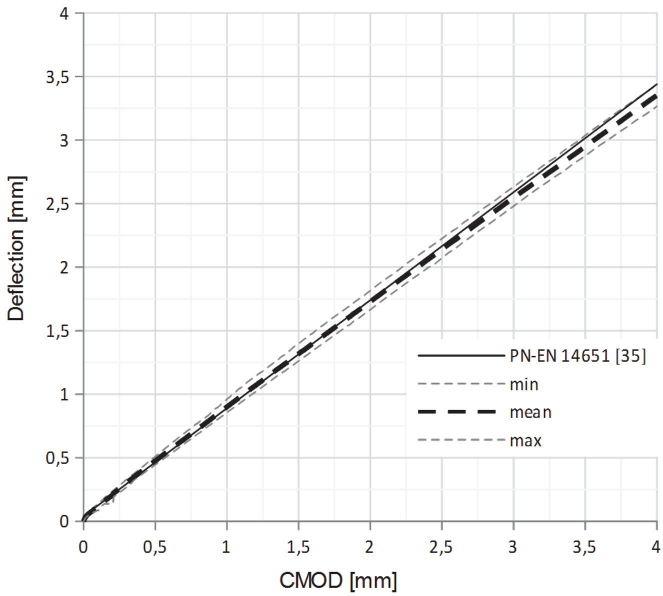

Fig. 10. Deflection-CMOD relation for the composite with the fibre content $V_f = 0.5\%$

According to the charts above, the experimental average values of *CMOD*-deflection relation correspond closely to the values proposed in the standard. Therefore, it is fully justified to use the standard for calculating residual strengths.

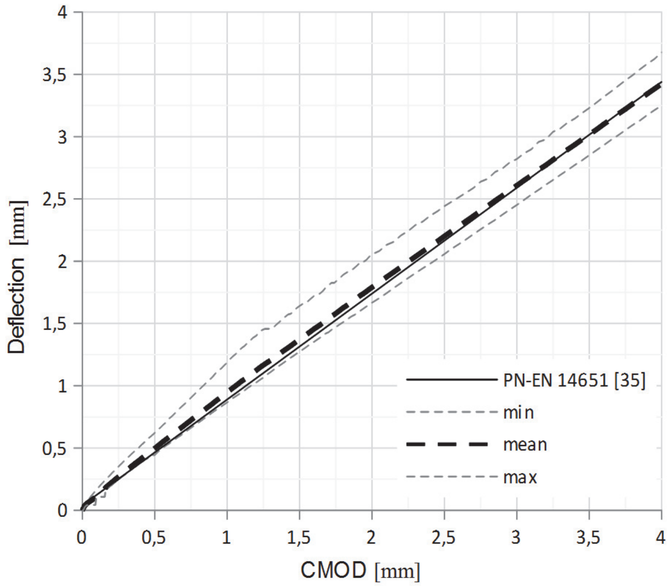

Fig. 11. Deflection-CMOD relation for the composite with the fibre content $V_f = 0.9\%$

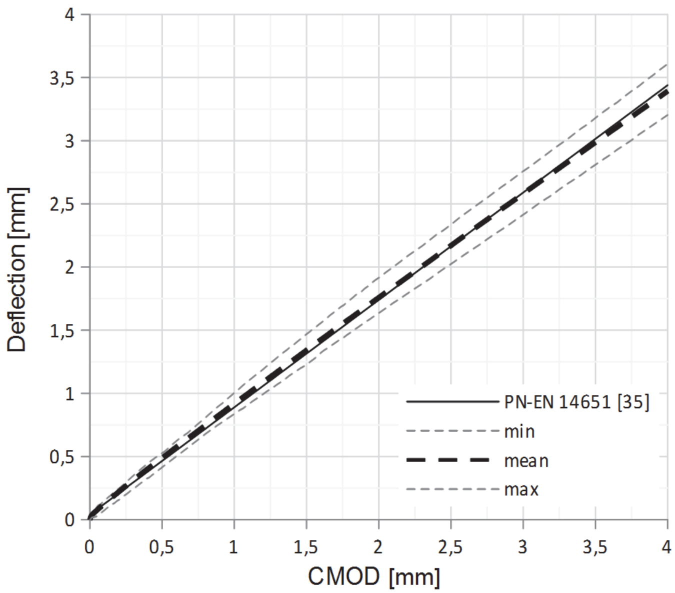

Fig. 12. Deflection-CMOD relation for the composite with the fibre content $V_f = 1.2\%$

6. Selected shear design methods – general characteristics

RILEM TC-162-TDF

Determining shear capacities of specimens made from fibre-reinforced composites in accordance with RILEM TC-162-TDF is based on Eurocode 2 (EN 1992 -1-1. 2004), which means it is based on truss system model S-T. The influence of fibres on shear capacity is defined as shear stress increment τ_{fd}, which is determined by means of residual strength $f_{R,4,k}$.
Shear capacity V_{Rd} is a sum of three factors:

$$V_{Rd} = V_{cd} + V_{fd} + V_{wd} \ [\mathrm{N}] \tag{3}$$

V_{cd} – specimen's shear capacity without shear reinforcement,

$$V_{cd} = \left[0{,}12 \cdot k \cdot \left(100 \cdot \rho_l \cdot f_{fck}\right)^{\frac{1}{3}}\right] \cdot b_w \cdot d \ [\mathrm{N}] \tag{4}$$

where:

$$k = 1 + \sqrt{\frac{200}{d}} \leq 2 \tag{5}$$

$$\rho_l = \frac{A_s}{b_w \cdot d} \leq 0{,}002 \ [-] \tag{6}$$

b_w, d width and effective depth of cross section (EN 1992 -1-1. 2004), [mm],
A_s – cross sectional area of reinforcement which is bonded beyoned the considered section (EN 1992 -1-1. 2004), [mm^2],
f_{fck} – characteristics cylinder compressive strength for concrete with fibers, [MPa],
V_{fd} – shear capacity increase due to steel fibre reinforcement:

$$V_{fd} = 0{,}7 \cdot k_f \cdot k \cdot \tau_{fd} \cdot b_w \cdot d \ [\mathrm{N}] \tag{7}$$

where:
k_f – factor taking into account the shape of the cross-section; for rectangular cross section beams k_f = 1,0

τ_{fd} - design value of incrase in shear strenght due to fibres, given by:

$$\tau_{fd} = 0{,}12 \cdot f_{R,4,k} \ [\mathrm{MPa}] \tag{8}$$

$f_{R,4,k}$ – residual strength corresponding to CMOD of 3,5 mm,
V_{wd} – shear capacity increase due to conventional shear reinforcement in accordance with (EN 1992-1-1.2004).

Fib Model Code

The fib Model Code method does not take residual strengths into direct consideration for determining shear capacities of fibre-reinforced composites. In tension zone, according to this method, the contribution of steel fibre reinforcement is defined by two strengths: serviceable residual strength f_{Fts} (post-crack strength for serviceability limit state), and ultimate residual strength f_{Ftu}. In order to determine shear capacities, fib Model Code recommends to use linear model describing cracked tension zone where tensile stresses are directly proportional to crack width w_u (Fig. 13). It is noteworthy that the stresses may increase or decrease along with crack width increments.

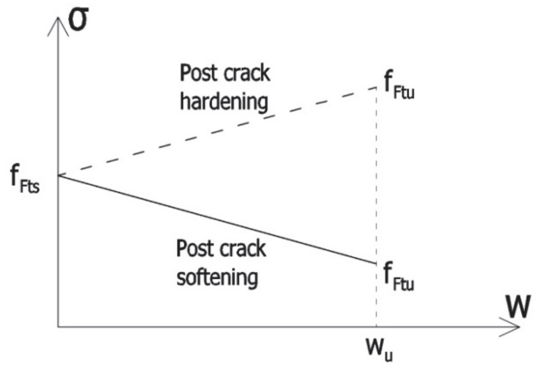

Fig. 13. Linear model describing cracked tension zone in bending cross-section of fibre-reinforced concrete in accordance with fib Model Code 2010: f_{Fts} – post-crack residual strength for serviceability limit state); f_{Ftu} – ultimate residual strength

Values f_{Fts} and f_{Ftu} are defined as:

$$f_{Fts} = 0{,}45 \cdot f_{R,1,k} \text{ [MPa]} \tag{9}$$

$$f_{Ftu} = f_{Fts} - \frac{w_u}{CMOD_3} \cdot \left(f_{Fts} - 0{,}5 \cdot f_{R,3,k} + 0{,}2 \cdot f_{R,1,k}\right) \geq 0; \quad w_u = 1{,}5mm \text{ [MPa]} \tag{10}$$

According to fib Model Code [24], the shear capacity of fibre-reinforced composites is presented as the sum of two capacities:

$$V_{Rd} = V_{Rd,f} + V_{Rd,s} \text{ [N]} \tag{11}$$

$V_{Rd,f}$ – design value of shear resistance in members with convencional longitudinal reinforcement and without convencional shear reinforcement is given by:

$$V_{Rd,f} = \left\{ \frac{0{,}18}{\gamma_c} \cdot k \cdot \left[100\rho_l \cdot \left(1 + 7{,}5 \cdot \frac{f_{Ftuk}}{f_{ctk}} \right) \cdot f_{fck} \right]^{1/3} \right\} \cdot b_w \cdot d \text{ [N]} \tag{12}$$

where:
γ_c – the partial safety factor for the concrete matrix without fibres,
f_{ctk} – characteristic value of tensile strength for the concrete matrix, [MPa],
V_{wd} – shear capacity increase due to conventional shear reinforcement in accordance with (EN 1992 -1-1. 2004).

An important aspect raised by fib Model Code is the minimum amount of traditional shear reinforcement in fibre-reinforced specimens:

$$f_{Ftuk} \geq 0{,}08 \cdot \sqrt{f_{ck}} \tag{13}$$

If the condition (13) is met, the minimum amount of transverse reinforcement is not required.

7. Calculating shear capacity using residual strengths

In order to prove the possibility of using SFRWSC with the fibre content equal to 1.2% as a construction material transmitting bending moment and transverse force, shear capacities of the prisms were calculated according to fib Model Code 2010 and RILEM- TC-162-TDF. In the analysis, two variants were considered. In the first variant, an assumption was made that the prisms have a constant cross-section (bxh = 200×300 mm) and their flexural reinforcement is variable. In the second variant, it was assumed that the flexural reinforcement ratio is constant (ρ_l = 0.01) and the prism's height is variable (h) with the proportion h/b = 1.5 maintained. A partial factor of safety equal to γ_f = 1.5 was used in the calculations.

Table 4 presents calculation results for shear capacities of the prisms with steel fibres and without steel fibres as well as the relation between these two values. This relation demonstrates the influence of steel fibres on shear capacity. The analysis revealed that adding steel fibres to the test composite significantly increases the specimen's shear capacity. According to Model Code 2010, the increase in shear capacity of the specimen with steel fibres is constant, regardless of the amount of main reinforcement, and is equal to 124% when compared to the increase in shear capacity of the specimen without fibres. In the case of RILEM – TC-162-TDF however, the opposite was observed. In the extreme case (i.e. for $\rho_l = 0.02$), shear capacity increase is equal to 75%.

Table 4. Selected calculation results for shear capacities of SFRWSC prisms in variant I

	Design methods						
	RILEM TC-162-TDF			Model Code 2010			
ρ_l [-]	V_{cd} [kN]	$V_{cd}+V_{fd}$ [kN]	$(V_{cd}+V_{fd})/V_{cd}$ [-]	$V_{Rd,c}$ [kN]	$V_{Rd,f}$ [kN]	$V_{Rd,f}/V_{Rd,c}$ [-]	f_{Ftu} [MPa]
0.008	41.02	81.13	1.98	41.02	91.89	2.24	2.18
0.010	44.19	84.67	1.92	44.19	98.99		
0.012	46.96	87.77	1.87	46.96	105.19		
0.014	49.44	90.53	1.83	49.44	110.74		
0.016	51.69	93.05	1.80	51.69	115.78		
0.018	53.76	95.36	1.77	53.76	120.41		
0.020	55.68	97.51	1.75	55.68	124.72		
ρ_l – tensile reinforcement ratio							

Analysing the shear capacity values (Table 5) calculated using RILEM method (variant II), it is safe to say that cross-section dimensions have a considerable influence on shear capacity increase with regard to the addition of fibres. The larger the cross-section of the prism is, the more the composite's shear capacity increases. However, analysing the results according to Model Code, one can conclude that changing the prism's cross-section has no influence on shear capacity increase in the case of a specimen made from fibre-reinforced composite. Another conclusion is that the fiber-reinforced specimen's shear capacity always increases proportionally by the same value in relation to the shear capacity of a specimen without fibres. In both calculation methods, shear capacity increase for different cross-sections at $\rho_l = 0.01$ exceeded 100%.

An important aspect raised in Model Code is that minimum shear reinforcement is required. This is understandable due to the problem of brittle fracture in specimens reinforced with steel fibres. In the case of the test composite, according to (13) one obtained:

$$f_{Ftuk} = 2{,}18 MPa > 0{,}08 \cdot \sqrt{f_{ck}} = 0{,}6 MPa$$

Table 5. Selected calculation results for shear capacities of SFRWSC prisms in variant II

bxh [mm]	Design methods						
	RILEM TC-162-TDF			Model Code 2010			
	V_{cd} [kN]	$V_{cd}+V_{fd}$ [kN]	$(V_{cd}+V_{fd})/V_{cd}$ -	$V_{Rd,c}$ [kN]	$V_{Rd,f}$ [kN]	$V_{Rd,f}/V_{Rd,c}$ -	f_{Ftu} [MPa]
160x240	29.19	60.85	2.08	29.19	65.49	2.24	2.18
187x280	38.88	82.67	2.13	38.88	87.24		
213x320	49.81	107.67	2.16	49.81	111.77		
240x360	61.97	135.84	2.19	61.97	139.04		
267x400	75.33	167.16	2.22	75.33	169.02		
293x440	89.88	201.60	2.24	89.88	201.67		
320x480	105.61	239.15	2.26	105.61	236.97		

8. Conclusions

Residual strengths are the major strength characteristics of a material. They may serve as basic values for designing structural elements reinforced with steel fibres. They also enable the composite's cracking resistance in bending to be determined. The defined four values of residual strength depend on *CMOD* value. It is noteworthy that the residual strength values are also related to the prisms' behaviour following the appearance of the first crack. In other words, these values vary depending on whether a given specimen is characterised by a decrease (*pcs*) or an increase in load along with an increase in *CMOD* value (*pch*). A decrease in load is related to a decrease in the other residual strength values just as an increase in load is related to an increase in the residual strength values.

Presented in article SFRWSC with the fibre content equal to 1.2% meets the requirements of construction materials and can be used, in some cases, as an alternative to ordinary concrete. The composite subject to analysis fulfils the standard requirements (Model Code 2010): $f_{R1}/f_{lk} > 0,4$, $f_{R3}/f_{R1} > 0,3$, which means that steel fibre reinforcement may partially replace conventional reinforcement at the ultimate limit state. Calculations done according to RILEM, fib Model Code show a considerable increase in the shear capacity of composites with the steel fibre content of 1.2%, which computationally leads to reduction of conventional shear reinforcement. Comparing the two methods, one should emphasize that RILEM regulations define shear capacity in a more simplified manner. Using only one residual strength $f_{R,4,k}$, a major aspect of the composite's behaviour following the appearance of the first crack (*pcs* or *pch*) would be omitted. Model Code, however, describes the issue of transmitting post-cracking stresses in more detail. Firstly, it defines the value f_{Ftsk}, which is determined directly from the value $f_{R1,k}$ – this occurs at the initial stage of cracking during the residual strength test. Next, the standard defines the value f_{Ftuk} which takes residual strengths into account for crack width equal to 0.5 mm and 2.5 mm as well as for limit crack width used in structural design.

Therefore, it is possible to conclude that the Model Code recommendation defines more accurately SFRWSC strength characteristics, which are used in structural design. Furthermore, the important issue of minimum conventional shear reinforcement should be emphasized. The RILEM method sets no conditions for reducing or omitting the minimum ratio of stirrup reinforcement in fibre-reinforced prisms.

Another conclusion is that, according to RILEM, the designed SFRWSC elements have to meet the requirements regarding the minimum reinforcement in the form of stirrups just like traditional reinforced concrete elements do. However, the Model Code standard does not require minimum stirrup reinforcement according to the formula (13), which has been proved in this article. Therefore, the condition (13) may evidently help improve reinforcement fixing at construction sites.

It should be also underlined that the composite is made from waste sand, which has an important ecological meaning. The possibility of using sand as an aggregate to produce structural material on an industrial scale would help manage waste sand accumulating in the Polish region of Pomerania. It would also make good use of the plentiful sand occurring in the Middle East and North Africa. Vast resources of fine aggregates in these regions may become a source of wealth by providing a component for the production of structural elements.

Notation

CMOD – crack mouth opening displacement
E_{cm} – static modulus of elasticity
E_d – dynamic modulus of elasticity
$f_{c,cyl}$ – cylinder compressive strength
$f_{c,cube}$ – cube compressive strength
$f_{ct,L}$ – limit of proportionality
f_{Fts} – serviceable residual strength
f_{Ftu} – ultimate residual strength
$f_{R,i}$ – residual tensile strength
$f_{t,spl}$ – split tensile strength
G_d – dynamic modulus of rigidity
k – homogeneity index
s – standard deviation

SFRWSC – steel fibre reinforced waste sand concrete
V_{cd} – specimen's shear capacity without shear reinforcement,
V_f – fibre content by volume
V_{fd} – shear capacity increase due to steel fibre reinforcement,
V_{Rd} – shear capacity
V_{wd} – shear capacity increase due to conventional shear reinforcement
γ_f – partial factor of safety
δ – prism's deflection value
ε_{cs} – shrinkage
λ – aspect ratio (l/d)
υ – coefficient of variation
ρ_l – tensile reinforcement ratio
τ_{fd} – shear stress increment

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Abstract

This article presents calculation results for shear capacity which were obtained using SFRWSC's residual strengths in accordance with fib Model Code and RILEM standards. Shear capacity was calculated in two variants: for constant cross-section of a specimen and for constant ratio of flexural reinforcement. The article also presents residual strength test results for SFRWSC with varying steel fibre content and shows the influence of fibre content on the composite's residual strengths. It has been proved that SFRWSC, which is an ecological composite and whose properties are similar or better than those of ordinary concrete, can be useful in the production of structural elements with regard to shear capacity. Additionally, one has observed that SFRWSC's strength characteristics, which are used in structural design, are determined more accurately in fib Model Code than in RILEM standard. Furthermore, the issue of minimum conventional shear reinforcement should be emphasized as RILEM recommendation sets no conditions for reducing or omitting this reinforcement.

Keywords:
Steel fiber-reinforced concrete, waste sand, residual strength, shear capacity

Nośność na ścinanie i wytrzymałości resztkowe fibrokompozytu na bazie piasków odpadowych

Streszczenie

W artykule przedstawiono wyniki obliczeń nośności na ścinanie przy zastosowaniu wytrzymałości resztkowych analizowanego materiału wg fib Model Code i RILEM. Obliczenia nośności na ścianie wykonano w dwóch wariantach: przy stałym przekroju elementu oraz przy stałym stopniu zbrojenia na zginanie. Zaprezentowano także wyniki badań wytrzymałości resztkowych dla fibrokompozytu o różnej zawartości włókien stalowych wytworzonego na bazie piasków odpadowych takiego fibrokompozytu. Przedstawiono wpływ zawartości zbrojenia rozproszonego na jego wytrzymałości resztkowe. Wykazano, że opracowany ekologiczny fibrokompozyt na bazie piasków odpadowych, którego właściwości są zbliżone lub lepsze niż betonu zwykłego, może być przydatny do wykonywania elementów konstrukcyjnych w aspekcie nośności na ścinanie. Ponadto stwierdzono, że norma fib Model Code bardziej wnikliwie niż norma RILEM określa cechy wytrzymałościowe fibrokompozytu, które następnie wykorzystuje się do wymiarowania elementów konstrukcyjnych. Dodatkowo należy podkreślić kwestię minimalnego zbrojenia konwencjonalnego na ścinanie. Rekomendacja RILEM nie wskazuje żadnych warunków zredukowania bądź pominięcia tego zbrojenia.

Słowa kluczowe:
fibrokompozyt, piasek odpadowy, wytrzymałość resztkowa, nośność na ścinanie

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Awareness of Waste Management in Single-Family and Multi-Family Housing Estates on the Example of Olsztyn

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1. Introduction

The problem of the negative impact of man on the natural environment results first of all from the willingness to maintain a high pace of economic development. This is mainly the result of over-demand and supply-driving consumption accompanied by low environmental awareness. This results in an increase in adverse external effects, which generate higher costs and reduce social welfare, resulting in ecosystems not being able to assimilate damage. One of the main problems in the context of environmental protection is the increase in the quantity of all types of waste, which is becoming more and more challenging to manage. Undoubtedly, over the centuries, waste generation has been an inseparable feature of human economic activity. However, a big problem becomes their management without causing any damage to the natural environment. This forces the necessity of proper waste management by limiting the space for storage, elimination of nuisance caused by emissions of pollutants to the environment and saving resources (*Zarządzanie środowiskiem*, 2007). People often have to bear individual costs in order for the environment to benefit (Steg et al., 2014).

It should be noted that this increased consumption leads to an increase in waste generation (Malinauskaite et al., 2017). In addition, the level of waste generation significantly depends on economic development – the richer the country, the more waste it produces (Minelgaite & Liobikiene, 2019). Therefore, legal regulations are introduced, which influence the decisions of both economic entities and households, which are to carry out rational waste management.

On average, the EU countries produce around 482 kg of waste per capita per year. However, there is a significant difference between the Member States.

The "leader" in waste generation is Denmark, where residents generate about 777 kg per capita per year. In Cyprus, Malta and Germany, the amount of waste is also one of the highest and reaches over 600 kg per capita. In Romania, Poland, Czech Republic and Slovakia, the amount of waste was almost twice as small (Minelgaite & Liobikiene, 2019). However, also in these countries, including Poland, the amount of waste has been increasing for many years, and forecasts indicate that this trend is continuing. According to the latest data published by the Central Statistical Office (GUS) (GUS, 2019a), 283 kg of municipal waste per capita was produced in 2015. In 2016, there was an increase of almost 15% (to over 300 kg) to reach 312 kg per person in 2017. Each year, however, the level of waste segregation and recycling is increasing. According to the official data of the Central Statistical Office (GUS) (GUS, 2019b), in 2015 the waste collected selectively in relation to the total amount of waste is 23.4%, in 2016 25.2% and a year later it reaches the level of 27.1%.

The necessity of rational exploitation of natural resources and environmental protection was considered to be the critical factors for the future development of Poland (Gawroński, 2019). Significant progress has been made in reducing environmental pressures over the last 30 years, but despite improvements, further steps need to be taken to improve the eco-efficiency and greening of the Polish economy (*Stan Środowiska w Polsce*, 2014). Therefore, the recently introduced regulations adopted by the ministers of the environment of the EU member states set new targets for the reuse and recycling of municipal waste: by 2025, the EU countries are obliged to manage 55% of waste in this way, by 2030 – 60%, and by 2035 – 65%.

Households can minimise waste and increase recycling through proper segregation and behavioural change (Van der Werff et al., 2019). Therefore, education and constant increase in awareness of the inhabitants have an essential role to play in waste management (Deluga, 2018). Environmental awareness is not only knowledge about the environment, but above all recognition of the environment as values and active measures to protect it (Tuszyńska, 2017). Environmental awareness can be broadly defined as the attitude regarding environmental consequences of human behaviour. Starting from the typical definition of attitude, environmental awareness is a pre-disposition to react to environmental issues in a certain manner (Culiberg & Rojšek, 2008; Ham et al., 2016).

The most important source of information for the public in this respect seems to be the Internet, as well as free information brochures distributed by municipal companies and local authorities. A large part of the public is convinced that with proper waste management, it is possible to protect the environment. In those communities where residents are convinced of their recycling potential, a great many people are involved in such activities (Tabernero et al., 2015). However, if not for the appropriate actions influencing people's way of thinking, their awareness at this level would be at a much lower level. Of course, it should be remembered that many factors determine the level of the environmental awareness. Therefore, in this paper, the thesis was formulated that residents are aware of the problems resulting from the generation of waste in households, but in some areas, it is necessary to improve their environmental awareness. This results from the existing significant differences in the level of knowledge, awareness, and behaviour of the inhabitants, related to rational waste management in the household, related to the type of housing in the place of residence (single and multi-family housing).

The aim of the paper is to evaluate the environmental awareness of city residents on the management of waste living in multi-family or single-family housing. The city of Olsztyn was chosen for testing due to the announcement of very high price increases for waste collection in 2019.

2. Method

2.1. Physical context

Two housing estates in Olsztyn were selected for the study, one in single-family housing - Brzeziny (B), the other in multi-family housing (primarily prefabricated buildings estates) – Osiedle Generałów (OG). Olsztyn is the capital of the Warmian-Masurian Region with a total population of 161291 permanent residents and about 30 000 temporary residents (including 20 126 students) (Adamska et al., 2018). The population of the analysed settlements is as follows: Brzeziny is inhabited by over 2 thousand people, which constitutes 1.28% of the total population of the city (respondents constituted about 3% of the total population of the estate), while Osiedle Generałów by 9 032 (5.52% of the total population of the city; respondents constituted about 0.7% of the total population of the estate)) (*Raport o stanie miasta Olsztyn za lata 2010*, 2011).

In Brzeziny, in 2017, over 993 Mg of waste was collected, which was about 0.48 Mg per capita. In turn, Osiedle Generałów was characterized by a level of nearly 2 887 Mg, which gave 0.32 Mg per capita.

2.2. Method of measurement

The primary variables were measured using a standardised interview questionnaire. It consisted of 21 closed and open questions, which concerned both socio-demographic variables such as gender, age, level of education and income, self-efficacy in relation to household and system waste management, satisfaction with the quality of services provided by waste collection companies and awareness of the costs of waste management.

2.3. Analysis of data

In order to compare the results of the study, a Chi-square (χ^2) test of the highest reliability (NW) was used, which tests the same hypothesis as Pearson's χ^2 statistics; however, its calculation method is based on the theory of the highest reliability:

$$\chi^2 = \sum_{i=1}^{n} \frac{(O_i - E_i)^2}{E_i} \tag{1}$$

where:
O – observed value,
E – expected value.

2.4. Respondents

The interview was conducted on one day (6 February 2019). Respondents were randomly selected because many of those who could potentially participate in the interview refused to respond. A total of 120 interviews were conducted with adults, 60 in each housing estate.

The largest group of respondents was between 36 and 45 years old, the smallest between 21 and 25 years old and over 65 years old (Table 1). On OG, respondents represented all age groups, which only slightly differed from each other in terms of numbers. On B, apparent domination of respondents aged 36-45 and 26-35 years was noted (Table 1).

Table 1. The age of respondents

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
21-25	9	15.0	5	8.3	14	11.7
26-35	6	10.0	22	36.7	28	23.3
36-45	14	23.3	30	50.0	44	36.7
46-65	17	28.3	3	5.0	20	16.7
above 65	14	23.3	0	0.0	14	11.7
Total	60	100	60	100	120	100

Source: own study

People with secondary education dominated both housing estates; however, a relatively large percentage of respondents with university education is noteworthy (Table 2).

Table 2. Education of respondents

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
basic education	4	6.7	1	1.7	5	4.2
secondary education	33	55.0	44	73.3	77	64.2
higher education	23	38.3	15	25.0	38	31.7
Total	60	100	60	100	120	100

Source: own study

The largest group of respondents declared monthly income in the range from 3 000 to 4 000 PLN, the smallest in the range from 1 500 to 3 000 PLN and from 6 000 to 7 000 PLN.

Table 3. Respondents' income per capita (PLN)

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
1500-3000	3	5.0	8	13.3	11	9.2
3000-4000	36	60.0	3	5.0	39	32.5
4000-5000	18	30.0	13	21.7	31	25.8
5000-6000	3	5.0	25	41.7	21	17.5
6000-7000	0	0.0	11	18.3	11	9.2
Total	60	100	60	100	120	100

Source: own study

3. Results

All respondents stated that they knew what the cost of collecting waste is per capita[1]. The vast majority of the respondents stated that they spent PLN 10 to 15 per month per family member on waste collection. This proves (especially in the case of B) that the respondents did not know the rates of charges, because the majority of OG residents and all of B stated that they sort waste, and the price, in this case, was below PLN 10. The $\chi 2$ analysis showed statistically significant differences in this respect between the investigated settlements. As can be seen from

[1] Rates until 31 March 2019 for residential properties: PLN 14.41 per month for a person living in a given property if waste is unsorted; PLN 9.80 per month for a person living in a given property if municipal waste is collected selectively.

the data in Table 4 for B, all residents indicated only this price range, as opposed to OG residents who declared charges in all price ranges.

Table 4. The monthly charge for waste collection per person

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
do 7 PLN	2	3.3	0	0	2	1.7
7-10 PLN	42	70.0	0	0	42	35.0
10-15PLN	10	16.7	60	100.0	70	58.3
above 15 PLN	6	10.0	0	0	6	5.0
Total	60	100	60	100	120	100

Statistics	χ^2 test values	p
7-10 PLN	54.72232	.00000
10-15 PLN	71.34277	.00000
above 15 PLN	5.755801	.01643

Source: own study

According to Slavik and Pavel (2013), the place of residence (single-family houses or multi-family buildings) affects the efficiency of collection of municipal waste charges. The situation is much worse in housing estates consisting of multi-family houses, which is associated with higher density, the anonymity of tenants or very frequent changes of residents. According to more than 70% of respondents, the level of waste collection fees is a large or considerable expense in the context of their household budgets. Only one-third of the population described it as small or average. The χ^2 analysis showed statistically significant differences in the opinions of respondents from both housing estates. The data contained in Table 5 show that the level of fees is much more negative to the residents of B than to OG.

According to Malinauskaite et al. (2017), waste management solutions should be not only environmentally sustainable but also cost-effective and socially acceptable. Therefore, the respondents' opinion on the willingness to pay a higher price for waste collection for environmental reasons was interesting. This is particularly important in view of the announcements of price increases as of 1 April 2019. Although more than 42% of the surveyed group responded positively to this issue, the rest were more or less strongly opposed to it. The χ^2 analysis showed that there were no statistically significant differences between the opinions of the residents of both housing estates only in the case of lack of consent to increase the number of waste collection fees. In both cases, one in ten respondents was strongly opposed to charging higher amounts for this service (Table 6).

Table 5. The opinion of respondents on the level of fees for the disposal of municipal waste

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
Small expense	45	7.5	3	5.0	8	6.3
Average expense	22	37.5	3	5.0	25	21.3
Considerable expense	27	45.0	8	13.3	35	29.2
Big expense	3	5.0	36	60.0	39	32.5
Very large expense	0	0.0	10	16.7	10	8.3
Hard to say	3	5.0	0	0.0	3	2.5
Total	60	100	60	100	120	100
Statistics		χ^2 test values			p	
average expense		13.95375			.00019	
considerable expense		8.870456			.00290	
big expense		31.17081			.00000	
very large expense		8.804787			.00300	

Source: own study

Table 6. The opinion of respondents on the allocation of more money to waste management for environmental reasons

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
Yes	36	60.0	15	25.0	51	42.5
No	6	10.0	6	10.0	12	10.0
Probably not	18	30.0	39	65.0	57	47.5
Total	60	100.0	60	100.0	120	100
Statistics	χ^2 test values			p		
Yes	10.26899			.00135		
No	.0014264			.96987		
Probably no	10.03859			.00153		

Source: own study

The research showed that the majority of residents of B and OG segregate municipal waste. However, the χ^2 compliance test showed that there were statistically significant differences between settlements. While in B segregation was declared by all residents, in OG more than every tenth respondent did not undertake such actions (Table 7). The higher tendency to segregate waste of single-family house residents compared to people living in multi-family buildings is confirmed by research Triguero et al. (2016). According to these authors, suburban residents are much more likely to segregate waste than those living in city centres or large housing estates who cede the problem to waste collection companies or are "free riding". There are also financial issues in favour of waste segregation, as Kiepas-Kokot et al. (2015) claim that the only economic incentive for environmentally friendly behaviour in the current municipal waste management system is the lower fee rate for selective waste collection.

Table 7. Waste sorting

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
Yes	53	88.3	60	100.0	113	94.2
No	7	11.7	0	0.0	7	5.8
Total	60	100	60	100	120	100
Statistics	χ^2 test values			p		
Yes	7.265052			.00703		
No	7.265052			.00703		

Source: own study

The residents of both housing estates declared that they segregate mostly paper, glass, and plastic. They were the least interested in the selection of metal and batteries and accumulators. The χ^2 analysis showed statistically significant differences in the approach to waste management in both housing estates for all types of waste. In the case of paper, glass, and plastic, only residents of single-family homes reported 100% segregation, but unlike the respondents from OG, they did not sort second-hand clothes, metal, medicines, and batteries (Table 8). A separate issue is the selection of organic waste. While in the case of residents of single-family houses they do not pose a problem due to, e.g., the possibility of composting, in the case of multi-family houses they become troublesome due to quick spoilage, therefore their utilisation requires increasing the frequency of collection, as well as supplying and increasing the capacity of containers for selective collection (Lorek, 2015). Another issue concerns waste such as medicines and batteries and accumulators. As the Jakubus & Tatuśko (2015) research shows, while the separation of the most popular fractions, such as paper, glass, metals or plastics, is not a problem, the remaining fractions of municipal waste are differently qualified by the residents.

Table 8. Type of sorted waste

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
paper and cardboard	53	88.3	60	100	113	94.2
glass	53	88.3	60	100	113	94.2
plastic	53	88.3	60	100	113	94.2
clothing and textiles	52	86.7	0	0	52	43.3
organic waste	8	13.3	25	42.5	50	41.7
metal	12	20,0	0	0	12	10,0
medications	8	13.3	0	0	8	6.7
batteries and accumulators	5	8.3	0	0	5	4.2
I don't do the selection	7	11.7	0	0	7	5.8
Statistics	χ^2 test values			p		
paper and cardboard	7.265052			.00703		
glass	7.265052			.00703		
plastic	7.265052			.00703		
metal	11.98108			.00054		
organic waste	0.000000			.0000		
clothing and textiles	79.50866			0.0000		
batteries and accumulators	4.275796			.03866		
medications	7.265052			.00703		
I don't do the selection	7.265052			.00703		

Source: own study

The vast majority of respondents from both housing estates stated that the waste collection and selection system is effective in their opinion (Table 9), which was confirmed by the χ^2 analysis.

Table 9. The opinion of respondents on the correct functioning of the waste collection system

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
Yes	47	78.3	53	88.3	100	83.3
No	13	21.7	5	8.3	18	15.0
Total	60	100	60	100	120	100
Statistics	χ^2 test values			p		
Yes	1.401510			.23647		
No	1.401510			.23647		

Source: own study

According to the majority of respondents (Table 10), municipal waste is collected systematically. The essential element of a well-designed system is "friendly and transparent" selective collection of waste "at source." Introduced systems should be intuitive and corrected for their effective functioning in a given area. In particular, this applies to multi-family buildings, where it is practically impossible to separate waste into several fractions into separate containers in an apartment (Banaszkiewicz et al., 2013). The χ^2 analysis did not reveal any statistically significant differences between the opinions of the inhabitants of both housing estates.

Table 10. The opinion of respondents on the regularity of municipal waste collection

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
Collected systematically	54	90.0	56	93.3	110	91.7
Is not collected systematically	6	10.0	4	6.7	10	8.3
Total	60	100	60	100	120	100
Statistics	χ^2 test values			p		
Yes	.1570461			.69189		
No	.2146889			.64312		

Source: own study

According to O'Connell (2011), although the level of social awareness related to the environment is still rising, it does not mean that it is possible to stop strengthening the solutions developed so far and searching for new ones. It was interesting to learn about the opinions of respondents on waste management activities in their place of residence. In the first place the respondents mentioned the improvement of the system of sorted waste management (mainly the frequency of waste collection), and in the second place - better information on issues related to the overall waste management system in their housing estate and the whole city (Table 11). The χ^2 analysis showed significant differences only in the case of information and education. The research carried out showed that the OG residents paid much more attention to this issue (Table 11).

The survey asked the respondents whether the number of waste bins was appropriate in their opinion. As shown in Table 12, nearly 70% of the residents of both housing estates believed that the situation is favourable in this respect. However, the χ^2 analysis showed significant differences between residents of single-family houses and multi-family buildings. The availability of waste containers was assessed much better by respondents from OG, where the lack of containers was noticed only by less than 12% of respondents, while the lack of containers was noted by 50% of respondents from B (Table 12).

Table 11. The opinion of respondents on the measures that are urgently needed for waste management

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
information and education of the local community	36	45.0	36	18.3	72	60.0
conducting efficient, selective waste collection	31	51.7	53	75.0	84	70.0
investments in infrastructure for waste management	1	3.3	3	6.7	4	3.3
Statistics	χ^2 test values			p		
information and education of the local community	7.224600			.00719		
conducting efficient, selective waste collection	4.436345			.03518		
investments in infrastructure for waste management	1.099134			.29446		

Source: own study

Table 12. The opinion of respondents on available waste containers

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
It's suitable	53	88.3	30	50.0	83	69.2
It is not suitable	7	11.7	30	50.0	37	30.8
Total	60	100	60	100	120	100
Statistics	χ^2 test values			p		
Yes	16.27988			p=.00005		
No	13.78043			p=.00021		

Source: own study

The question of the number of waste bins available to the respondents is related to the above. The research carried out showed that most often there were three containers in their place of residence, which was related to the segregation carried out (Table 13)[2]. However, the χ^2 analysis showed significant differences between settlements. At OG dominated respondents indicating three containers for waste segregation and B by respondents indicating four containers for waste segregation. This may be due to the fact that the residents of single-family houses have a much larger surface area, and thus a higher possibility to have more containers

[2] As of March 2018, the amended regulations are in force and there should be at least five containers.

than those living in a multi-family building. It is also important that the residents of single-family homes are in charge of segregation themselves, while various types of management serve those living in multi-family buildings.

Table 13. Number of containers to which respondents have access

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
5 containers	8	13.3	8	13.3	16	13.3
4 containers	9	15.0	37	61.7	46	38.3
3 containers	39	65.0	15	25.0	54	45.0
2 containers	4	6.7	0	0.0	4	3.3
1 container	0	0.0	0	0.0	0	0.0
Total	60	100	60	100	120	100
Statistics	χ^2 test values			p		
5 containers	0.000000			1.0000		
4 containers	20.07688			.00001		
3 containers	13.31967			.00026		
2 containers	5.755801			.01643		

Source: own study

The assumption of the selective collection system of municipal waste is to obtain the largest possible amount of high-quality raw materials suitable for recycling. This objective can only be achieved with a high level of public involvement. In order to encourage residents to segregate waste, it is not enough just to provide them with access to containers. An essential element is the environmental awareness of the society and the conviction that selective collection has a measurable impact on the state of the natural environment (Pasiecznik et al., 2016). Research carried out in two housing estates in Olsztyn showed that the majority of respondents found the information on waste segregation sufficient. However, it is worth noting that more than one-third of respondents were of the opinion that their environmental awareness was still limited (Table 14). The $\chi 2$ analysis showed that there were significant differences between settlements. Much better environmental awareness was assessed by OG residents, among whom only one in ten had some doubts about this issue. Similar results were obtained by Pietrzyk et al. (2014), who researched one of the municipalities in Lesser Poland Region. According to them, only half of the municipality inhabitants were of the opinion that educational activities were conducted on a large scale, while 29% of the respondents were unable to answer such a question. It is, therefore, necessary to increase the emphasis on education in this area, especially since, as Ma and Hipel (2016), Song et al. (2016) and Siedlecka (2017) claim, knowledge is a key factor influencing public awareness in the context of waste management systems and, consequently, environmental protection.

Table 14. The opinion of respondents on information on waste segregation

Specification	Osiedle Generałów		Brzeziny		Total	
	n	%	n	%	n	%
It's suitable	54	90.0	24	40.0	78	65.0
It is not suitable	6	10.0	36	60.0	42	35.0
Total	60	100	60	100	120	100
Statistics	χ^2 test values			p		
It's suitable	20.79234			.00001		
It is not suitable	23.74389			.00000		

Source: own study

4. Conclusions

Over the last three decades, significant progress has been made in reducing human pressure on the environment. Despite the improvement of the situation, further actions should be taken to improve the effectiveness of waste management in Poland. As mentioned in the introduction, the main objective of the research was to assess the level of the environmental awareness of residents of multi-family and single-family housing in Olsztyn on waste management on the example of two housing estates. Although the research is not representative, the results obtained indicate certain tendencies indicated in the works of other authors (Deluga, 2018).

Based on the research, conclusions were formulated that could be used by city authorities in the future:

1. Residents are aware of the waste problems, but some issues require improvement of the environmental awareness and actions at the household level. This is particularly important against the background of numerous information indicating the need to reduce the amount of waste, especially those that are very difficult to manage effectively.
2. The majority of respondents did not know the level of waste collection fees. This concerned mainly people living in single-family houses. This is surprising, as most of them declared to sort waste, which is associated with a lower price. It is important that at the time of field measurements, a very high (over 100%) increase in rates was already known, and according to over 70% of respondents, the level of per capita fees related to waste was already a high expense, especially for the residents of single-family houses. Most respondents were sceptical about the increase in waste fees, but more than 40% were willing to pay more for environmental reasons.

3. The majority of the respondents stated that they segregated waste, but the inhabitants of single-family houses were more inclined to do so. This may be due to the fact that waste management in single-family houses is more transparent and easier to control, which limits abuse. In turn in multi-family buildings, inhabitants are decisively more anonymous what can cause even the so-called "free riding".
4. The residents of both settlements segregated mainly paper, glass, and plastic. However, only the residents of single-family houses showed full segregation. Despite this, unlike the respondents from multi-family housing, they did not declare sorting of used clothes, metal, medicines or batteries. Organic waste (BIO) was not a problem for the inhabitants of single-family houses (possibility of composting), but in the case of a multi-family building, it can be troublesome, as evidenced by a small percentage of respondents undertaking such actions.
5. In the opinion of respondents from both housing estates, the waste collection and selection system is effective, and waste is collected systematically. This is at odds with the expectations of respondents regarding investments in waste management in their place of residence. The majority of respondents mentioned (especially those living in single-family houses) the increase in the frequency of waste collection in the first place and the optimisation of the waste management information system in the second place. Even though since March 2018 the regulations on increasing the number of containers have been in force, respondents from multi-family buildings usually had three containers, while respondents from single-family houses had four.

The research carried out confirmed the thesis made at the beginning of the article. An important element of waste management is the environmental awareness of society and the conviction that selective collection has a measurable impact on the state of the environment. The majority of respondents considered the available information on waste segregation sufficient. However, it is worrying that more than one-third of them felt that their environmental awareness was too limited. It is, therefore, necessary to intensify the efforts of institutions responsible for waste management in order to inform all the inhabitants of the city about it adequately.

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Abstract

One of the main problems in the context of environmental protection is the increase in the quantity of all types of waste, which is becoming more and more challenging to manage. The aim of the paper is to evaluate the environmental awareness of city residents on the management of waste living in multi-family or single-family housing. The city of Olsztyn was chosen for testing. Two housing estates in Olsztyn were selected for the study, one in single-family housing – Brzeziny, the other in multi-family housing – Osiedle Generałów. The primary variables were measured using a standardised inter-view questionnaire. It consisted of 21 closed and open questions. A total of 120 interviews were conducted with adults, 60 in each housing estate. Surveys have confirmed that residents are aware of the waste problems, but some issues require improvement of the environmental awareness and actions at the household level. Most of the respondents did not know the level of waste collection fees. This concerned mainly people living in single-family houses. The majority of the respondents stated that they segregated waste, but the inhabitants of single-family houses were more inclined to do so. The residents of both settlements segregated mainly paper, glass, and plastic. However, only the residents of single-family houses showed full segregation. Organic waste (BIO) was not a problem for the inhabitants of single-family houses (possibility of composting), but in the case of a multi-family building, it can be troublesome, as evidenced by a small percentage of respondents undertaking such actions. In the opinion of respondents from both housing estates, the waste collection and selection system is effective, and waste is collected systematically.

Keywords:
waste management, environmental awareness,
single-family and multi-family housing estates, waste sorting, costs

Świadomość dotycząca gospodarowania odpadami mieszkańców osiedli w zabudowie jednorodzinnej i wielorodzinnej na przykładzie Olsztyna

Streszczenie

Jednym z głównych problemów w kontekście ochrony środowiska jest zwiększanie się ilości wszelkiego rodzaju odpadów, które są coraz trudniejsze do zagospodarowania. Celem artykułu jest ocena poziomu świadomości ekologicznej mieszkańców miasta na temat gospodarowania odpadami mieszkającymi w zabudowie wielorodzinnej lub jednorodzinnej. Do testowania wybrano miasto Olsztyn. Do badań wytypowano dwa osiedla mieszkaniowe w Olsztynie, jedno w zabudowie jednorodzinnej – Brzeziny, drugie w wielorodzinnej – Osiedle Generałów. Do pomiaru pierwotnego zmiennych wykorzystano standaryzowany kwestionariusz wywiadu. Zbudowany był z 21 pytań zamkniętych i otwartych. Przeprowadzono 120 wywiadów z osobami dorosłymi, po 60 w każdym z osiedli. Badania potwierdziły, że mieszkańcy są świadomi problemów związanych z odpadami, jednak w niektórych kwestiach konieczna jest poprawa stanu wiedzy oraz działań na poziomie gospodarstw domowych. Większość respondentów nie znała wysokości stawek opłat za odbiór od-padów. Dotyczyło to przede wszystkim osób zamieszkujących domy jednorodzinne. Większość badanych stwierdziło, że segreguje odpady, przy czym większą skłonność do takiego działania mieli mieszkańcy domów jedno-rodzinnych. Mieszkańcy obu osiedli segregowali przede wszystkim papier, szkło i plastik. Pełną segregację wykazali się jednak tylko mieszkańcy domów jednorodzinnych. Odpady organiczne (BIO) nie stanowiły problemu dla mieszkańców domów jednorodzinnych (możliwość kompostowania), jednak w przypadku budynków wielorodzinnych bywa to kłopotliwe o czym świadczy niewielki odsetek badanych podejmujących takie działania. W opinii respondentów z obu osiedli system odbioru i selekcji odpadów jest efektywny, a odpady odbierane są systematycznie.

Słowa kluczowe:
gospodarka odpadami, świadomość ekologiczna,
osiedla w zabudowie jednorodzinnej i wielorodzinnej, segregacja odpadów, koszty

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Characteristics of Sludge Node Operation at Wastewater Treatment Plant in Żory

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1. Introduction

Proper operation of a wastewater treatment plant (WWTP) consists in achieving an appropriate level of the wastewater treatment and carrying out the technological process in accordance with the adopted technology. Therefore, it requires adapting the conducted wastewater treatment processes to the changing functional characteristics of the treatment plant elements, including inhomogeneous volume flow and the wastewater composition. Disruptions and disabilities in the operation of the wastewater treatment plant cause, that the increased amounts of pollutants are introduced into aquatic ecosystems. The by-product of the processes taking place at the wastewater treatment plant is, among others, the sewage sludge (Dymaczewski et al. 1997). According to the Polish regulations (Dz. U. 2019 item 701), the municipal sewage sludge is defined as the "coming from the wastewater treatment plants sludge from the anaerobic digesters and other installations used for the treatment of the municipal wastewater, and other wastewater with a composition similar to the composition of the municipal wastewater". In turn, indirectly, as a result of running processes of the sludge treatment, there are produced leachates from the sludge dewatering processes. The leachates are characterized by varying in time load of pollutants, especially nitrogen and phosphorus compounds. The issue of leachates is a key problem in terms of returning into the technological line the additional load of nitrogen, phosphorus and organic carbon. In addition, they are a factor with a potentially very large negative impact on the effects of nitrogen removal in the main treatment line (Gajewska & Pempkowiak-Obarska 2008). In connection with the above, in the work an analysis was prepared of the functioning of the sewage sludge part of the wastewater treatment plant in Żory, in the years 2015-2017.

2. Objective of the work

The subject of the study was the analysis of data regarding the functioning of the sewage sludge part of the wastewater treatment plant in Żory. The study included analysis of the functioning of the sewage sludge part of the Żory wastewater treatment plant in the period from 2015 to 2017. The assessment of work of this part of the wastewater treatment plant was based on results of the physical and chemical parameters of sludges and leachates after the dewatering process.

3. General characteristics of the object

The wastewater treatment plant in Żory is located in the Silesian Voivodship, on the left bank of the River Ruda, at 43 + 450 km of its course. In terms of technology, the treatment plant is divided into two parts: wastewater and sewage sludge. The wastewater is treated using the mechanical and biological methods along with anaerobic treatment of the sludge. The wastewater treatment is carried out using the low-load sludge technology based on the classical, 3-stage Bardenpho system, referred to as the A2/O system (Figure 1). According to the assumptions of the process, the wastewater along with the activated sludge flows sequentially through a chamber or a separate anaerobic (non-oxygen), anoxic (hypoxic) and aerobic (oxygen) zone (Heidrich & Witkowski 2005). In the three-phase type A2/O system, both organic phosphorus and total nitrogen are removed from the wastewater.

The excessive sludge from the secondary settling tanks after compaction on a belt compactor is directed to anaerobic digesters, where it is fermented together with the raw sludge from the primary settling tank in the process of mesophilic fermentation at 38°C. The hydraulic retention time (HRT) amounts to 20-21 days. The chambers are heated by spiral heat exchangers through recirculation of the sludge contained in them. Mixing in the anaerobic digesters is carried out by means of mechanical agitators, and the mixing process is additionally supported by the pump system for recirculation. The sludge from the anaerobic digester (AD) is discharged using the overflow pipeline to a two-chamber retention basin of the digested sludge, equipped with agitators. The next stage of processing the sludge is its dewatering on the belt press. The dewatered sludge is stored under a roofed place of temporary sludge collection and then directed for further management.

The functioning anaerobic digesters are equipped with installations for collecting biogas, which after the desulphurisation and drainage process is used for the production of electricity and heat in cogeneration units. The biogas produced in the fermentation process is collected in the shell gas tank, and its excess is burned in a torch.

The projected average daily capacity of the treatment plant amounts to $Q_{d,avg.}$ = 9 596.0 m^3/d, while the maximum daily capacity is $Q_{d,max}$ = 19 200.0 m^3/d. The equivalent number of inhabitants was defined at the level 69 791 PE.

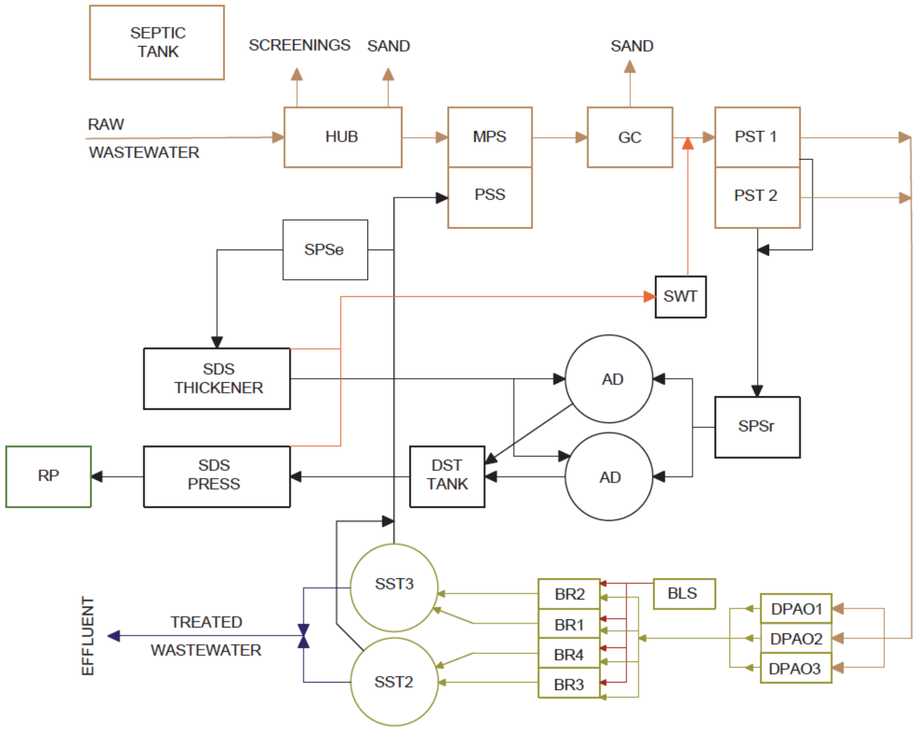

Fig. 1. Block diagram of the wastewater treatment plant in Żory. Source (Own materials of PWiK Żory 2018; Zdebik et al. 2018)
Meaning of symbols: HUB – sand separator with screen, MPS – main pump station, PSS – pump station for the recirculated sludge, GC – grit chamber, PST – primary settling tank, DPAO – dephosphatation chamber, BLS – blower station, BR – biological reactor, SST – secondary settling tank, SPSr – raw sludge pump station, SPSe – excessive sludge pumping station, AD – anaerobic digester, DST – digested sludge tank, SDS – sludge digestion station, RP – roofed place, SWT – supernatant storage tank

Average daily inflow of raw wastewater to the treatment plant in the years 2015-2017 amounted ca. 8 177.0 m^3/d. The data regarding the quantity and quality of wastewater flowing into the wastewater treatment plant in the years 2015-2017 are presented in Table 1. It was found that the hydraulic load and pollutants loads in the wastewater inflow conditions, in the rainless periods, did not exceed the assumed design parameters Analysing the annual distribution of the BOD_5 load, which amounted to 2 444 kg/d, it was lower by 1 743.0 kg /d than the design parameters. The total phosphorus load was lower than the assumed design parameters, while in the case of total nitrogen, the assumed load of these pollutants was exceeded. With reference to the design values, the total nitrogen load was higher by 114.3 kg/d. A observable increase in the nitrogen load in raw wastewater may be caused by an increased amount of inflowing wastewater in a certain month. Another of the reasons could be the low temperature of the raw wastewater (Brzezińska 2011). For example in 2016 it was 8.7°C.

Table 1. Comparison of design and actual parameters of the wastewater flowing into the WWTP in the years 2015-2017. Own study based on (Own materials of PWiK Żory 2018)

Parameter	Design parameters	Actual parameters
PE*	69 791	44 283
$Q_{d,avg.}$, m^3/d	9 596.0	8 177.0
BOD_5, kg/d	4 187.0	2 444.0
COD, kg/d	8 375.0	5 825.5
TSS, kg/d	4 536.0	3 266.3
TN, kg/d	768.0	882.3
TP, kg/d	126.0	119.0

*Population Equivalent

4. Analysis of functioning of the sewage sludge part

Table 2 shows the characteristics of the sludge produced in the various stages of its processing. The properties of sludge generated in the wastewater treatment process at WWTP Żory are typical for municipal wastewater treatment plants (Bień 2007) and for this characteristics of sewage sludges and wastewaters the wastewater treatment plant has been designed. The physico-chemical properties of the sediments were similar to the designed values. However, due to increasing amount of sewage sludges, their value exceeded the designed values which resulted in partial overloading of sewage sludges equipment. The raw sludge from the primary settling tanks was characterized by hydration of 96.27% and the volatile solids of 2.83%. The thickened waste sludge had lower hydration (at the level of about 94%). The volatile solids amounted to about 4.5%. The lowest content of the volatile solids was characteristic for the digested sludge (1.68%). The last stage of the sewage sludge treatment is the dewatering process.

Thanks to this process, the sludge obtained the dry matter content of around 20.4% in the analysed period.

Table 2. Characteristics of the specific types of sludge according to design and operational data from 2015-2017. Based on (Own materials of PWiK Żory 2018)

Sludge			
Raw	Thickened	Digested	Dewatered
Daily sludge volume, m^3/d (operational data / design data)			
64.08 / 67.00	49.01 / 53.00	113.09 / 110.00	11.98 / 10.00
Moisture content, %			
96.27 / 97.50	94.12 / 95.00	97.34 / 97.50	79.58 / 78.00
Dry matter content, %			
3.70 / 2.50	5.88 / 5.00	2.66 / 2.50	20.42 / 22.00
Organic matter content, %			
2.83 / n.d.*	4.48 / n.d.	1.68 / n.d.	14.09 / n.d.

n.d. – no data

The data regarding the average daily balance of sludge was used to assess the load of process equipment in the sewage sludge line. The analysis of the data presented in Table 3, i.e. the differences between the designed and the current state, indicates changes in regime of the equipment operation in the sewage sludge part of the treatment plant.

In the technological line of the sludge processing it was omitted the hydrolyser, which was out of service by the end of 2017. In the analysed period (2015-2017), two instead of three secondary settling tanks were used. The time of the wastewater retention in the secondary settling tanks, calculated on the base of the average daily volume of the wastewater ($Q_{d,avg.}$ = 8 177.0 m^3/d), including their capacity, increased from the designed value of 7.8 h to 9.14 h. The excessive sludge thickener, with the assumed 24-hour excessive sludge amount of 270.4 m^3/d, works approx. 5.4 h/day, i.e. longer than assumed in the project (4.9 h/day). For an average HRT, calculated on the base of the average daily amount of the excessive thickened sludge (48.0 m^3/d) and raw sludge (64.1 m^3/d), reaching the WKF, the hydraulic retention time is on average 21 days, i.e. 5 days shorter than in the design assumptions for the WKF chambers.

Table 3. Comparison of the designed capacity with the actual cycle of work of the sludge processing equipment. Based on (Own materials of PWiK Żory 2018)

Device	Parameter	Unit	Design parameter	HRT
			Value	
Hydrolyzer	Capacity	m^3	196	-
Primary settling tank	Capacity	m^3	2x400	
	Mean retention time	h	1.3	1.2
Secondary sedimentation tank	Capacity	m^3	3x1556	2x1556
	Mean retention time	h	7.8	9.14
	Diameter	m	3x25	
Thickener	Output	m^3/h	50	
	Mean work time	h/d	4.9	5.4
Mixed sludge storage tank	Capacity	m^3	14.5	
	Fill time	h	b.d.	7.3
Anaerobic digester	Capacity	m^3	2x1200	
	HRT	d	26.6 (summer) 25.4 (winter)	21.0 (avg.)
Post-fermentation storage tank	Capacity	m^3	300	
	Sludge retention time	d	6.4-7.8	2.6
Filter press	Output	m^3/h	5-10	
	Mean work time	h/d	4.1	11.9
Supernatant water storage tank	Capacity	m^3	1100	
	Retention time	d	6.3 (winter) 7.7 (summer)	16.4 (avg.)

Due to the fact that the amount of mixture of the sludge directed to fermentation has increased, in the future it should be considered possibility of expanding the system with an additional WKF chamber, or a system of thermal sludge hydrolysis. The possible retention time in the digested sludge tank, calculated taking into account the current data on the amount of the digested sludge, is shorter than the assumed time (6.4-7.8 d) and amounts to 2.6 d. Near three-fold increase in the average working time of the belt press was found (from 4.1 h/d to 11.9 h/d). This value was determined on the base of the average daily amount of the digested sludge and the maximum capacity of the equipment (10 m^3/h). In turn, the possibility of retaining leachates in the tank of the supernatants is greater than the designed one (about 7 d) and amounts to 16.4 d. The increase in the amount of wastewater flowing into the treatment plant and the related increase in the amount of generated sludge have an impact on the presented discrepancies between the designed and the actual state. The belt press and the digested sludge tank are particularly loaded in the system. The constantly increasing amount of sludge generated in the wastewater treatment plant may cause overloading of the technological system of sludge processing and, as a consequence, deterioration of the digested and dewatered sludge parameters.

5. The effect of pollutant loads in the leachates on the efficiency of work in the main technological line

The source of pollutants supplied to the main technological line, in addition to these coming from the municipal wastewater flowing into the WWTP, make the leachates generated after dewatering of the sludges, coming from the fermentation process. The leachates from dewatering of the sludge are a key problem in the aspect of returning to the production process of an additional nitrogen load, also phosphorus and organic compounds. The issue of pollutant load in the leachates is a factor with a potentially very large negative effect on the results of TN (Total Nitrogen) removal in the main treatment line. On the basis of data regarding the qualitative composition of the raw wastewater, initially treated and the leachates, it was determined their potential impact on the efficiency of pollutant decomposition in the biological reactors (Table 4). In the WWTP Żory the amount of arising leachates is not measured, therefore for further analysis it was adopted the target value specified in the construction and executive design of 2006, made by the Consulting Inżynieria Technologia, which is presented in Table 5.

The digested sludge produced in the WWTP Żory is dewatered by the filter belt press. During dewatering of sludges, the formed leachates are discharged by gravitation into the supernatant storage tank. For this need it was adapted the object previously functioning as the Imhoff settler. To the supernatant storage tank there are also directed waters from the emergency overflow of the digested sludge tanks, leachates from the temporary sludge repository and the rinsing water. From the leachate storage tank the leachates are discharged through a gate valve with electric drive, enabling regulation of the runoff to the inflow into the wastewater treatment plant.

Table 4. Quality assessment of the raw wastewaters, wastewaters after the primary settling tank and leachates coming from the filter presses in the years 2015-2017. On the base of (Own materials of PWiK Żory 2018)

Parameter	Unit	Raw wastewater	Wastewater after primary settling tank	Leachates from filter press	Treated wastewater
TN	mg/dm^3	107.9 σ = 21,78	75.9 σ = 18,42	664.8 σ = 221,73	14.7 σ = 3,36
N_{NH4}		82.5 σ = 23,40	61.7 σ = 15,06	592.6 σ = 215,01	1.3 σ = 4,20
TP		14.6 σ = 6,17	8.2 σ = 3,35	197.7 σ = 105,39	0.2 σ = 0,65
PO_4		39.2 σ = 18,94	39.1 σ = 199,44	*nt.*	*nt.*
COD		712.4 σ = 169,64	548.0 σ = 79,73	386.9 σ = 168,74	52.0 σ = 40,82
BOD_5		297.9 σ = 95,30	243.0 σ = 59,08	66.4 σ = 75,00	5.0 σ = 2,84
TSS		399.4 σ = 122,87	263.0 σ = 71,74	1100.9 σ = 1008,10	13.9 σ = 16,41
BOD_5/TN	-	2.8	3.2	0.1	0.3
COD/TN		6.6	7.2	0.58	3.5
COD/BOD_5		2.39	2.26	5.83	10.40

nt. – not tested, TN – Total Nitrogen, TP – Total Phosphorus,
TSS – Total Suspended Solids

Table 5. The amount of effluents from the filter presses. Source (Consulting Inżynieria Technologia 2006)

Parameter	Unit	Value	
		Summer	Winter
Amount of leachates	m^3/d	65.8	68.8
Individual amount of rinsing water	m^3/h	10.0	10.0
Amount of rinsing water	m^3/d	77.4	81.0
Total amount of leachates	m^3/d	143.3	149.8

On the base of data from the period of 2015-2017, an analysis of the qualitative composition of the leachates, produced during dewatering of the digested sludge on the filter presses, was conducted.

The analysis of the presented data shows that in the leachates there is a high content of ammonium nitrogen, total phosphorus, as well as periodically very high content of the total suspended solids. The maximum measured concentration of the total suspended solids during this period amounted to 3627.0 mg/dm^3, ammonium nitrogen 935.4 mg/dm^3, total phosphorus 668.2 mg/dm^3. The leachates after the filter presses were characterized by similar concentration of the COD as in the raw wastewaters. This value was on average 683.0 mg O_2/dm^3 in the raw wastewaters, and 386.9 mg O_2/dm^3 in the leachates. On the other hand, the value BOD_5 of the leachates coming from the presses was 4.5 times smaller than in the raw wastewaters and almost 4 times smaller than in the wastewater after the primary settling tank. Accordingly, the value of the ratio COD/BOD_5 was 5.83, indicating that there are recycled to the main technological line the hardly biodegradable organic substances that reduce effectiveness of the biological decomposition processes. The leachates discharged from the filter presses are a source of the secondary pollutants returned to the technological line of the wastewater treatment plant.

High content of the nitrogen and phosphorus compounds and a relatively small amount of organic compounds cause that the leachates have a significant contribution to the inflow of pollutants load into the biological part and under conditions of deficiency of organic compounds in the raw wastewaters, they can affect the inhibition of the biological process of the wastewater decomposition. The above observations have been confirmed in the studies carried out, among others, by (Fux et al. 2002; Janus & van der Roest 1997). For example, in the wastewater treatment plant in Minworth (England), the concentration of the total suspended solids was from about 220.0 to 2340.0 mg/dm^3, and $N\text{-}NH_4$ from 450 to 750 mg/dm^3. In turn, in the leachates coming from the Luggage Pot (Australia) treatment plant, the concentration of the ammonium nitrogen amounted from 943.0 to 1710.0 mg/dm^3, and the total suspended solids from 95.0 to 6132.0 mg/dm^3.

Next, it was estimated the value of load of the pollutants supplied to the technological wastewater treatment line (Table 6). The daily quantity of the leachates was determined on the base of the data contained in Table 5. The average value from the summer-winter period was assumed to be equal 146.6 m^3/d.

Table 6. Loads of pollutants in the wastewater in the years 2015-2017. Source (Own materials of PWiK Żory 2018)

Wastewater	Parameter	Value [kg/d]		
		Average	Max.	Min.
Raw wastewater	TN	859.5	1334.3	474.0
	N_{NH4}	691.7	1802.6	284.1
	TP	106.4	266.5	24.4
	COD	5591.0	8930.9	2979.7
	BOD_5	2488.5	4174.9	843.2
	TSS	2979.7	7244.6	1514.4
After primary settling tank	TN	621.3	1105.1	137.5
	N_{NH4}	505.1	894.7	90.9
	TP	67.1	190.7	0.00
	COD	4485.9	5689.3	2709.6
	BOD_5	1989.2	3266.2	1219.7
	TSS	2152.9	4346.77	826.8
Leachates from filter press	TN	97.45	156.86	12.31
	N_{NH4}	86.87	137.14	6.10
	TP	28.98	97.96	1.32
	COD	56.72	158.33	5.39
	BOD_5	9.73	50.72	2.79
	TSS	161.39	531.72	4.40
Treated wastewater	TN	120.30	253.70	96.57
	N_{NH4}	11.05	463.70	0.81
	TP	1.63	36.00	0.08
	COD	6.35	2659.80	204.6
	BOD_5	40.92	122.76	0.08
	TSS	113.76	1980.52	57.29

Based on the conducted analyses. it was found that the leachates coming from the filter presses carried a significant load of total phosphorus. which constitutes on average 27.2% of the total load flowing into the treatment plant. as well as total suspension and total nitrogen. which maximum load is respectively 5.4% and 11.3% of the total load flowing into the treatment plant. On the other hand. the COD and BOD_5 load constitutes only a small part of the raw wastewater load. i.e. below 1% (Figure 6).

The unfavourable COD/BOD_5 ratio of the supernatants inflowing to the main technological line causes periodical deterioration of the efficiency of nitrogen compounds removal in the wastewater treatment plant. This is due to the poor load of organic pollutants flowing into the wastewater treatment plant. The denitrification process works best when the BOD_5/TN ratio is higher than 4.0, while the very low value of this parameter in the supernatants inhibits the growth of denitrifying bacteria, which reduces the effectiveness of nitrogen compounds elimination. The increased amount of total suspended solids in supernatants entering into the primary settling tank increases its hydraulic load and negatively affects the degree of pollutants removal.

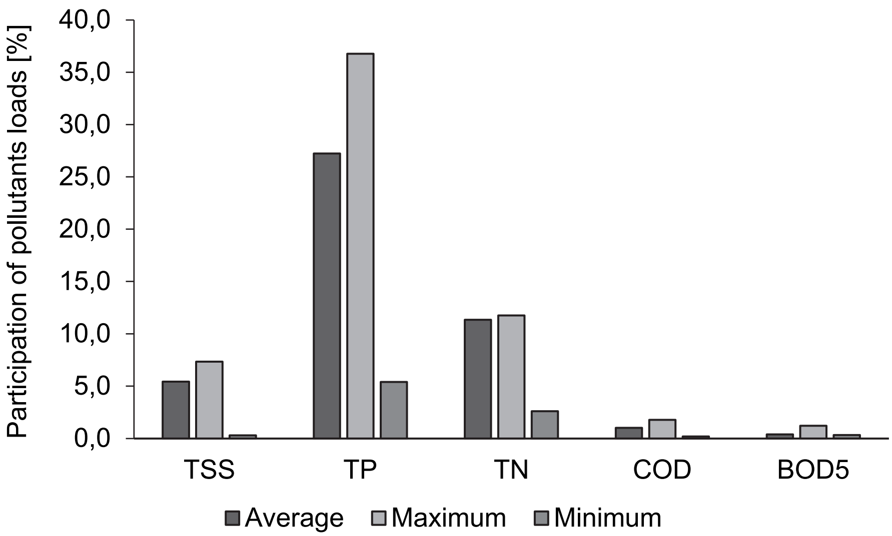

Fig. 2. Percentage relation of the pollutants load in the leachates. coming from dewatering. to the total load in the raw wastewater. Own study based on (Own materials of PWiK Żory 2018

Despite the adverse impact of the leachates quality on the efficiency of biological wastewater treatment, the quality of the wastewater discharged to the receiver meets the requirements set out in the conditions of the water permit. The organic pollutants load expressed as COD is reduced by about 92%, BOD_5 by over 98%, while totals suspended solids by about 96%. Similarly, high removal efficiency is observed for phosphorus compounds, which are reduced by almost 99%. Total phosphorus concentrations in treated wastewater range from 0 to 0.2 mg P/dm^3, while the permissible value is 2 mg P/dm^3. The wastewater treatment plant is also characterized by quite good efficiency of removing total nitrogen. In this case, the removal efficiency is on average of 83%. In periods, when leachates with particularly unfavourable composition flow into the main technological line, the efficiency of ammonium nitrogen removal is 75% compared to nearly 99% reduction in other periods of work (Zdebik et al. 2018).

Due to the large and time-varying load of pollutants which characterize leachates. especially those of general nitrogen. total phosphorus and suspended matter. consideration should be given to the treatment of the leachates before returning them to the technological wastewater treatment line. Due to the high content of nitrogen and phosphorus compounds and unfavourable C:N and C:P ratio. which cause that this type of wastewater is difficult to biodegrade. discharging the leachate waters in the case of a deficit. the inflow of easily biodegradable organic compounds in the wastewater may cause a reduction in the effectiveness of biogenic compounds removal (nitrogen and phosphorus compounds) in the biological process of the wastewater treatment. There are several methods for reducing pollutants found in supernatants. These include physico-chemical methods, e.g. ammonia stripping, ion exchange, chlorination, struvite precipitation and biological methods, including modern and effective activated sludge processes such as the DEMON, BABE, SHARON and SHARON-ANAMMOX processes (Barbusiński 2016; Dereszewka & Cytawa 2016). Due to the high content of nitrogen compounds in the supernatants, it is advisable to pre-treat them in the deammonification process. The deammonification process involves nitrogen removal by partial nitrification and ANAMMOX technology in SBR reactor under strict pH control (Wett 2007).

In the case of sludge dewatering process, a common problem arising during the exploitation of sewage sludge dewatering equipment is the precipitation of hard sediment of ammonium magnesium phosphate ($(NH_4)Mg(PO_4)\cdot 6H_2O$), also known as struvite. Struvite is a mineral with a characteristic crystalline structure, which is formed by regular PO_4^{3-} tetrahedrons, deformed $Mg(H_2O)_6^{2+}$ octahedrons and NH_4^+ group bonded through hydrogen bonds. Struvite precipitation is also possible under controlled conditions, eg. in reactors such as the Struvia™, Crystalactor®, PhosnixUnitaka®, PEARL® or PHOSPAQ™. The precipitated struvite is a product of commercial values due to its very good fertilizing properties. Due to the poor solubility in water, minerals contained in struvite (i.e. nitrogen, phosphorus, magnesium) are released slowly and gradually. In granular form, it can be applied to the soil in amounts significantly exceeding the dose of conventional fertilizers used, without overdosing (Czajkowska & Siwiec 2011).

6. Conclusions

The results of the carried out tests and the assessment of operation of the wastewater treatment plant. including the centre of the sludge treatment. allow to present the following conclusions:

- The quality of sewage sludges was characterized by similar chemical composition and physical properties to the sludge design characteristics. Daily sludge volume from the wastewater treatment plant was higher than according to the designed values wjich resulted in overloading of some sewage sludge processing equipment.
- Performed calculations. checking the efficiency of individual equipment. showed that the existing excessive sludge thickening system does not have sufficient capacity and was designed for other values of concentrations of pollutants in the sludge and the leachates stream.
- On the base of analyses and own calculations it was found that the charge of pollutants introduced from the leachates into the technological system affects the final concentration of total nitrogen in the treated wastewaters.
- In order to increase the efficiency of nitrogen removal in the main technological line. it is proposed to introduce the deammonification process of the leachates coming from the sludge dewatering. to reduce the load of ammonium nitrogen entering the biological part of the treatment plant. After the deammonification process. it will be possible to use the struvite precipitation process.
- Despite the observable. increasing concentrations of pollutants and the amount of treated wastewater. the plant meets the requirements for the quality of the wastewater discharged to the receiver. as required by the conditions of the water permit and in the Regulation of the Minister of the Environment.

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Abstract

The purpose of this work was to analyze work of the sludge part of the wastewater treatment plant in Żory. During the analysed period (years 2015-2017) the wastewater treatment plant in Żory worked in conditions typical for the municipal facilities. The characterization of the sludge generated in the wastewater treatment process has also shown that the sludge properties are typical for the municipal wastewater treatment plants. Based on the data provided by the PWiK Sp. z o. o. in Żory. the characteristics of the technological process were made. This characteristics in a detailed way includes the sludge part of the treatment plant. The analysis of the functioning of the sludge part was performed and the influence of the pollutants load in leachates on the effectiveness of work in the main technological line was characterized. Studies on the functioning of the sludge part showed discrepancies between the design status of the wastewater treatment plant and the real state. This is due to the increasing amount of the wastewater flowing into the treatment plant and the associated increase in the amount of the occurring sludge. The belt press and the digested sludge tank are particularly loaded. The belt press works for about 11.9 h/d with assumed 4.1 h/d. In turn. the residence time of the sludge in the digested sludge tank is about 3 times shorter than assumed. Despite the observed. increasing concentrations of pollutants and the amount of treated wastewater. the plant meets the legal requirements regarding the quality of the wastewater discharged to the receiver by the water-legal permit and the Regulation of the Minister of the Environment. Based on the results of laboratory tests of the wastewater and leachates generated in the process of dewatering on the filter presses. their impact on the efficiency of treatment in the main technological line was characterized. The amount of leachates in relation to the amount of the wastewater flowing into the treatment plant was 1.8%. The leachates had high content of ammonium nitrogen. total phosphorus and total suspended solids. The average concentrations of these parameters were: S_{NNH4} = 592.6 mg/dm^3, S_{Nog} = 664.8 mg/dm^3, S_{Pog} = 197.7 mg/dm^3 and S_{Zog} = 1100.9 mg/dm^3. The average values of BOD_5 and COD indices were S_{BOD5} = 66.4 mg/dm^3, and S_{COD} = 386.9 mg/dm^3. The leachates coming from the filter presses carried a significant load of total phosphorus. which constituted on average 27.3% of the total load flowing into the treatment plant. as well as the total suspension and total nitrogen. which maximum load constituted 7.3% (Z_{og}) and 11.8% (N_{og}) of the total load flowing into the treatment plant. The ratio of COD/BOD_5 indices of pollutants of the leachates from the presses was 5.83. which indicated the introduction of hardly biodegradable compounds into the main technological line. In order to increase the efficiency of nitrogen removal in the main technological line it was proposed the implementation of deammonification process of the leachates from the sludge dewatering. aiming to reduce the ammonium nitrogen load. introduced to the biological part of the treatment plant.

Key words:
wastewater treatment plant, activated sludge, sewage sludges, quality of the wastewater, leachate, sewage sludge management

Charakterystyka funkcjonowania węzła przeróbki osadów ściekowych na oczyszczalni ścieków w Żorach

Streszczenie

Celem niniejszej pracy była analiza pracy części osadowej oczyszczalni ścieków w Żorach. Oczyszczalnia ścieków w Żorach w analizowanym okresie (lata 2015-2017) pracowała w warunkach typowych dla miejskich obiektów komunalnych. Również charakterystyka osadów powstających w procesie oczyszczania ścieków wykazała. że właściwości osadów są typowe dla miejskich oczyszczalni ścieków. Na podstawie danych udostępnionych przez PWiK Sp. z o.o. w Żorach. dokonano charakterystyki procesu technologicznego. Charakterystyka w sposób szczegółowy uwzględnienia część osadową oczyszczalni. Dokonano analizy funkcjonowania części osadowej oraz scharakteryzowano wpływ ładunku zanieczyszczeń w odciekach na skuteczność pracy w głównym ciągu technologicznym. Badania dotyczące funkcjonowania części osadowej wykazały rozbieżności między stanem projektowym oczyszczalni ścieków. a stanem rzeczywistym. Wynika to z faktu zwiększającej się ilości ścieków dopływających na oczyszczalnię oraz związanym z tym przyrostem ilości powstających osadów. Szczególnie obciążone w układzie są prasa taśmowa oraz zbiornik osadu przefermentowanego. Prasa taśmowa pracuje przez około 11.9 h/d przy zakładanych 4.1 h/d. Z kolei czas przebywania osadów w zbiorniku osadu przefermentowanego jest około 3 razy krótszy od zakładanego. Pomimo obserwowanych. zwiększających się stężeń zanieczyszczeń oraz ilości oczyszczanych ścieków. oczyszczalnia spełnia wymagania prawne dotyczące jakości ścieków odprowadzanych do odbiornika nadane przez pozwolenie wodnoprawne oraz Rozporządzenie Ministra Środowiska. W opraciu o wyniki badań laboratoryjnych ścieków i odcieków powstałych w procesie odwadniania na prasach filtracyjnych. scharakteryzowano ich wpływ na skuteczność oczyszczania w głównym ciągu technologicznym. Ilość odcieków w stosunku do ilości ścieków dopływających do oczyszczalni wynosiła 1.8%. W odciekach stwierdzono wysoką zawartość azotu amonowego. fosforu ogólnego oraz zawiesiny ogólnej. Średnie stężenia wymienionych parametrów wynosiły: S_{NNH4} = 592.6 mg/dm^3, S_{Nog} = 664.8 mg/dm^3, S_{Pog} = 197.7 mg/dm^3 oraz S_{Zog} = 1100.9 mg/dm^3. Średnie wartości wskaźników BOD_5 oraz COD wynosiły S_{BOD5} = 66.4 mg/dm^3 i S_{COD} = 386.9 mg/dm^3. Odcieki z pras filtracyjnych niosły znaczny ładunek fosforu ogólnego. który stanowił średnio 27.3% całkowitego ładunku dopływającego do oczyszczalni oraz zawiesiny ogólnej i azotu ogólnego. których ładunek maksymalny stanowił 7.3% (Z_{og}) oraz 11.8% (N_{og}) całkowitego ładunku dopływającego do oczyszczalni. Stosunek wskaźników zanieczyszczeń COD/BOD_5 odcieków z pras wynosił 5.83. co wskazywało na wprowadzanie do głównego ciągu technologiczne związków trudno rozkładalnych. W celu zwiększenia efektywności usuwania azotu w głównym ciągu technologicznym zaproponowano implementację procesu deamonifikacji odcieków z odwadniania osadów w celu redukcji ładunku azotu amonowego wprowadzanego do części biologicznej oczyszczalni.

Słowa kluczowe:
oczyszczalnia ścieków, osad czynny, osady ściekowe, jakość ścieków, odciek, gospodarka osadowa

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Analysis of Benefits and Barriers in Implementing the Eco-Management and Audit Scheme in Selected Organisations

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1. Introduction

Proper management of a modern enterprise should lead not only to economic but also to ecological and social effects. Implementation of the principles of sustainable development at the level of each enterprise is very important because it counteracts the excessive burden on the environment on the local and global scale. (Lee & Lam 2012, Szyszka & Matuszak-Flejszman 2016, Venkatesh 2010.) The growing importance of environmental protection in the economy is the result of the growing ecological awareness of society.(Szyszka & Matuszak-Flejszman 2017). This awareness translates into pressure exerted on business entities and administrations (Pawłowski 2009, Harris et al.2001). The results of the research indicate that it is very important to popularize environmental management systems. Implementation of such systems in companies has an effect on products, processes and green supply chain management. (Prajogo, et al. 2014). However, it is important to point out that the effective implementation of environmental management systems within the company requires complementing organizational capabilities and resources to implement proactive environmental strategies (Martín-de Castro et al. 2016).The Eco-Management and Audit Scheme(EMAS) is an environmental management system in which various organisations like enterprises, institutions and offices can participate voluntarily. Institutions such as hospitals are also increasingly implementing EMAS. The purpose of EMAS registration for hospitals is to combine quality of services with environmental protection. (Seifert 2018; Lizzi et al. 2017).The main assumption of the system is to distinguish those organisations that go beyond the scope of minimum compliance with the regulations and constantly improve the effects of their environmental activities (Mazzi et al.2016). The basic principles of the system are set out in the Regulation (EC) No 1221/2009 of the European Parliament and of the Council of 25 November 2009 on the voluntary participation by organisations in a Community eco-management and audit scheme (EMAS), also referred to as EMAS III. It is worth noting that in recent years there has been a revision of the Regulation repealing the annexes (Commission Regulation (EU) 2017/1505 of 28 August 2017 amending Annexes I, II and III to Regulation (EC) No 1221/2009 of the European Parliament and of the Council on the voluntary participation by organisations in a Community eco-management and audit scheme (EMAS) and Commission Regulation (EU) 2018/2026 of 19 December 2018 amending Annex IV to Regulation (EC) No 1221/2009 of the European Parliament and of the Council on the voluntary participation by organisations in a Community eco-management and audit scheme (EMAS). The issue of companies' impact on the environment and the implementation of various activities for its protection is and will be important, e.g. promoting the implementation of EMAS system, which was emphasised – among others – during the UN Global Climate Summit – COP24 in Katowice in 2018. The involvement of individual countries in the promotion of EMAS is diverse, as evidenced by the number of organisations registered in the system. The leaders in the number of organisations registered in EMAS per population are: Austria, Spain, Germany, Denmark and Italy. In recent years, there has been a dynamic growth in registered organisations in some countries, in others – a significant reduction. Although the EMAS system has been operating in Poland since May 1st, 2004, it is not implemented on a large scale in Polish enterprises. This state is not the result of the lack of environmental awareness of the organisations' management but refers to the barriers and difficulties in implementing EMAS. Implementation of the system involves additional costs, preparation of documentation, often reorganisation of the enterprise, etc.(Bernardo et al.2015). In spite of these difficulties, however, Polish companies decide to implement this system concentrating on its specific benefits (Ociepa-Kubicka 2015).

The aim of the article is to indicate, analyse and assess the benefits and most important barriers in the EMAS implementation process in selected Polish organisations. The article was prepared on the basis of the results of a survey addressed to enterprises which had implemented EMAS, and literature review.

2. Materials and methods

For the purposes of this publication a survey was carried out (the questionnaire was conducted in 2018/2019). The research aimed at obtaining information on the benefits and barriers of the functioning EMAS environmental management system in various organisations located in Poland. The following issues were analysed:

- factors that were the reason for implementing the EMAS system,
- difficulties that occurred in organisations when implementing the system,
- incurred implementation costs,
- external and internal benefits arising from the implementation of EMAS,
- the duration of the system implementation,
- analysis of the possibilities of the implementation costs reimbursement.

The research was based on a written survey form to be filled in by the organisations. The questionnaire was prepared by the author of the publication. It was sent via e-mail to 50 organisations (these were service-providing and production companies) that had implemented the EMAS system. 17 organisations returned comprehensively completed surveys which could be analysed for the research purposes. The questionnaire comprised 7 closed-ended questions in which the respondents were to indicate the most significant factors among the answers provided. There was also an open-ended option of including "other factors" as own answer. The survey was anonymous. It asked about the number of employees in the organisation: less than 10 employees – 1 organisation, between 10-50 employees – 2 organisations, 51-250 employees – 9 organisations, above 250 employees – 5 organisations.

3. Results and discussion

Most of the surveyed organisations had already operated other EMS systems, e.g. the ISO 14001 standard or the international ISO 9001. In order to identify the factors that led the respondents to implement additional EMS – EMAS – they were asked to highlight the most significant ones that determined their decisions of EMAS implementation (Fig. 1).

The surveyed enterprises implementing the EMS were primarily focused on: aiming at the improvement of the image of the company and its competitiveness on the market (11 indications) and the will to improve the condition of the environment (8 indications). Furthermore, the studies published by other authors have indicated that the organizations implementing EMAS are guided by factors such as image improvement or gaining a competitive advantage on the market (Morrow & Rondinelli 2002). The enterprises implemented EMAS also in order to expand their current quality management systems with EMAS (7 indications) and to raise ecological knowledge and awareness of the employees (7 indications).The outcome proves the growing ecological awareness of entrepreneurs. Smaller importance was attributed to the strive to improve competitiveness and innovation (5), the desire to adapt to the expectations or requirements of recipients (4) or to facilitate the acquisition of additional funds (2). The organisations also pointed to the fact that the reason for introducing EMAS was to conduct a better dialogue with the public and to set an example to the beneficiaries (2 indications).In order to determine the basic difficulties, the enterprises had to face, the survey asked to identify those the most crucial for the respondents (Fig. 2).

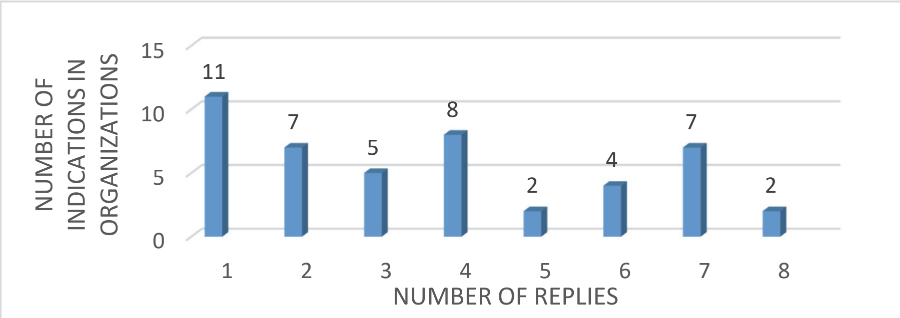

Fig. 1. Cause(s) of EMAS implementation in company

1. aiming at the improvement of the company's image and competitiveness in the market
2. willingness to expand the functionality of the quality management system with EMAS,
3. aiming at the improvement of competitiveness and innovativeness of the company,
4. aiming at the improvement of the condition of the natural environment (reduction of energy and raw materials consumption, reduction of emissions, etc.),
5. facilitating the access to the financial means, e.g. from various funds designated for environmental protection or more beneficial loans,
6. desire to adapt to the expectations or requirements of the customers and/or the market,
7. aiming at the raise of ecological knowledge and awareness among employees,
8. other.

The greatest difficulty for the respondents was the substantive and organisational aspects of the implementation (9 indications), as well as the time of preparations and implementation (8 indications). Serafin Ch. (Serafin 2018) pointed to difficulties related to the preparation of documents and the correct analysis of legal acts.

Also, the limited knowledge of the implementation process was pinpointed as a hindrance (6 indications). In 4 cases, the problem was the resistance of the employees against the planned changes. Another barrier discouraging organizations to implement EMAS is the fact that, as underlined by the authors, there is no or only minimal support from the public administration for companies that use EMAS (initiatives to promote the company, increase the possibility of getting discounts, etc.) (Kivi &Gurvits 2017; Merli et al.2014).

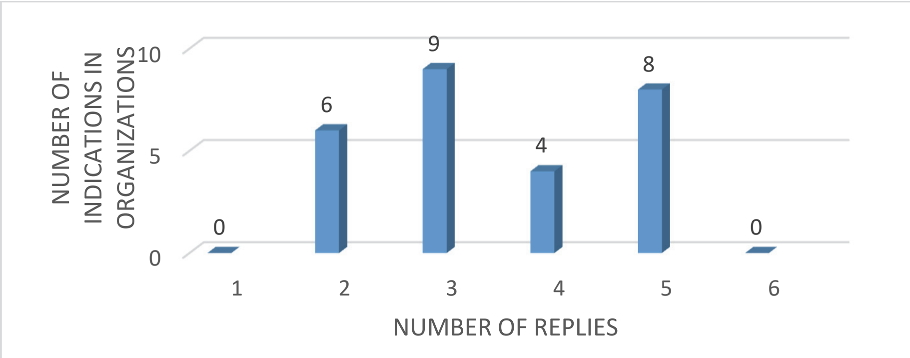

Fig. 2. Difficulties encounter during EMAS implementation

1. financial problems – additional costs related to the implementation of, e.g., equipment, training, technologies, certification fees, etc.
2. limited knowledge about the rules of the system implementation,
3. substantive difficulties and organisational problems with the necessary documentation,
4. limited knowledge of the staff concerning the benefits of the implementation or resistance to the implementation of changes,
5. time-consuming preparation and implementation,
6. other.

In one of the questions, the respondents were asked to indicate the period they needed for the implementation of the system in their organisations. Majority of answers indicated 6-12 months (9 indications), and 6 months (5 indications). There were 3 organisations which took 12-24 months to implement the system.

Implementation of EMAS generated additional costs. Many authors have emphasized the fact that the costs associated with the implementation of EMAS systems in organizations represent a serious barrier for them.(Alvarez-Garcia & RioRoma 2016; Daddi et al.2017; Del Brio et al.2001; Iraldo et al.2009; Kivi &Gurvits 2017; Merli et al.2014; Seifert 2018).

They also indicate that high costs of implementing and maintaining the system are, among others, the reason for resignation from the EMAS system (Preziosi 2016).

The survey asked which expenses were the greatest (Fig. 3).

The most important were the costs of certificates, audits (12 indications) and costs incurred for the environmental protection investments (5 indications). Lower importance was assigned to the costs of staff training or the costs of company modernisation and technological advancement. The survey asked in what period the incurred costs could be reimbursed. Most of the organisations found it difficult to determine such time (11 indications), 4 organisations selected 5 years, 2 organisations – 10-20 years. Implementation of the system represents an investment for enterprises, bringing measurable results and numerous benefits. Internal benefits are related to financial results and the effectiveness of business operations, while external benefits had an impact on shaping the relationship between the internal environment and the competitive environment of the enterprise (Fig. 4, 5) (Brzeszczak 2018).

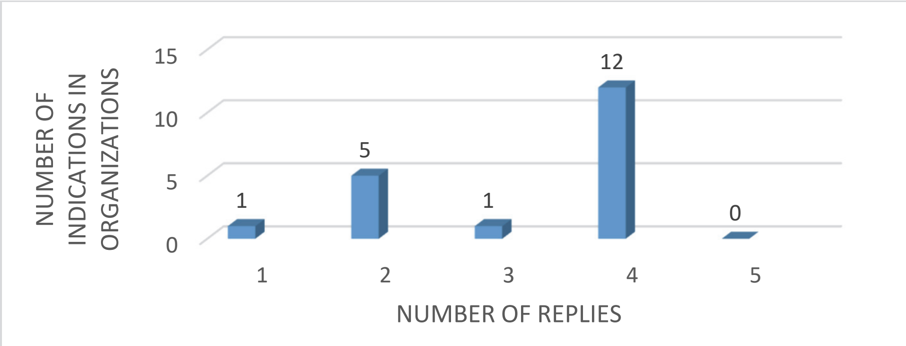

Fig. 3. Implementation expenses in company
1. costs of enterprise modernisation, investments, changes in technology,
2. increase in the environmental protection investments,
3. costs of staff training,
4. costs of certification and audits,
5. other.

The survey asked for the most significant internal benefits resulting from the implementation of EMAS.

The most important for the surveyed companies was achieving compliance with the regulations and raising environmental protection standards (16 indications), improving the functioning of a company operating according to the EMAS concepts (12 indications) and increasing ecological awareness of employees (9 indications). In the studies of other authors, the fact of meeting the regulations was also very important and perceived as one of the most substantial benefits. (Hillary 2004; Tesa et al. 2018). Montobbito and Solito pointed to another advantage: the adoption of EMAS promotes greater innovativeness at company level (Montobbito & Solito 2018).

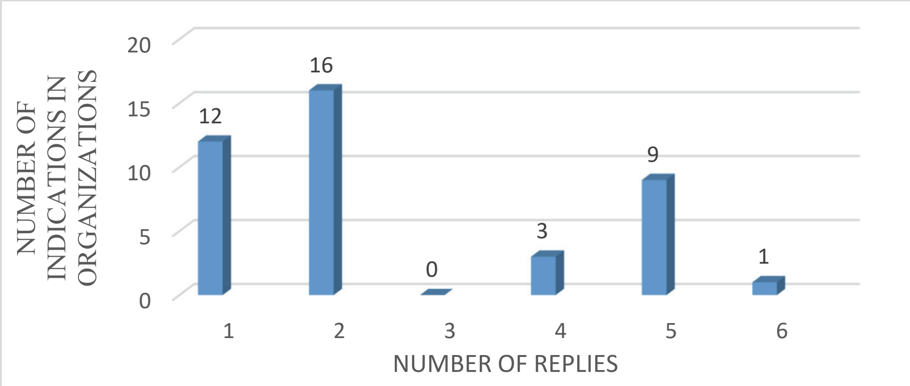

Fig. 4. Internal benefits stemming from EMAS implementation

1. improvement of the functioning of an enterprise operating according to the EMAS concept,
2. obtaining the compliance with regulations, raising the standards of environmental protection,
3. greater availability of more beneficial bank loans and funds from various sources,
4. improvement of the economic effects of the company's operations by the reduction of production costs (materials, natural resources, increased sales) and reduction of the current costs of environmental protection,
5. increase of the environmental awareness among the employees,
6. other.

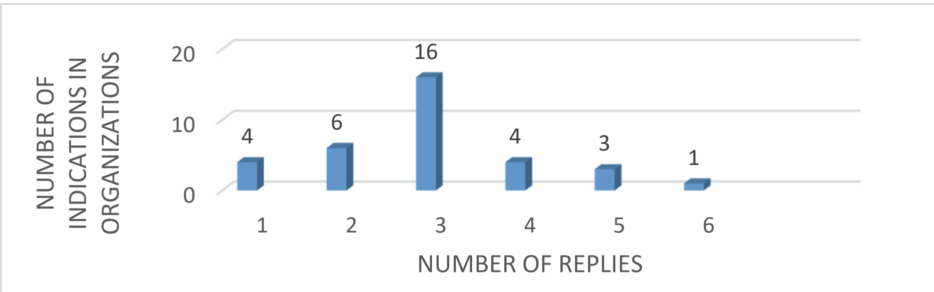

Fig. 5. External benefits stemming from EMAS implementation

1. increase of the company's attractiveness for potential clients,
2. increasing competitiveness of the company in the market,
3. better, pro-ecological image of the company,
4. improvement in the environment and ecological safety of the company's activity,
5. increase in trust and improvement of relations with the local community,
6. other.

The improvement of the economic effects of the organisation's activities was of lesser importance (3 indications), while none of the surveyed organisations indicated greater access to better loans and obtaining additional funds as benefits. As additional asset, however, the surveyed pinpointed the ongoing monitoring of the environmental objectives. Enterprises also indicated external benefits resulting from the implementation of the EMAS system.

In the opinion of the surveyed organisations, the implementation of the environmental management system contributed to a better pro-ecological image of the company (16 indications) and to the increase of company's competitiveness on the market (6 indications). To a lesser extent, the surveyed enterprises observed the increasing attractiveness for clients (4 indications), the improvement of the environment condition and ecological safety of the run activities (4 indications), or the increase of trust and improvement of relations with the local community (3 indications). Furthermore, in a study by Martín-Peña et.al., good relations with the customers are seen as important benefits of the implementation of EMAS.(Martín-Peña et al. 2014). Furthermore, Schmidt-Räntsch et.al. show in their study that minimising environmental problems is also a very important factor seen as a benefit.(Schmidt-Räntsch et al. 2012).

4. Conclusions

Socio-economic development in the modern world is related to ever-lesser access to natural resources, environmental pollution and climate change. Thanks to the rational use of environmental resources, we counteract the excessive burden of all the natural environment elements. Responsible organisations, adjusting to these limitations, should rationally manage the resources, support the materials recycling process and reduce the carbon footprint throughout the entire life cycle of the product. Each of the operating organisations is co-responsible for achieving the goals of sustainable development. Production companies play particularly crucial role. Considering social and environmental issues of their activities, at every stage of the supply chain, they can set new pro-ecological trends in the sectors in which they operate.

That is why it is so important to invest in fulfilling commitments concerning the goals of sustainable development. The presented research results allow to conclude that they comprise formalised management systems, in particular the EMAS environmental management system.

Enterprises deciding to implement the EMAS system were primarily interested in the improvement of their image and competitiveness on the market, but also the enhancement of the state of the natural environment (the reduction of energy consumption and emissions, etc.). Assessing the internal benefits resulting from the implementation, the EMAS system most often indicated obtaining the compliance with the law, the increase of the standards of environmental protection, the company's improvement of its functioning and the increase of the environmental protection awareness among the employees. Also, the analysis of the external benefits of the EMAS system implementation included the companies' pursuit of a better, environmentally-friendly image of their operations. The answers indicate the growing ecological awareness of and responsibility for the state of the environment among the company's management. The organisations did not indicate the economic aspects as the most important in relation to the EMAS system implementation and operation.

During the implementation of the environmental management systems the surveyed entities encountered a number of difficulties, for example: limited knowledge about the system implementation principles and the time required for the preparation and implementation process. Most enterprises needed around 1 year for the EMAS implementation. Moreover, the companies struggled with the processing of the additional documentation. This indicates insufficient knowledge related to the implementation process and the necessity of adequate staff training. Advisory services to develop a pro-ecological systems implementation programme should become more common.The incurred costs turned out to be a significant problem. The examined companies listed the following as the most expensive elements related directly to EMAS implementation: certification, external audits and costs incurred for investment activities related to environmental protection. The mentioned organizational difficulties and costs of EMAS implementation may be potentially discouraging for new entrepreneurs. Even though the system is more and more popular and appreciated world-wide, it turns out that it is a struggle to launch. It is therefore proposed to encourage companies that already have EMAS to share their experience with other companies, which can make it easier to implement this system in other companies. Most organisations could not define the time in which the incurred EMAS expenses would be reimbursed. Lack of specific financial calculations may be the cause of companies' discouragement from further activities and unwillingness to implement and maintain the EMAS eco-management system.

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Abstract

The development of enterprises in the 21st century must involve care for the natural environment. Owing to the introduction of ecological activities, entrepreneurs gain in the economic, ecological and social sphere. That is why it is so important to implement and disseminate ecological management in companies. Although undoubtedly the environmental awareness of entrepreneurs is increasing, there is a lack of much interest in implementing additional systems such as the EMAS Eco-Management and Audit Scheme. The purpose of the present study was to determine the impact of a functioning EMAS management system on the activities of organisations that have implemented this system. The basis for the evaluation was the results of research and a review of domestic and foreign literature. The results of the research show that the organisations undertook to implement EMAS observing a number of benefits. However, at the implementation stage, there were numerous, not always foreseen, difficulties which extended the planned implementation period. The conducted research can be the basis for the development of new procedures facilitating the implementation of the systems in the enterprise. They can provide valuable information for various organizations supporting and disseminating the development of pro-ecological management.

Keywords:
environmental management system, EMAS, ecology, management

Analiza korzyści i barier przy wdrażaniu System Ekozarządzania i Audytu w wybranych organizacjach

Streszczenie

Rozwój przedsiębiorstw w XXI wieku musi wiązać się z troską o środowisko naturalne. Dzięki wprowadzaniu działań ekologicznych przedsiębiorcy zyskują na płaszczyźnie ekonomicznej, ekologicznej i społecznej. Dlatego tak ważne jest wdrażanie oraz upowszechnianie zarządzania ekologicznego w firmach. Chociaż niewątpliwie świadomość ekologiczna przedsiębiorców wzrasta obserwuje się brak dużego zainteresowania wprowadzaniem dodatkowych systemów jak System Ekozarządzania i Audytu EMAS. Celem pracy było określenie wpływu funkcjonującego systemu zarządzania EMAS na działalność organizacji, które wdrożyły ten system. Podstawą do oceny były wyniki badań oraz przegląd literatury krajowej i zagranicznej. Wyniki przeprowadzonych badań wskazują, że organizacje podejmowały się wdrożenia EMAS widząc szereg korzyści. Jednak na etapie wdrożenia wystąpiły liczne trudności, na które nie zawsze były przygotowane i które wydłużyły planowany okres wdrażania. Przeprowadzone badania mogą być podstawą opracowania nowych procedur ułatwiających wdrożenie systemów zarządzania środowiskowego w przedsiębiorstwie. Mogą stanowić cenną informacje dla różnych organizacji wspierających i upowszechniających rozwój proekologicznego zarządzania. Tematyka artykułu jest ważna i aktualna ze względu na konieczności ograniczania wpływu organizacji na środowisko i wdrażania zasad zrównoważonego rozwoju.

Słowa kluczowe:
systemy zarządzania środowiskowego, EMAS, ekologia, zarządzanie

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Assessment of the Ecological Status and the Need for Renovation of Drainage Ditches in the Strumień Junikowski Catchment

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1. Introduction

In order to ensure proper water relations in any catchment it is crucial to maintain an adequate condition of drainage ditches. Drainage systems are responsible not only for appropriate moisture levels in agriculturally utilised soils, but also for the elimination of the negative impact of excess waters coming from spring thaw and torrential rains. In view of climate change and the resulting increasing frequency of extreme weather conditions, such as short-term abundant precipitation and droughts, elements of drainage systems will play an even more vital role (Bykowski et al. 2011, Liberacki & Olejniczak 2013). Considering the above, it is of critical importance to ensure serviceability of these systems (Sojka et al. 2019).

To maintain drainage structures in operable condition it is necessary to follow guidelines for their proper use and to perform maintenance operations at the required frequency. Maintenance of ditches consists in the preservation of the desired transverse shape and downgrade of the ditch bottom as well as the elimination and repair of all ditch bottom damage (Bielecki & Klus 1970). Basic maintenance operations include mowing of vegetation overgrowth, hoeing of plants rooted in the bottom and sediment removal (Kozaczyk et al. 2016). In practice these operations are frequently performed at excessively long intervals, resulting in massive ditch overgrowth and thus their reduced flow capacity. This leads to water bursting their banks and to flooding of adjacent agriculturally utilised land and urbanised areas. In the case of an insufficient flow rate in a ditch the amount of sediments also increases, resulting in a deterioration of water quality and promoting eutrophication. As it was stated by Joel et al. (2015), overgrown ditches cease to serve their function of discharge outlets for excessive phosphorus compounds and start to be their generators. Hydraulic structures being elements of drainage systems, such as gates and weirs installed at ditches, also need to be adequately maintained. Maintenance of these structures consists e.g. in flushing of culverts under roads as well as inspections and repairs of their rings.

In Poland the problem related with an inadequate serviceability of drainage systems is much more complicated. Inadequate frequency of maintenance operations is not the only factor causing their improper functioning. Another problem is also connected with the depreciation of many drainage structures, built in the 1970's and 1980's and currently being in the final stages of their structural lifetime (Bykowski et al. 2011). Damaged and unserviceable drainage structures need to be reconstructed. Funds allocated in the past to their repairs as a rule were insufficient to meet the needs and covered only a small percentage of the actual requirements. In the Poznań county in the years 2010-2016 money transferred from public funds to finance maintenance and operation of drainage structures met only 5.5% annual demand (Stachowski et al. 2017).

Apart from the progressing depreciation of drainage structures another problem is also related with the identification of areas requiring maintenance works. For this reason researchers are focusing on the development of a method to estimate relative relevance of drainage in individual regions. It may prove useful in the preparation of a development strategy for a given area. Based on the results provided by such a method the scope of maintenance works and modernisation of drainage structures may be planned for specific regions (Kaca 2017). The condition of ditches is increasingly often evaluated applying the MADRAS (Minnesota Agricultural Ditch Research Assessment for Stability) method and the HEC-RAS programme. These tools take into consideration stability of banks and escarpments, their shape, slope and susceptibility to erosion, vegetation, as well as deposition and transport of sediments in the ditch (Avilés et al. 2018, Joel et al. 2015). As it has been observed by many researchers, in Poland the technical condition of these structures is most frequently assessed using a method proposed by Kaca and Interewicz (1991) with later modifications (Bykowski et al. 2014, Liberacki & Olejniczak 2013, Oleszczuk et al. 2017, Przybyła et al. 2017). This method only assesses the technical condition of drainage structures. It does not take into consideration the ecological status of the watercourse, even though these aspects are interrelated. Maintenance works performed on ditches (mowing of their banks and cleanout of the ditch bottom) have a significant environmental impact and may contribute to adverse environmental changes (Bodnar-Nowakowska 2007). Also such procedures as dredging and chemical weeding of ditches pose a significant threat endangering biodiversity (Dollinger et al. 2015).

For this reason the condition of a drainage system may not be definitely classified as good or bad solely depending on its technical condition. In view of the above the authors of this paper decided to undertake a comprehensive evaluation of both the need to renovate the system of drainage ditches and to assess its current ecological status.

2. The study area

The study was conducted on the catchment of the Strumień Junikowski, covering 48.89 km^2 and located in the central part of the Wielkopolskie province. It is situated in the city of Poznań and the town of Luboń as well as the neighbouring communes of Dopiewo, Tarnowo Podgórne and Komorniki (Fig. 1). According to the physico-geographical regionalisation system proposed by Kondracki (2013) this area is included in the mesoregion of the Poznańskie Lake District (315.51), being a part of the subprovince of the South Baltic Lake District (315) and the macroregion of the Wielkopolskie Lake Ditrict (315.5). The Strumień Junikowski of 11.7 km in length is the primary watercourse of the catchment.

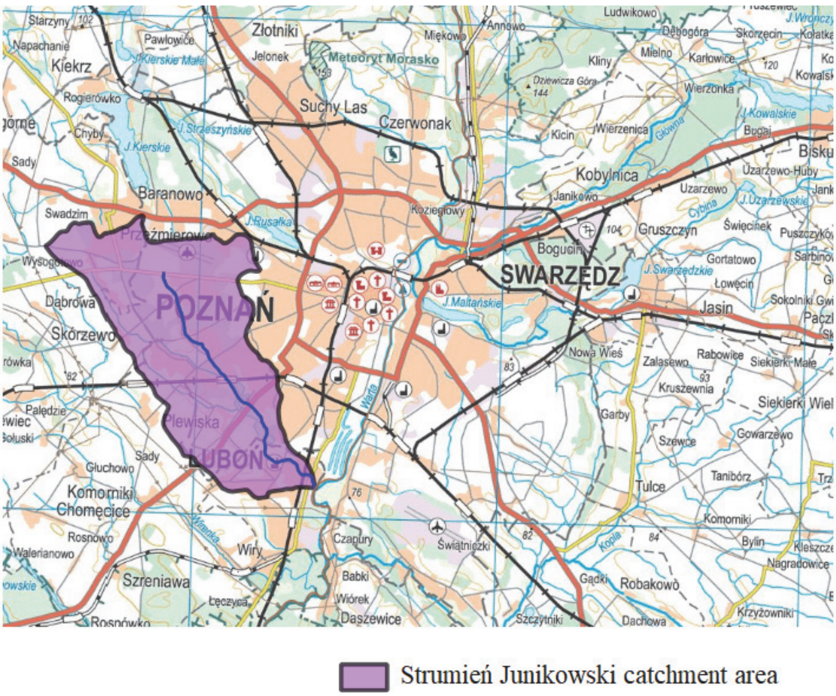

Fig. 1. Location of the Strumień Junikowski catchment area

Drainage ditches found in the analysed area were classified to three categories:

1. 1st order ditch – the Strumień Junikowski, as the main outlet,
2. 2nd order ditches – tributaries of the Strumień Junikowski (the Skórzynka, Ławica, Plewianka, Ceglanka),
3. 3rd order ditches – smaller ditches classified as drainage or roadside ditches flowing into 1st and 2nd order ditches.

It needs to be remembered that despite the extensive drainage network the analysed catchment is exposed to intensive anthropogenic pressure. The agricultural areas in that region are increasingly often subjected to urban sprawl. These processes cause a considerable increase in the paved surface area in the catchment, which is connected with increased surface runoff of waters from spring thaw and torrential rains.

3. Material and methods

The aim of this study was to assess the ecological status and needs for maintenance and renovation for drainage ditches in the Strumień Junikowski catchment. For this purpose available technical documentation of the drainage structures and base maps of the catchment were analysed. A site inspection was conducted (in April 2018), during which structures within the Strumień Junikowski and the other watercourses in the catchment were surveyed. Their technical condition was evaluated following the method proposed by Kaca and Interewicz (1991). The method was modified, eliminating the separate classification of operability and serviceability of these structure and replacing them with the general evaluation of their condition using descriptive notes of good, satisfactory and unsatisfactory (Bykowski et al. 2014), following the criteria used in Table 1. In the case of the other ditches in the analysed catchment (2nd and 3rd order ditches) a descriptive assessment of their need for renovation and modernisation was applied.

In the course of field inspections the degree of degradation was also evaluated in the Strumień Junikowski. It included the characteristics of habitats within the watercourse and bioindicator analyses applying the Macrophyte River Assessment Method (Szoszkiewicz et al. 2010). The method is based on the qualitative and quantitative assessment of the macrophyte species composition in the waters. MMOR research was conducted during the growing season in August 2018, when the plants were fully developed and identifiable. Aquatic plants were analysed along a 100m representative river stretch. Only macrophytes growing in the water were recorded (or at least rooted within the waters). Representative sections for habitats most commonly found near the river were selected for the study. The first point was dominated by patches of ruderal vegetation and bushes. The second point was dominated by a forest habitat with patches of ruderal vegetation, small fragments of meadows and allotments. The third point is a typical wetland habitat. The fourth point was dominated by reeds and wastelands. The fifth point was located in the area of industrial development. Macrophytes were identified to species. Only in the case of algae identification to genus was considered sufficient. The presence of each taxon was recorded with a percentage, 9-point scale: 1 for 0.1%, 2 for 0.1-1%, 3 for 1-2.5%, 4 for 2.5-5%, 5 for 5- 10%, 6 for 10-25%, 7 for 25-50%, 8 for 50-75% and 9 for 75%, respectively. Based on the obtained Macrophyte Index for Rivers (MIR) and the Water Framework Directive the ecological status of catchment waters was evaluated. The assessment was performed only in the main watercourse of the catchment, assuming that the Strumień Junikowski is the receiving water of the other ditches and as a consequence its condition reflects the ecological status of the entire catchment.

Table 1. Assessment criteria for the technical condition of linear, hydraulic and communication structures (Bykowski et al. 2014)

Assessment criteria of the technical condition of linear structures				
Lp	**criterion**	**structure condition**		
		good	**satisfactory**	**unsatisfactory**
1	Singular ditches			
	◦ average depth [cm]	80 - 120	60 - 80 i 120 - 150	< 60 i > 150
	◦ silting [cm]	< 10	10 - 30	> 30
	◦ plants' average height [cm]			
	a) at the bottom	< 25	25 - 35	> 35
	b) on the scarp	< 25	25 - 50	> 50
2	Collective ditches			
	◦ average depth [cm]	90 - 130	70 - 90 i 130 - 160	< 70 i > 160
	◦ silting [cm]	< 10	10 - 20	> 20
	◦ plants' average height [cm]			
	a) at the bottom	< 20	20 - 30	< 70 i > 160
	b) on the scarp	< 10	10 - 20	> 20
Assessment criteria of the hydraulic & communication structures				
Lp	**criterion**	**structure condition**		
		good	**satisfactory**	**unsatisfactory**
1	Culvert's pipeline			
	◦ silting	< 10 %	10 - 30 %	> 30 %
	◦ cover	> 50 cm	30 - 50 cm	< 30 cm
	◦ concrete rings' arrangenent	proper arrangenent of rings	proper arrangenent of rings	rings misplaced, damaged
2	Road over the culvert			
	◦ ruts	no / < 10 cm	10 - 20 cm	ruts reaching rings
3	buldings bridgeheads	no fracture	small fractures	deep fractures

4. Assessment of the technical condition of drainage structures in terms of their maintenance and renovation

The field studies provided a survey of 38 concrete culverts over the entire length of the Strumień Junikowski and 31 box culverts in the Skórzynka watercourse. Their status was assessed, showing that for most structures located in the Strumień Junikowski it is good or satisfactory (Fig. 2). The greatest effect on this status was exerted by silting of the waters, which in extreme cases exceeded 30%. Another evaluated parameter was the structure headwater, which as a rule met the requirements of a good condition, i.e. over 50 cm. The primary problem for the culverts in the analysed watercourse was connected with progressing silting and overgrowing of these structures. In some of them concrete damage would also need to be repaired. During the field research it was observed that there are no small water retention devices on the watercourse. In the era of current climate changes and drought, it is extremely important to slow down the outflow. It is therefore necessary to increase the number of retention devices on the watercourse by building groundsills, barrages, sluice gates and small reservoirs. The implementation of such investments will also contribute to increasing the flood safety of urbanised catchment areas.

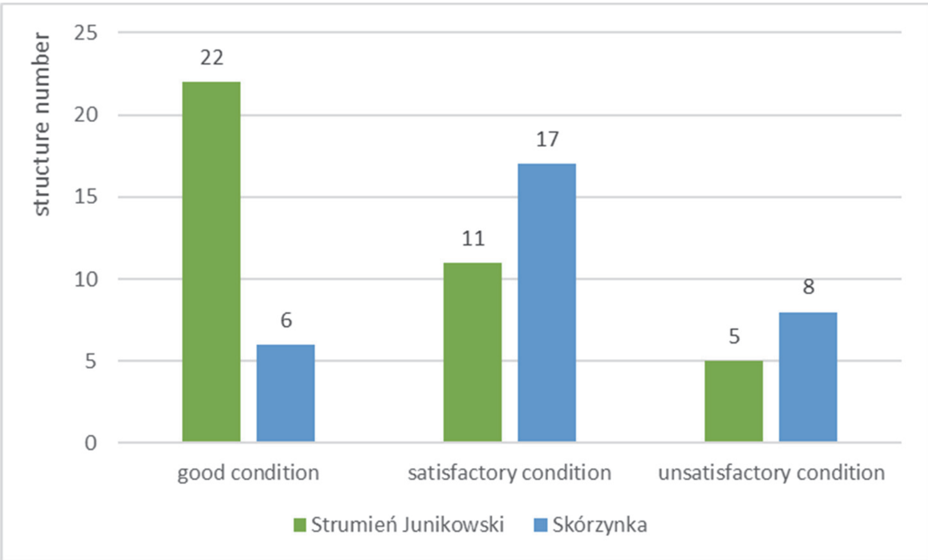

Fig. 2. Assessment of the condition of drainage structures

Field studies have shown that, in contrast to the Strumień Junikowski, the structures in the Skórzynka watercourse are in a worse condition. In 8 out of 31 culverts their condition was classified as inadmissible, i.e. not serving their function. One culvert is completely obstructed by the fallen bank openwork slabs. The parameter connected with headwater levels in the culverts was assessed as much better, as in none of the inspected structures it was classified as inadmissible. Within the administrative limits of the city of Poznań the structures are in optimal condition and they were classified as good (5 structures) and satisfactory (1 structure).

In the course of the conducted studies and field inspections the condition of linear structures was also assessed. This was based on such parameters as the mean depth of the watercourse, the degree of silting and the height of vegetation on the bottom and the escarpments. The condition of the linear structures in the Strumień Junikowski was assessed as satisfactory in over 60% of all cases (Fig. 3). Areas evaluated as being in the best condition, classified as good, included the initial segment of the watercourse, located near the airport, and the fragment at the outlet. The greatest problem observed in the Strumień Junikowski is related to the deposition of considerable amounts of rubbish and debris, particularly in the middle stretch of its course. Also numerous dead trees lying on the bottom obstruct water flow and contribute to increased silting. Over approx. 60% length of the Skórzynka watercourse its condition was assessed as satisfactory. In this case the greatest negative aspect, resulting in the deterioration of its evaluated status, is connected with the process of its vegetation overgrowth. The height of bank vegetation very often is greater than the satisfactory value and exceeds 50 cm. The relatively low flow rate in the Skórzynka watercourse contributes to accelerated ditch overgrowth. Another problem is also related with the observed high degree of silting (over 30 cm). For several years now the level of silting has not improved, as confirmed by earlier studies. Field measurements conducted in 2010 showed that the entire length of the Skórzynka watercourse is subject to observed high degree of silting with a thickness of approx. 35 cm (Przybyła et al. 2011).

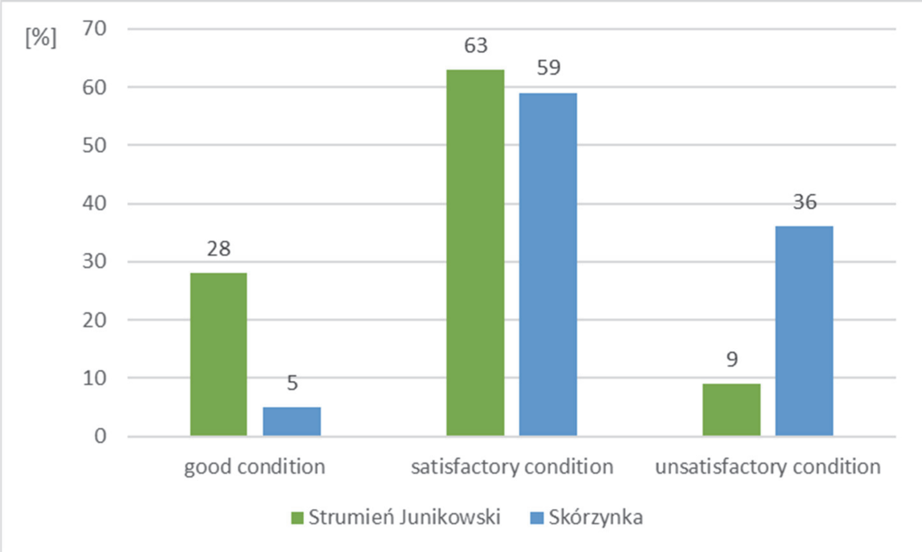

Fig. 3. Assessment of condition of linear structures

The conducted field inspection facilitated also an assessment of needs for maintenance and renovation in the lower order watercourses in the Strumień Junikowski catchment. The condition of the channels in 3rd order ditches was classified as unsatisfactory. As a result of long-term neglect their basic parameters determining water flow have greatly deteriorated. These ditches are overgrown and silted to a considerable degree. Culverts located in those ditches (approx. 60) are damaged and silted. Most of the 3rd order tributaries need to be thoroughly renovated by mowing of their bottoms and banks (minimum twice a year), cleanout of silting to a depth of min. 30 cm as well as restoration of the original cannel parameters (sloping). Damaged or improperly prepared culverts either require modernisation or need to be replaced. It was found that in relation to the total length of 3rd order ditches flowing to the Ławica watercourse (1242 m) over 70% require renovation. In the Plewianka watercourse 100% 3rd order tributaries require mowing of the vegetation overgrowth and removal of bottom silting. An analogous situation was observed in ditches flowing into the Ceglanka watercourse. In contrast, the Skórzynka has no tributaries. The conducted analysis showed that also 2nd order drainage ditches, i.e. the Ławica, Skórzynka, Plewianka and Ceglanka watercourses, as well as their drainage structures need to be renovated. This is determined mainly by the accelerated inflow of waters from the catchment, resulting from its intensive management and the increased area of impermeable (building development). The largest number of structures which need to be replaced is located in the Skórzynka watercourse (15 culverts). In turn, the lowest number of culverts classified as requiring renovation was found in the Ławica and Ceglanka (3 structures each). In the Plewianka watercourse 6 culverts need to be replaced (Table 2).

Table 2. A list of 2nd order ditches that require renovation

2nd order ditches' name	the mouth of Strumień Junikowski [km]	total length of the river [km]	lenght in the need of renovation [km]	lenght in the need of renovation [%]	total number of structures	structures in the need of modernisation	structures in the need of modernisation [%]
Ławica	9+750	2,30	1,30	56,5	8	3	37,5
Skórzynka	5+778	7,75	3,00	38,7	31	15	48,4
Plewianka	5+240	4,37	3,20	73,2	11	6	54,5
Ceglanka	4+480	2,23	1,50	67,3	8	3	37,5

5. Survey and phytosociological valuation of the watercourse

The Strumień Junikowski practically over its entire length is characterised by a high degree of anthropisation. Natural and semi-natural habitats accompany the dominant ruderal habitats, as confirmed by studies conducted to date (Dyderski & Wrońska - Pilarek 2018). Large areas along the river banks are covered by synanthropic species, primarily allochthonous. *Impatiens glandulifera* have been reported in the source section of the river. Naturally, it occurs in Central Asia, in the western Himalayas. It was imported as an ornamental plant and is an expansive synanthrope limiting biodiversity of river valleys. At present it is found not only in Asia and Europe, but it is a problem also in North America and New Zealand. Among synanthropes *(Echinocystis lobata)* was also observed here. It is an annual climber from the *Cucurbitaceae* family. In Poland its cultivation, breeding and sale are strictly controlled. In the middle stretch of the river at Junikowo, at Rzepińska street and at Niezłomnych street, large patches of *Reynoutria sachalinensis* were also reported. The latter is one of the 20 most expansive plants in the world. It is a perennial, forming underground rhizomes, which hinders effective control of this species. It is found most frequently in habitats located along watercourses. In Poland it is recommended as an energy crop, although opinions on this subject vary. Due to its rapid growth, dynamic spread and threat to native biodiversity all cultures of this plant are controlled. At the Junikowski Cemetery in the vicinity of old drainage ditches a unique association of *Selino carvifoliae-Molinietum* meadows is found, which has been threatened for almost two decades now (Borysiak 2001). The molinia meadows of varying moisture levels *(Molinion)* are Natura 2000 habitats (6410) with its representative species, purple moor-grass *(Molinia caerulea)*. Habitat 6410 is a semi-natural biotope, which developed as a secondary habitat replacing cleared forests. Both its formation and maintenance are connected with a specific management system, consisting in the annual late mowing performed in late August or even early September. These biotopes affect biodiversity also due to the system of their use. Neglected meadows excluded from use are transformed through natural succession into tall herb or shrub communities or forests. In rebogged sites they may be transformed into sedge beds. Molinia meadows are connected with mineral and organogenic soils with a very wide trophic amplitude – from poor, weakly acid soils to very fertile, alkaline soils, frequently with marked gleying (Kącki and Michalska 2010). A characteristic feature of these habitats is connected with the variable ground water table. In the beginning of the vegetation season it is very high and meadows are often flooded. In the summer season the groundwater level falls very low, frequently below the rhizosphere of many plant species. Water circulation in soil may result from natural conditions or be artificially generated by wetland drainage operations. Slightly different conditions are found in sieve-molinia grasslands (subtype 6210-2). These habitats develop on more acidic soils relatively poor in nutrients. Their vegetation composition floristically resembles acid sedge fens and fens. Water circulation in the soil is not very dynamic and the habitat is permanently moist (Matuszkiewicz 2018).

In selected sampling points (Fig. 4) bioindicator analyses were performed using the Macrophyte River Assessment Method (MMOR), assessing the degree of watercourse degradation, primarily in terms of the trophic status. A total of 22 macrophyte species were identified, including algae (1 taxon), pteridophytes (1 taxon), mosses (1 taxon), monocotyledonous (7 taxa) and dicotyledonous plants (12 taxa). Using the survey data the metric, i.e. the Macrophyte River Index (MIR), was calculated, which when referred to reference vales for a given macrophyte type facilitates evaluation of the ecological status as defined by the Water Framework Directive (2000/60/EC) (Szoszkiewicz et al. 2010).

Obtained MIR values indicate high variation in the ecological status of the Strumień Junikowski over its entire length (Fig. 5). The highest index value was recorded at Rzepińska street at the Junikowski Cemetery (point 2). This index classified waters to the very good ecological status based on the MIR boundary values for 5 classes of ecological status for lowland sandy and organic rivers. Waters in point no. 4 below the ponds were also classified as having a very good ecological status. The headwater and outlet points were found within the good ecological status according to the EU WFD. The lowest class was recorded for water flowing next to ponds in Kopanina. The recorded index classified water to the poor ecological status class.

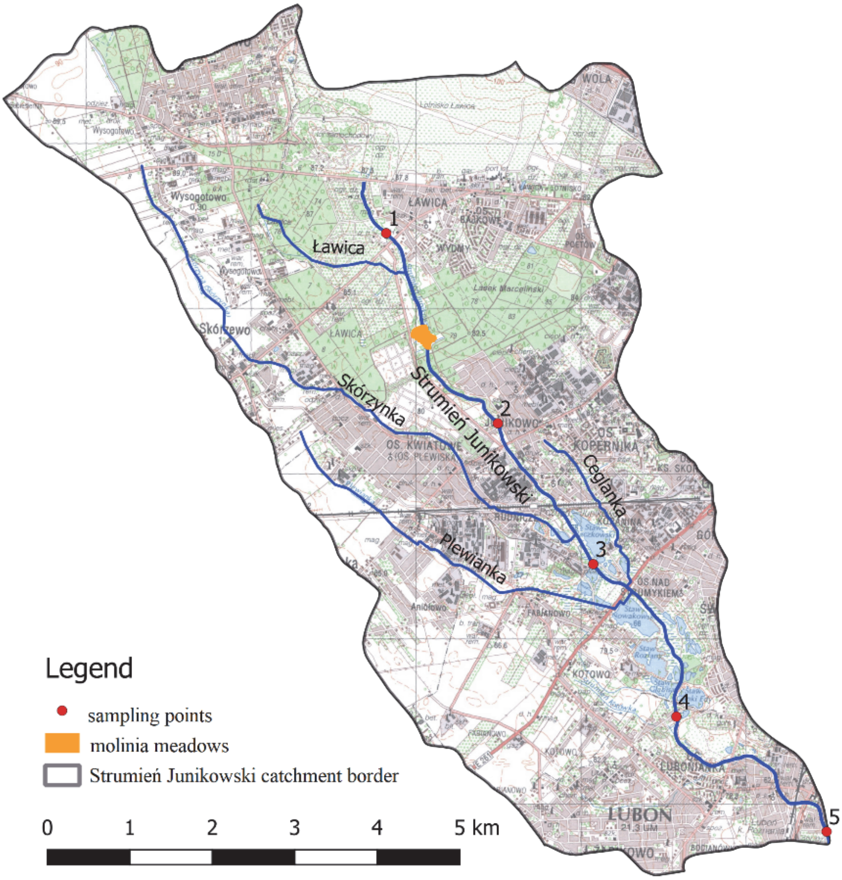

Fig. 4. Location of sampling points of the Macrophyte River Assessment Method

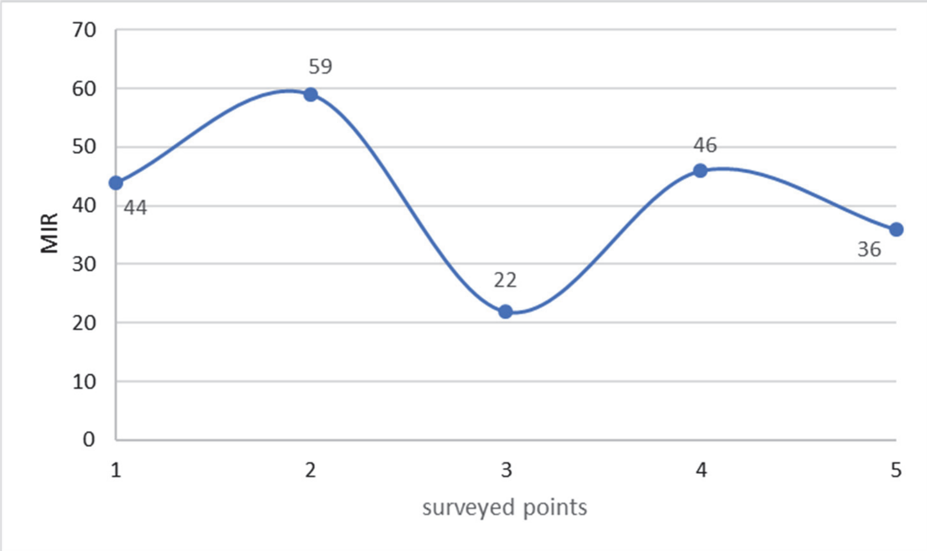

Fig. 5. Results of the Polish Macrophyte Index for Rivers in the surveyed points of the watercourse

In the course of macrophyte analyses colonies of rare slime molds *(Myxomycota, Mycetozoa,* also referred to as *Eumycetozoa)* were also identified. Formerly the group comprising several hundred species had been classified to fungi and later to fungus-like protists. At present it is classified to eukaryotic organisms belonging to *Amoebozoa,* i.e. a taxon of eukaryotes with a supergroup status. Although they had been considered to be a class of cryptogams, particularly fungi, they are closer to typically animal *Protista* (protozoans). This is indicated by the occurrence of mobile forms and feeding through phagocytosis. Thus they are not directly related with plants, animals or fungi.

6. Conclusions

Studies conducted on the ecological status and requirements for renovation and maintenance of drainage ditches in the Strumień Junikowski catchment provided grounds for the formulation of the following conclusions:

1. The Strumień Junikowski catchment is undergoing gradual degradation due to the increasing share of urbanised areas.
2. Obtained values of the Macrophyte Index for Rivers (MIR) indicate considerable variation in the ecological status of the Strumień Junikowski catchment, which may also result from the technical condition of drainage structures in that area, modifying its hydromorphological conditions.

3. Analyses conducted using the Macrophyte River Assessment Method showed that in the stretch between Ławica and Grunwaldzka street the degree of anthropopressure on the watercourse, resulting from habitat transformations and influx of pollutants, is the smallest. This is indicated by the highest MIR value and the identified macrophyte species, characterised by a narrow ecological amplitude.
4. Evaluation of the condition of drainage structures located in the Strumień Junikowski showed that they are in good condition. In contrast, the condition of the 3rd order watercourses was classified as unsatisfactory. Their immediate renovation (cleanout of silt deposits and mowing of vegetation overgrowth) are recommended.
5. The Strumień Junikowski catchment is constantly being developed, which leads to an accelerated and increased outflow of precipitation and spring thaw waters. For this reason maintenance of the drainage ditches in optimal condition is crucial and has a tremendous impact on the reduction of flooding risk in the areas adjacent to the watercourse.
6. In order to increase the flood safety of urbanised areas in the Strumień Junikowski catchment it is recommended to build small retention reservoirs and gates in the analysed watercourse, thus improving its retention capacity.

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Abstract

Drainage systems are responsible for maintaining adequate soil moisture levels and alleviating negative consequences of excess water coming from the spring thaw as well as torrential rains. In the face of the climate change and pervasive extreme weather conditions, the importance of these ameliorative measures will be increasing. It is imperative to ensure appropriate functioning of these drainage systems. To be effective they need to be adequately operated and maintained, with maintenance measures performed appropriately and with required frequency. Basic ditch conservation procedures include mowing to remove vegetation overgrowth and cleanout to remove sediment. A significant problem in Poland results from an insufficient number of renovation and conservation operations performed on drainage systems, their gradual deterioration and depreciation. As a result, it is crucial to assess the need for renovation and modernisation of drainage ditches. It needs to be remembered that these operations interfere with the environment and may cause some unfavourable ecological changes. In view of the above, the authors of this publication conducted a thorough evaluation of both the required renovation of the investigated drainage ditch system and its current ecological status. The study area comprised the Strumień Junikowski catchment with the main outlet, i.e. Strumień Junikowski, its tributaries (the Skórzynka, Ławica, Plewianka, Ceglanka) as the main collection ditches and field ditches. During the field inspection the existing drainage structures were inventoried, with their technical condition assessed according to Kaca and Interewicz (1991). In this paper the characteristics of habitats found in the drainage area of the watercourse are presented along with the bioindicator analysis performed using the Macrophyte River Assessment Method. Based on the MIR index the ecological status of the stream was assessed and classified in accordance with the Water Framework Directive. The results demonstrate a significant variation of the ecological state of Strumień Junikowski over its entire course. The condition of the drainage structures in the drainage area varies. In the main watercourse of Strumień Junikowski the inspected culverts are in a good condition in contrast to the ones located on the tributaries. Vegetation overgrowth and sediment deposition in the ditches are major problems of the drainage area. This is caused by a lack of effective and systematic maintenance and renovation of the watercourses. The Strumień Junikowski drainage area is further being developed, which is associated with a rapid and increased discharge of rainwater and snowmelt. Thus it is necessary to maintain drainage ditches to ensure their optimal condition, which is essential to decrease the risk of flooding in the urban areas adjacent to the watercourse.

Keywords:
renovation, modernisation, maintenance, drainage ditches, drainage measures, ecological status, Macrophyte River Assessment Method

Ocena stanu ekologicznego oraz potrzeb renowacji rowów odwadniających zlewni Strumienia Junikowskiego

Streszczenie

Systemy melioracyjne odpowiadają za zapewnienie prawidłowego uwilgotnienia gleb oraz niwelowanie negatywnych skutków nadmiaru wód pochodzących z roztopów oraz deszczy nawalnych. W obliczu zmian klimatycznych oraz coraz częstszego występowania ekstremalnych zjawisk pogodowych rola urządzeń melioracyjnych będzie wzrastać. Niezwykle ważne jest zatem zapewnienie prawidłowego funkcjonowania tych systemów. Warunkiem skutecznego działania urządzeń wodnomelioracyjnych jest ich właściwa eksploatacja, a także konserwacja, prowadzona w odpowiednim zakresie oraz z określoną częstością robót. W Polsce dużym problemem jest niewystarczająca ilość przeprowadzanych renowacji i konserwacji urządzeń melioracyjnych oraz ich stopniowe starzenie się i dekapitalizacja. Dlatego też niezwykle ważne jest dokonanie oceny potrzeb renowacji i modernizacji rowów melioracyjnych. Należy pamiętać przy tym, że zabiegi te istotnie ingerują w środowisko i mogą przyczynić się do niekorzystnych zmian ekologicznych. Autorzy niniejszej publikacji przeprowadzili kompleksową ocenę zarówno potrzeb renowacji systemu rowów odwadniających jak i jego aktualnego stanu ekologicznego. Obiekt badań stanowiła zlewnia Strumienia Junikowskiego z rowem pierwszego rzędu – Strumieniem Junikowskim (główny odbiornik), rowami drugiego rzędu – dopływy Strumienia Junikowskiego (Skórzynka, Ławica, Plewianka, Ceglanka) oraz rowami trzeciego rzędu. Podczas wizji terenowej zinwentaryzowano istniejące budowle wodnomelioracyjne oraz oceniono ich stan techniczny według metody Kacy i Interewicza (1991). W pracy przedstawiono również charakterystykę siedlisk występujących w obrębie cieku oraz wykonano badania bioindykacyjne z wykorzystaniem Makrofitowej Metody Oceny Rzek (MMOR). Na podstawie otrzymanego wskaźnika MIR (Makrofitowego Indeksu Rzecznego) sklasyfikowano stan ekologiczny wód strumienia wg wytycznych Ramowej Dyrektywy Wodnej. Otrzymane wyniki badań wskazują na duże zróżnicowanie stanu ekologicznego Strumienia Junikowskiego na całej jego długości. Stan budowli melioracyjnych w zlewni również nie jest jednolity. W obrębie głównego cieku – Strumienia Junikowskiego, zinwentaryzowane przepusty są w dobrym stanie w przeciwieństwie do tych znajdujących się na jego dopływach. Dużym problemem zlewni jest też wzrastające zarastanie oraz zamulenie rowów. Przyczyną tego stanu jest brak wystarczającej i systematycznej konserwacji i renowacji cieków. Zlewnia Strumienia Junikowskiego cały czas jest poddawana dalszej zabudowie, co wiąże się nagłym i zwiększonym odpływem wód opadowych i roztopowych. Z tego powodu zachowanie rowów odwadniających w optymalnym stanie jest bardzo ważne i ma ogromny wpływ na zmniejszenie ryzyka podtapiania terenów zurbanizowanych przyległych do cieku.

Słowa kluczowe:
renowacja, modernizacja, konserwacja, rowy odwadniające,
urządzenia wodnomelioracyjne, stan ekologiczny, Makrofitowa Metoda Oceny Rzek

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Study of the Outflow Conditions of the Weir Skoki on the Paklica River

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1. Introduction

Relatively small water resources in Poland and their uneven time and spatial distribution necessitate an increase in the number of investments designed for appropriate management of available water. The above assumption is supported by means of different types of water structures (Bednarczyk et al. 2009). When a damming structure includes other water facilities located in its immediate vicinity, i.e. a hydroelectric power plant, a fish pass, a sailing lock, and sometimes even a water intake, the whole system constitutes a water barrage.

Exploitation of reservoirs is associated with various problems. These are, i.e., vegetation overgrowing the riverbed below and above the reservoir, or erosion and material accumulation upstream and downstream of water structures.

Vegetation overgrowth in the riverbed reduces the flow rate capacity, and by leading to an increase in the water table level it may cause the flooding of adjacent areas. Kubrak et al. (2013) presented factors transforming the water flow resistance in lowland rivers of a complex cross-section nature. In the article, the authors characterised the vegetation growing in the floodplains of the Vistula riverbed and its impact on the water flow capacity. They pointed out that it is necessary to define the rules for removing vegetation from the riverbeds of high waters. Banasik and Krzyżanowski (2015) indicated the flow resistance resulting from variability of proper channel routing and riparian vegetation in floodplain areas as the most influencing factors affecting both the capacity of the Odra River and the forecasts of its flow-state relation. The work of a small hydropower plant located on small watercourses takes place in an annual cycle covering growing and post-growing seasons – including autumn and winter with lower temperatures

(Bajkowski and Olifirowicz 2014). Each of these seasons faces different operational problems related to the work of a small hydroelectric plant (Walczak 2018).

Tarnawski and Michalec (2007), who analysed the possibility of hydraulic transmission of high water through the weir on the Uszwica river in Brzesko. Previously, during the field research consisting in the technical assessment of the weir conducted in 2005, it was found that despite visible damages, the weir met the standards necessary for correct operation.Changes in sediment transport processes are also disadvantageous due to their dynamics, particularly in the downstream of the water structure. The most hazardous factor here is local erosion, which, if it develops in an uncontrolled way, can lead to local scouring below the water structure. Urbański (2009) presented the effect of water flow conditions on the characteristics of this phenomenon. On the basis of the study he stated that an increase in the water table level below the weir extends the time needed for creating local scouring, and a double increase in the flow rate causes an eightfold increase in the depth of scouring. Dąbkowski et al. (2007) investigated through their research the process of scouring below of the tired construction with outflow over and above the gate and demonstrated that bigger depths of scour make outflow above the gate. Głowski and Parzonka (2007) analyzed the functioning and impact of the Brzeg Dolny reservoir, taking into account the provision of adequate water quantity and bleed for the proper functioning of the hydroelectric power plant and electricity production. Studies related to this issue were also conducted by Hämmerling et al. (2013) and Hämmerling et al. (2019). On the basis of laboratory and field tests, the researchers identified the parameters of the mathematical model and presented an analysis of local scouring formation using a three-dimensional SSIIM modelling program.

Water management of retention and flow reservoirs requires regulating the flow of water through damming structures. However, the use of these structures for a long time has a significant impact on their safety, durability and functional characteristics. The natural environment negatively affects their technical condition and contributes to the ageing processes they are subject to. Each structure fulfils its assumed functions at the moment when it is newly built, however, over time, these functions become more and more limited due to aging processes. The solution to this problem is repair works that allow for restoring initial properties of a damming structure. Despite undertaking such works, a decrease in its utility value will be inevitably observed. When the renovation is technically required, though, economically unjustified, the facility is temporarily shut down (Zawadzki 2005).

Each damming structure divides a watercourse into two parts: the downstream – below the structure (downstream water) and the upstream – above the structure (upstream water). The division has a significant impact on the current river regime. The difference between upstream and downstream water is called the water surface elevation. By means of sluice devices in a damming structure, it is possible to regulate the outflow, hence the water surface elevation. When a reservoir is created, the water velocity in the upstream also changes, followed by the change in the regime of water table levels. A new phenomenon appears – waterborne bedload is deposited near the structure in the upstream, initiating the process of reservoir silting. Downstream water, which has excess energy and is sediment-free, begins to destroy intensely the riverbed below the structure (Bednarczyk et al., 2009). In order to maintain the safety of a damming structure, it is important to make appropriate hydraulic, strength and stability calculations. The calculations should take into account the entire structure and all its individual elements. Each element is designed not only to ensure the stability of the system, but also to operate reliably throughout its entire lifetime. The degree of reliability and safety of a structure corresponds to proper correction coefficients chosen for theoretical calculations and the assumed coefficients for natural parameters of materials used. Each structure designed or renovated requires special attention in relation to physical and mechanical phenomena that may have a negative impact on its safety and correct operation (Bednarczyk et al., 2009).

Table 1. Summary of major dam failures (structures higher than 15 m) that occurred between 1900-1975 acc. to International Commission on Large Dams (Kowalski 2017)

No.	Cause	Concrete dams	Earth dams	Other i.e. Steel dams	Total
1	Spillway breach	9	25	3	37
2	Erosion	3	31	–	34
3	Damage to escarpment protective elements	–	13	–	13
4	Leakage and penetration in the dam	–	37	–	37
5	Leakage and penetration in the ground	11	54	1	66
6	Landslides	7	28	–	35
7	Deflections	2	32	3	37
8	Deterioration of quality	6	5	–	11
9	Earthquakes	–	3	–	3
10	Faulty structures	2	3	–	5
11	Damage to shutters/sluices	3	4	–	7
	Total	43	235	7	285

Failures and catastrophes were the result of errors arising at various stages of construction or subsequent operation, including incorrect assessment regarding the technical condition of facilities, made by contractors who did not notice or could not foresee imminent hazards. For this reason, a person assessing a technical condition of a given facility should be responsible for own decisions and indications that have led to failure, as it is in the case of a chief designer (Parylak, 2007).

Common causes of dam failure, which are numerous, can be divided into anthropogenic and naturogenic actions. These include, among others, the following determinants: errors in design and construction, errors in concrete technology and workmanship as well as damage caused as a result of mechanical loads, physical impact or chemical aggression. Therefore, in order to ensure that a hydrotechnical structure and its elements function as long as possible in a safe and sustainable way at each stage (design, construction and operation), it is necessary to systematically and correctly conduct maintenance inspections of the investment.

1.1. Description of the research object

The research object was an uncontrolled section of the Paklica watercourse located at 6 + 400 km (Fig. 1). The water node includes a mill weir and a power plant, located in Skoki, commune Międzyrzecz, county Międzyrzecki.

The facility is directly adjacent to the county road leading from Brójec to Międzyrzecz, and more specifically to the road bridge over the Paklica River. Behind the bridge, to the south, there are: Wyszanowskie Lake and Bukowieckie Lake.

Paklica is a river about 40,0 km long, flowing through the Lubuskie Lakeland. It is a left tributary of the Obra River, where it flows into in the town of Międzyrzecz at 42 + 400 km, and flows out of Paklicko Małe Lake in the village of Wysoka. The surface of the lake is 51.0 ha, while its average depth is around 5,0 m. The total catchment area is 253,21 km^2 (Czarnecka 2005). The length of the catchment area equals the total length of the river and amounts to 40,0 km, the average width, i.e. the ratio of area to length is 7.0 km, and the average decrease is 0.74%. The river basin is located in the Łęgowski Lakeland and Bruzda Zbąszyńska, and belongs to the proglacial valley of the Warta River, which forms 22 water reservoirs. The borders of the catchment area are local elevations of land created by the accumulation of glacial sands (outwash plain surfaces). The southern border is indicated by an artificial elevation of the area, closed by an old route and embankments of the railway line between the villages of Rzepin and Zbąszyń. All towns located within the catchment area are agricultural or agricultural-forestry. The way of nearby land use is directly attributable to the nature of these localities: arable lands, approx. 65% of the total area, including 9% of green areas, 33% of forests, 2% of fishery land. The catchment is mostly located in the subsurface zone, with formations of high permeability, what makes this area characterised by high afforestation.

Fig. 1. The barrage in Skoki on the map (own study)

The mill weir is constructed of a channel with concrete sidewalls and a partially reinforced bottom. It was designed to accumulate water for the water mill located in Skoki Villge. The channel ends with two working sluices, which form the inlet to the hydroelectric turbines, located on both sides of the idle sluice. The idle sluice in the mill weir is a reinforced concrete structure, which together with two working sluices constitutes a complementary unit, as illustrated in Fig. 2 (Olek, 2014a).

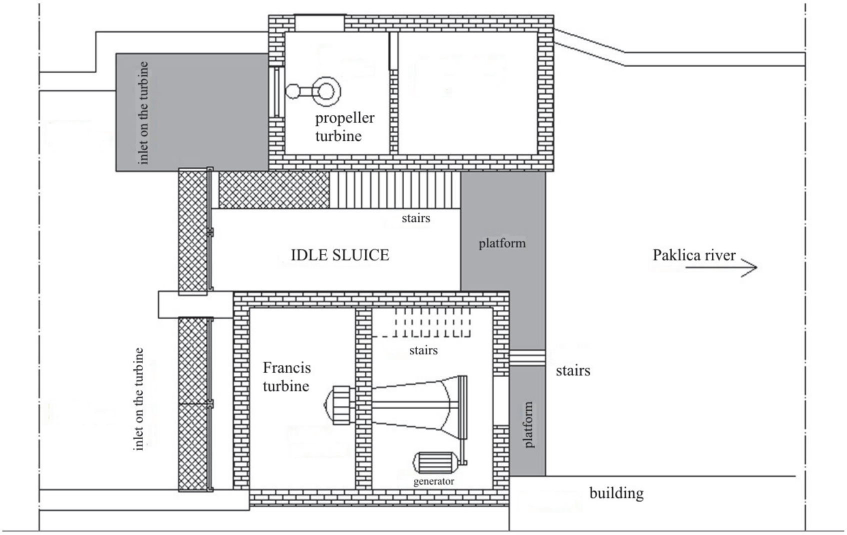

Fig. 2. Scheme of the barrage on the Paklica River

The water turbines are located in two buildings. They are part of the mill weir and can generate electricity. The first hydropower plant houses a Francis turbine with the following characteristics: water discharge $Q = 1.02$ m^3/s, rotor diameter D = 900 mm, efficiency coefficient $n < 60$ and nominal power up to 28 kW. Whereas, in the second building, there is a propeller turbine with water discharge $Q = 0.50$ m^3/s and nominal power of 14 kW. From the north, the hydroelectric power station borders with a plot of land where there is a bottom outlet with an eel basket and a fish trap placed at the artificially created outflow of water from Bukowieckie Lake. The bottom outlet consists of two inlets, with an opening of $B = 2.00 + 2.00 = 4.00$ m, connected with 30.0 m long construction pipes, ended with the fish trap and the eel basket (Olek, 2014b).

2. Methodology

Water flow velocity values were measured using Valeport Model 801 EM Flow Meter. An electromagnetic flow meter is used to accurately measure the water flow rate in open channels with an accuracy of ± 0,5%. It measures instantaneous velocity with a resolution of up to 1 mm/s, but also averages the results with a standard deviation. The water flow velocity measurements were taken for 5 cross-sections of the riverbed (Fig. 3). The selected cross-sections (3, 4, 5, 6, 8) were considered significant since they were located at the characteristic points of the studied section of the riverbed. They included: −main channel −outflow of water from the downstream, above the connection with the inflow (cross-section 3), –side channel –inflow to the main channel (cross-section 4), –main channel – below the connection of the main channel with a tributary, located behind a clump of vegetation (cross-section 5), –main channel –above the bridge (section 6), and –main channel –below the bridge, at the footbridge with an installed water gauge (section 8).

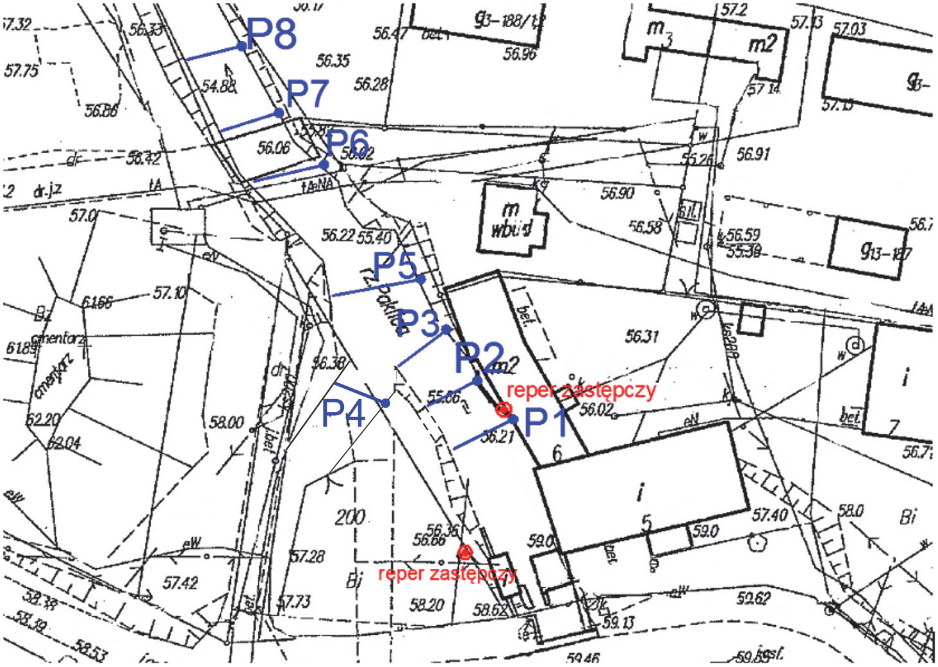

Fig. 3. Diagram of the Paklica River section with marked cross-sections

The velocity measurements in the determined cross-sections (Fig. 3) was carried out over the entire width of the riverbed, where the hydrometric verticals were spaced approximately 1.0 m apart, at points located at a distance of 0.05 m from each other. The obtained results were used to prepare the velocity distribution in individual cross-sections of the riverbed as well as throughout the entire section of the river below the Skoki barrage.

For the purpose of the present article there was also carried out an analysis of spillway capacity using the empirical relationship (Kisielev 1972, Franzini & Finnemore 1972, Sobota 1994, Lewandowski 2006) for flow rate Q regarding a free outflow broad-crested weir (Fig. 4):

$$Q = mb\sqrt{2g}H_0^{\frac{3}{2}}$$

where:
m – discharge coefficient,
b – length of the crest [m],
$H_0 = H + \frac{\alpha v_0^2}{2g}$ (weir head+velocity head) [m].

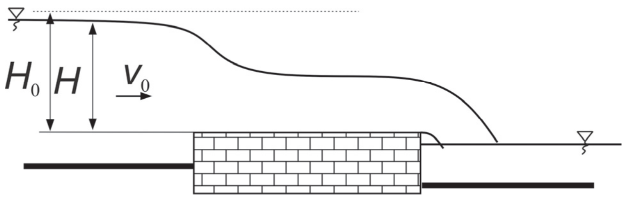

Fig. 4. Diagram of the free outflow broad-crested weir

The values of the expenditure factor m of a broad-crested rectangular weir range from 0.295 to 0.365 (Kisielev 1972, Kubrak 1989). This is influenced by, among others the shape of the edge of the threshold at the inlet (rounded, cut off, or sharp) and the roughness of the surface of the rectangular weir range.

3. Results

The water flow velocity measurements were taken using a flow metre in the studied section of the Paklica River for 5 cross-sections of the riverbed. The analysed section of the watercourse was characterised by highly varied water velocity. The reasons for these disturbances were, among others: variable water depths in each cross-section, overgrown riverbed embankments, dense grassy vegetation and a poor technical condition of the water barrage. During the measurements, the sluices of the hydraulic structure were closed, however, due to the poor technical condition of the entire facility, numerous water leakages could be observed. As a result, there was a small amount of flowing water, and consequently – low flow velocity values in cross-sections below the barrage (cross-section 3), a significantly larger amount of water, and higher flow velocity values in the inlet channel, below the fish trap (cross-section 4). Cross-section 5 was the section below the connection of the main channel to the inflow channel, behind a clump of plants (axis of the river bed). This cross-section was characterised by large flow velocity fluctuations in relation to its depth due to the occurrence of rich river vegetation. Cross-sections 6 and 8 demonstrated a gradual stabilisation of water flow velocities, because they were in a proper distance from the barrage and there were no elements in the area that could disturb the water flow rate (i.e. aquatic vegetation).

The graphical representation of the results of water velocity measurements in the riverbed includes only selected characteristic points. All the presented velocity distributions concerned the hydrometric verticals located in the central part of the measurement cross-section.

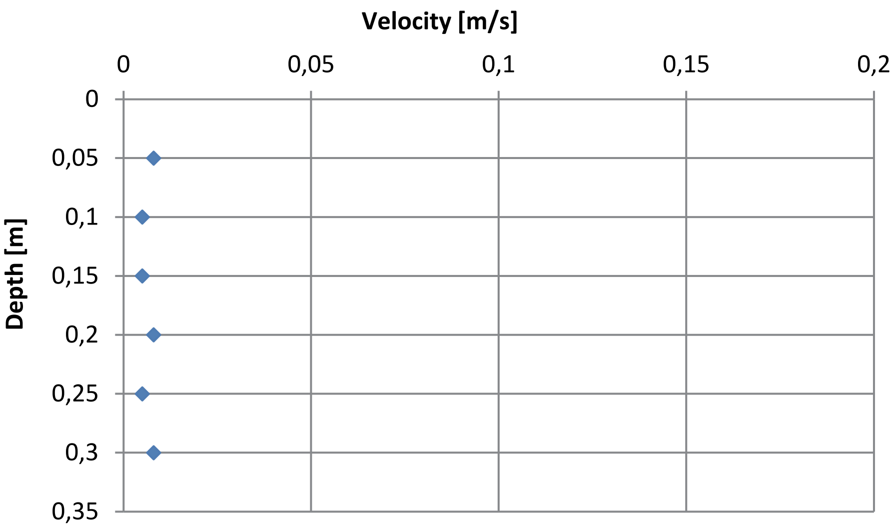

Fig. 5. Vertical velocities distribution in axis of cross-section 3 on the Paklica River

Velocity distributions in the central part of the cross-section (Fig. 5) were characterised by a low value of water flow rate resulting from a small depth of the riverbed and a specific location. Velocity values in the hydrometric vertical did not exceed 0.1 m/s.

However, an increase in velocity by almost 100% was observed in cross-section 4 (Fig. 6), which was located in the inflow channel where there is a fish trap. The lowest average velocity was measured at a depth of 0.35 m, and the highest 0.1 m from the bottom.

The average water velocity (approx. 0.1 m/s) was also measured in cross-section 5 (Fig. 7), although the velocities for individual depths varied significantly by up to 0.03 m/s. Variability in velocity values with a simultaneous increase in depth was caused by the location of the cross-section including the connection of the main channel to the inflow channel and the resultant local water accumulation as a direct effect of a large clump of grassy vegetation (Fig. 8).

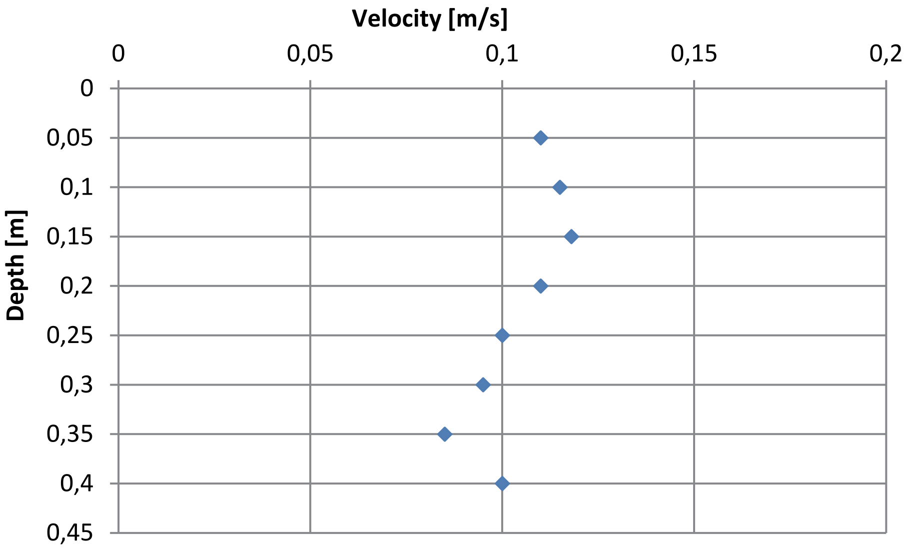

Fig. 6. Vertical velocities distribution in axis of cross-section 4 on the Paklica River

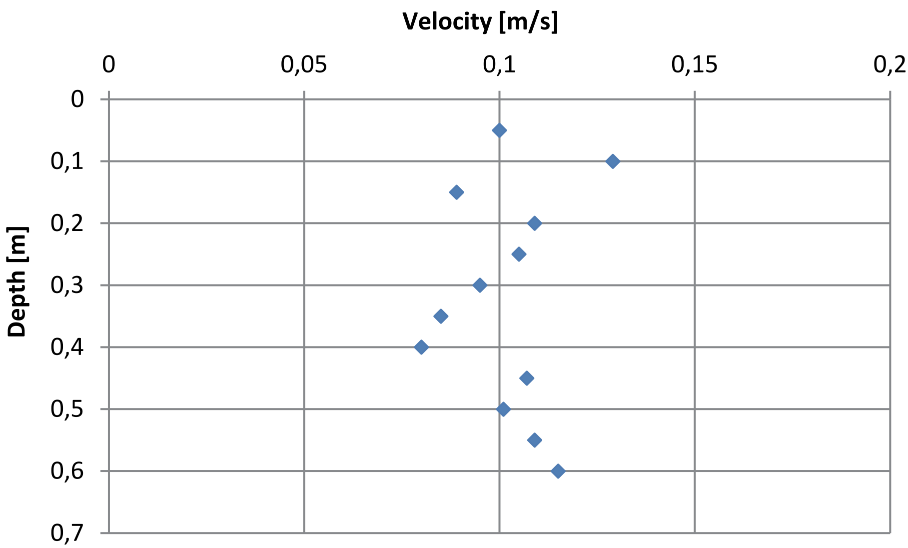

Fig. 7. Vertical velocities distribution 2 m from BL in cross-section 5 on the Paklica River

Fig. 8. Measurement of water flow velocities on the Paklica River

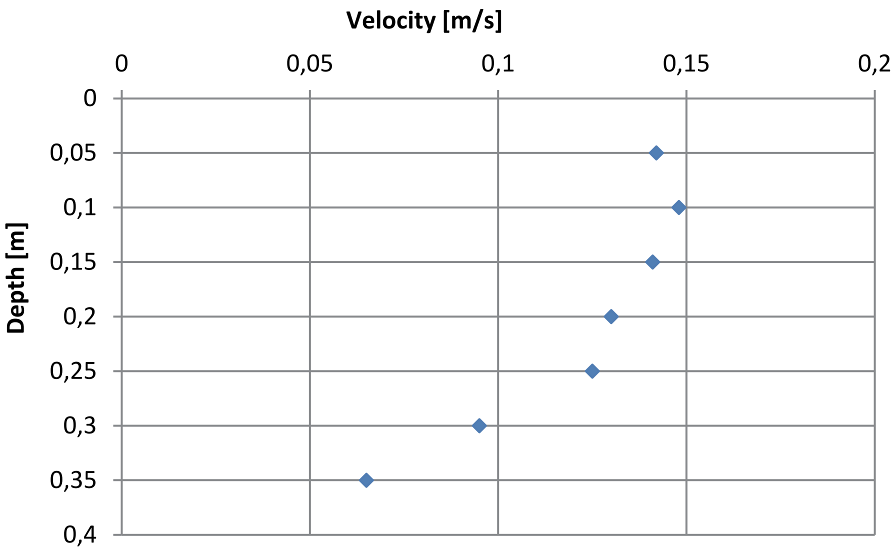

Fig. 9. Vertical velocities distribution in axis of cross-section 8 on the Paklica River

A significant effect of grassy vegetation on velocity values was observed in analyzed cross section (Fig. 8), located in the area with intensive biological development represented by reed on both sides of the cross-section. Riparian vegetation additionally affected the narrowing of the cross-section, particularly at the level of water table. The bottom zone had the velocity values higher by half than the average. (Local vegetation has the shape of cylindrical elements, through which water flows without much resistance).

The highest average velocity values were measured in the axis of cross-section number P8, which is shown in Figure 9. The location of the measurement cross-section (equal to 10 m) was important here. The area lacks riparian vegetation, and the hydro-technical structure itself is in such a distance that it does not affect flow conditions.

In order to properly assess the weir's capacity, it was assumed that the length of the crest is 2.76 m, and the values for water height above the crest fall within 5 cm to 100 cm. Calculations of the flow capacity of a broad-crested rectangular weir at the barren drop of the barrage were made taking into account two values of the flow rate coeficient: m = 0.292 (current state, damaged concrete surfaces of the overflow) and m = 0.365 (after modernization). The results are calculated in the Fig. 10.

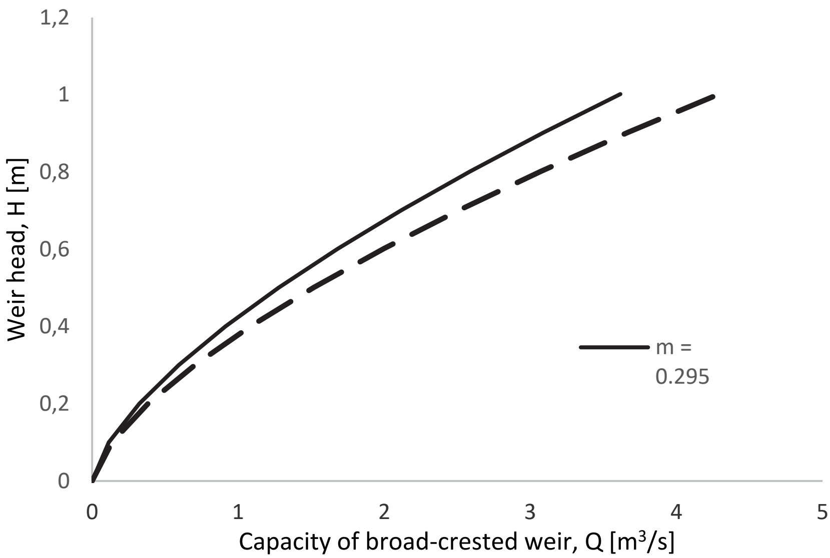

Fig. 10. Capacity of broad-crested part of the Skoki weir

The expenditure of a broad-crested rectangular weir at the idle drop of a water step at NPP = 58.40 m above sea level (H = 0.8 m) is 2.57 m^3/s and together with other overflow devices it allows safe passage of large waters. The modernization of this broad-crested rectangular weir (rounding the inlet edge, smoothing the broad-crested rectangular weir) would increase its capacity by approx. 19%. It would also be necessary to equip the overflow with a modern steel movable closure, e.g. a flat gate valve (Novak et al. 2001).

4. Discussion

The effect of flow resistance of vegetation on the riverbed capacity was the subject matter considered among others by Walczak et al. (2015), who studied the influence of seasonal changes in vegetation on river flow velocity values. Kozioł et al. (2016) stated that the method of Shiono and Knight allows for predicting the lateral velocity profile averaged in depth in compound channels with high vegetation in floodplains compliant with laboratory hydraulic measurements. Walczak et al. (2018) analysed the development of vegetation over a 12-year period and confirmed that reduction in the flow rate can reach 45% for scenarios in which the only considered factor is an increase in the diameter (at constant density), and up to 70% in the case of an increase in the vegetation density. Fig. 7 and 9 show the logarithmic distribution of water velocities that occurs in the areas without elements blocking free flow rate.

On the basis of on-site verification and empirical calculations, it can be noticed that direct proximity of shrubby vegetation on Bukowiec Lake does not affect the weir's capacity. Only elastic vegetation, represented by leaves and branches of grasses, can be found at the inlet trash racks of the weir. The poor technical condition of the weir's concrete elements subject to aging processes does not allow for impounding water. Lack of measuring and control devices as well as fish passes, plus the insufficient capacity necessitate modernisation of the weir.

5. Summary

For the purpose of this work, there were analysed: spillway capacity and water flow conditions below the damming structure on the Paklica River. As the technical condition of individual elements of the damming structure confirmed, it was found that the system could not perform its functions effectively. A small amount of water (due to leakage through the flat gates) flowed through the weir channel and HP, hence the occurrence of low water flow rates within the section from the weir to the connection with the fish trap channel. It was stated that the flow rates were much higher in the channel discharging water from the fish trap than in the channel discharging water from the hydroelectric power plant and the weir, which was caused by a poor technical condition of the fish trap and numerous leaks. Local changes and disturbances of water velocity in cross-sections were strongly shaped by vegetation overgrowing the riverbed. It can be observed that the cross-sections located in the areas of grassy vegetation were characterised by high variability of velocity values, which directly affected the flow rate. Field studies were conducted during the period of full vegetation, therefore the analyzed speed distributions take into account its occurrence in cross-section.

Modernization of the broad-crested rectangular weir located on the Paklica River by rounding the inlet edge and smoothing the broad-crested rectangular weir would increase its capacity by approx. 19%. Equipping the broad-crested rectangular weir with a modern steel movable closure would allow more accurate flow control on the barrage.

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Abstract

The paper presents an assessment analysis of the flow capacity of the barrage on the Paklica river. The analysed barrage consists of a mill weir and bottom outlets, and is supplied with water from Bukowiecki Lake. The reasons for addressing this subject matter were: from the need to determine the technical condition as well as the ecological condition of the lower position. The environmental status of the area below the system was considered as equally important. Field research included photographic documentation of the technical condition of the weir, taking into account the state below and above the structure, its abutments and the threshold. Additionally, there were made velocity distribution measurements in the downstream during the growing season, assuming this period as the least favourable with respect to hydraulic conditions.

Keywords:
broad-crested rectangular weir, velocity, flow rate coeficient

Badanie warunków odpływu z jazu Skoki na rzece Paklica

Streszczenie

W artykule oceniona została przepustowość stopnia wodnego na rzece Paklica. Analizowany stopień składa się z jazu młyńskiego i upustów dennych i jest zasilana wodą z jeziora Bukowieckiego. Przyczyny podjęcia tego tematu były następujące: potrzeba ustalenia stanu technicznego, a także stan ekologiczny analizowanego obiektu. Równie ważny był stan środowiskowy obszaru poniżej stopnia wodnego. W czasie badań terenowych wykonano dokumentację fotograficzną stanu technicznego jazu z uwzględnieniem stanu górnego i dolnego stanowiska, przyczółków oraz progu. Dodatkowo wykonano pomiary rozkładu prędkości w dolnym stanowisku w czasie wegetacji przyjmując ten okres za najmniej korzystny ze względów hydraulicznych.

Słowa kluczowe:
przelew o szerokiej koronie, prędkości, współczynnik wydatku

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Bending Moment of the Waste Fine Aggregate Concrete Beams

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1. Introduction

The strength of fiber reinforced concrete meant as load carrying capacity, resistance to cracking or limiting magnitude of strain and shifting is a decisive factor on its suitability in concrete structures (Głodkowska & Ziarkiewicz, 2018), (Błaszczyński & Przybylska-Fałek, 2015). The fibres cause, in every case, significant increase of energy needed to destroy the element for any type of loading (Sucharda, Pająk, Ponikiewski, & Konecny, 2017), (Sadowska-Buraczewska, 2016), (Domski, 2015), (Seitl, Keršner, Bílek, & Knésl, 2010), (Kormeling, Reinhardt, & Shah, 1980). The strength increases with the number and performance of steel fibres (Maidl, 1995), (Meda, Minelli, & Plizzari, 2012), (Pająk & Kühn, 2016), (Domski & Głodkowska, 2017). The highest influence of steel fibres is obtained in the case of bending, which depends on, among other things, arrangement of the fibres within the cross-section. The fibres located in the element tension zone, particularly at the element edge, are used most efficiently (Yazıcı, İnan, & Tabak, 2007), (Ponikiewski, Katzer, Bugdol, & Rudzki, 2014), (Sadowska-Buraczewska & Skrzypczak, 2019).

The method of calculation of the fiber reinforced concrete beams load carrying capacity depends on the adopted distribution of stress-strain in the compressed and stretched zones. Authors of the article (Henager & Doherty, 1976) adopted in the seventies a simplified model of stress pattern and linear variability of strain at beam's height. The method was accepted for application by the American Concrete Institute (ACI-544.4R-88, 1994) at the maximum value of compressive strain fixed by (Henager & Doherty, 1976) at 0.003. Pearlman, Swamy and Al-Ta`an, Hassoun and Sahebjam, Lok and Xiao proposed different value of the maximum strain in the compressed zone making it dependent on, for example, amount of the fibres applied. There are also some other methods of calculation of load carrying capacity of fiber reinforced concrete beams proposed by, among others, (Swamy & Al-Ta`an, 1981) (Narayanan & Kareem-Palanjian, 1986), (Craig, Decker, Dombrowski, Laurencelle, & Federovich, 1987), (Lim, Paramasivam, & Lee, 1987), (Ezeldin & Shiah, 1995), (Imam, Vandewalle, & Mortelmans, 1995), (RILEM TC 162-TDF, 2003), (Padmarajaiah & Ramaswamy, 2004), (fib Bulletin 55, 2010) but they are not included within this paper.

The laboratory test results for the critical load carrying condition of beam elements made of plain concrete and waste fine aggregate concrete containing steel fibres 50/0.80 and 30/0.55 (Zarzycki, Katzer, & Domski, 2017) have been shown in this paper. The destruction moments obtained during the experiments were compared with analytical values acquired by application of some selected calculation methods.

2. Description of experiments

The experiments were carried out in six beams dimensioned 150×200×3300 mm. Sixteen beams were made of waste fine aggregate concrete and two of plain concrete. The beams were loaded with two concentrated forces applied at 1/3 beam span. The beam test loading diagram is shown in Fig. 1.

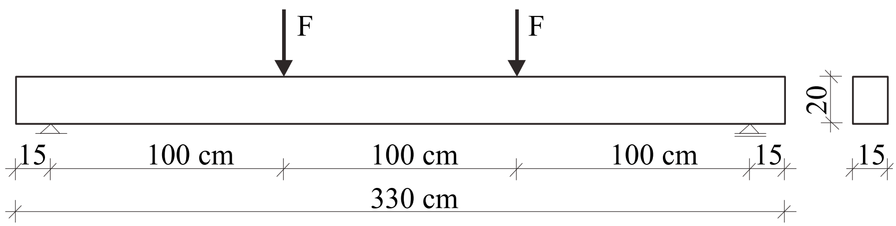

Fig. 1. Beam geometry and loading arrangement diagram

The magnitude of the loading applied was controlled by beam support reaction reading using SAD 256 data acquisition computer system. The system was used, in the presented study, also for measurement of beam tensioned reinforcement strain. It was measured with foil strain gauge glued (before concrete pouring) to two tensioned rods. TFs-5/120 foil strain gauges (120.3 Ω ± 0.2% resistance and gauge factor k = 2.15 ± 0.5%) connected to SAD 256 system via the so-called Wheatstone's bridge have been applied. The longitudinal beam reinforcement was made of ribbed steel (34GS grade) dia. 10, 12 and 14 mm, whereas the transversal reinforcement was made of smooth steel (St3SX-b grade) dia. 4.5 mm. Only ribbed steel was tested for its mechanical properties. The yield point within 424-454 MPa range, tensile strength from 695 MPa to 714 MPa and modulus of elasticity from 220 GPa to 223 GPa were obtained. It appears from the tests performed that ribbed steel used in this study featured a very distinct yield point.

The marking, beam characteristics and strength features of concrete applied are shown in Table 1. The tensile strength while in splitting ($f_{ct,sp}$) experiments were carried out on 150 mm cubes. The cylindrical compressive strength (f_c) and modulus of elasticity (E_c) were established for cylindrical samples featuring diameter of 150 mm and height of 300 mm, received by cutting samples featuring height of 450 mm on both ends.

Table 1. Beam characteristics and associated test results

<table>
<tr><th rowspan="2">Beam marking</th><th rowspan="2">Fibres l/d_f [mm/mm]</th><th colspan="2">Longitudinal and transversal reinforcement</th><th colspan="3">Concrete mechanical features</th></tr>
<tr><th>Top rods / bottom rods</th><th>Stirrups and their spacing</th><th>$f_{ct,sp}$ [MPa]</th><th>f_c [MPa]</th><th>E_c [GPa]</th></tr>
<tr><td>B–1, B–2</td><td rowspan="3">50/0.80</td><td>2#8 / 3#10</td><td rowspan="7">ϕ 4.5 mm at 130 mm</td><td rowspan="3">3.57</td><td rowspan="3">50.2</td><td rowspan="3">34.2</td></tr>
<tr><td>C–1, C–2</td><td>2#8 / 3#12</td></tr>
<tr><td>G–1, G–2</td><td>2#8 / 3#14</td></tr>
<tr><td>H–1, H–2</td><td rowspan="3">30/0.55</td><td>2#8 / 3#14</td><td rowspan="3">2.89</td><td rowspan="3">38.4</td><td rowspan="3">26.0</td></tr>
<tr><td>I–1, I–2</td><td>2#8 / 3#12</td></tr>
<tr><td>J–1, J–2</td><td>2#8 / 3#10</td></tr>
<tr><td>F–1, F–2</td><td>–</td><td>2#8 / 3#10</td><td>3.82</td><td>51.9</td><td>33.4</td></tr>
</table>

To produce the B, C, G, H, I and J series beams natural fraction aggregate (0-4) mm, being the residue of aggregate hydroclasification in the gravel pit in Sępólno Wielkie (West Pomerania) was used. 30/0.55 or 50/0.80 hooked steel fibres (Zarzycki, Katzer, & Domski, 2017) featuring slenderness ratio 54.5 and 62.5 respectively were added alternately to the fine aggregate concrete mix. Plain commercial concrete, class C35/45, produced in „Dźwigbet" in Koszalin was used to produce the F series beams. The waste fine aggregate concrete containing steel fibres mix compositions (Domski, 2016) are shown in Table 2.

Table 2. Fine aggregate concrete compositions [kg/m^3]

Mix components (Domski, 2016)	H, I, J series	B, C, G series
Waste sand (0-4 mm)	1855	1835
CEM II/B-V 32.5 R cement	378	374
Water	140	150
FM 34 superplasticiser	3.83	3.78
Steel fibres	34	33

3. Test results and their analysis

The value of the moment at which it was assumed that the beam was destroyed (Fig. 2), was being established from the reinforcement steel strain and bending moment relationship graph. The moment magnitude at which the reinforcement steel "flew", registered by an electric resistance wire strain gauge glued to the reinforcing rods, was being taken form the graph. All the beams under review were destroyed due to arrival at the yield point of the stretched steel reinforcement.

Fig. 2. View of the damaged beam

Figure 3 shows examples of the bending moment and reinforcing steel strain relationship graphs. The horizontal line (at strain value approx. 0.2 percent) at the graph (Fig. 3) shows the reinforcing steel yield point calculated on the basis of the accompanying experiments assuming the linear relationship of σ-ε. All the analysed beams were destroyed at the higher than calculated level of steel strain. Also strain values in beam lateral surfaces were being determined for the load at which the yield point was being reached using linear transducer gauge measurements.

According to (Henager & Doherty, 1976) the location of the neutral axis for plain concrete doesn't change much with increase of the load i.e. between 0.42 and 1.0 of the destructive force value the neutral axis stays practically at the same position whereas in the steel fibre containing beams the location of the neutral axis shifts along with increase of the load towards the compressed reinforcement. The above relationship for fine aggregate concrete was recorded in the presented own research but the phenomenon described by Henager and Doherty for plain concrete was not observed during said research work. Figure 4 shows examples of graphs of strain occurring at beam height in the middle of its span. No significant difference in graph shape and in strain values between plain concrete and fine aggregate concrete was established.

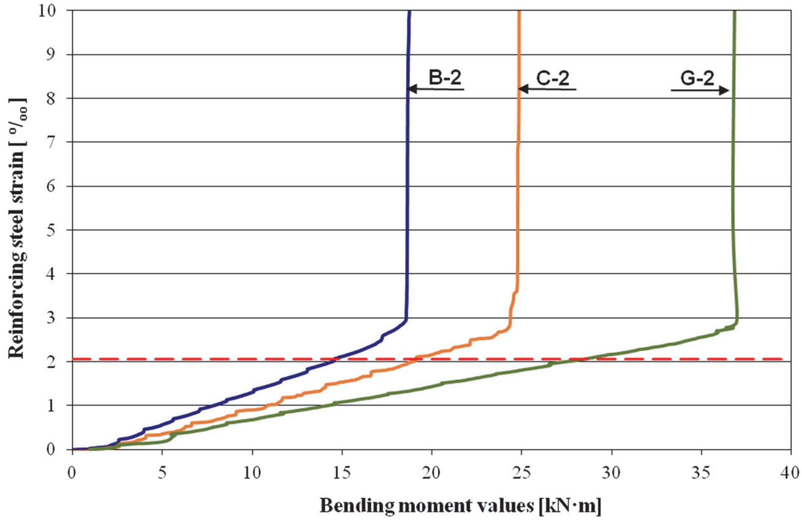

Fig. 3. The bending moment in function of the reinforcing steel strain for selected beams

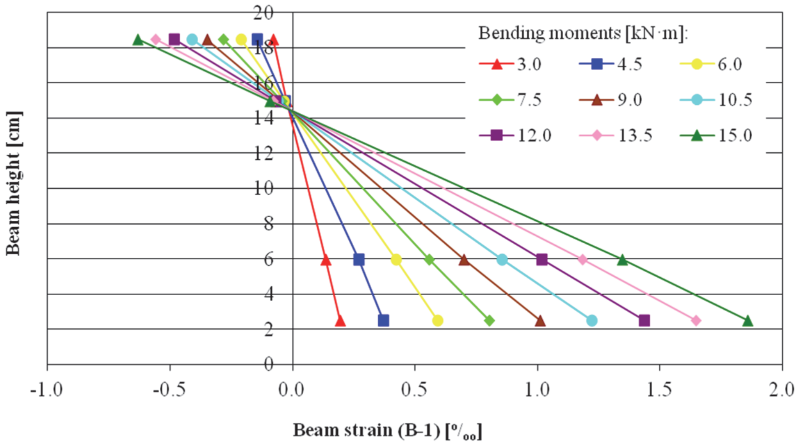

Fig. 4. Lateral strain of beam surface (B-1)

The results of the load carrying capacity of fine aggregate concrete beams were compared with the values calculated on the grounds of American Concrete Institute method (ACI-544.4R-88, 1994), the diagrams of which are shown in Figure 5.

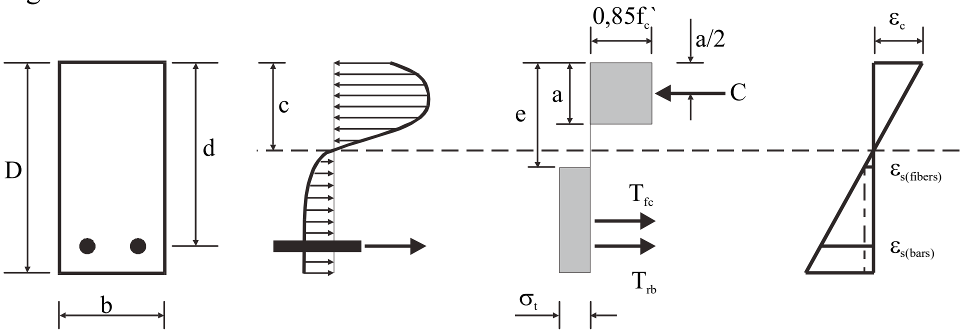

Fig. 5. The diagram of calculation of the carrying capacity of beams containing steel fibres according to (Henager & Doherty, 1976)

Assuming the distribution of stress as in Fig. 5 the load carrying capacity of the cross-section can be calculated from equation (1) (notations as those used in Fig. 5).

$$M_t = A_s f_y \left(d - \frac{a}{2} \right) + \sigma_t b (D - e) \left(\frac{D}{2} + \frac{e}{2} - \frac{a}{2} \right) \tag{1}$$

The distance "e" shall be determined from Fig. 5 assuming that the maximum strain of the outermost compressed fibre (ε_c) is 0.003:

$$e = \frac{\left(\varepsilon_{s(fibres)} + 0.003\right) \cdot c}{0.003} \tag{2}$$

where:

$$\varepsilon_{s(fibres)} = \frac{\sigma_f}{E_s} = \frac{2\tau_d F_{be} l}{d_f E_s} \tag{3}$$

whereas "σ_t" strain is, according to formula (4):

$$\sigma_t = 0.00772 \frac{l}{d_f} \rho_f F_{be} \tag{4}$$

In the above formula ρ_f means the steel fibre content by volume (percentage) whereas F_{be} is a factor which depends on fibre shape taking values from 1.0 for straight fibres to 1.2 for hooked ones. Where l is the length, d_f is the diameter of the fibres and τ_d is the dynamic bond stress between the fiber and the matrix.

The calculated and measured breaking moment values compared with results obtained by other authors are shown in Table 3 and Figure 6.

Table 3. Load carrying capacities of the tested beams

Beam marking	Breaking moments		M_C / M_T
	Tested M_T [kN·m]	Calculated M_C [kN·m]	
B–1; B–2	18.39; 18.82	18.45*	1.00; 0.98
C–1; C–2	24.70; 24.40	24.18*	0.98; 0.99
G–1; G–2	35.94; 36.94	33.72*	0.94; 0,91
H–1; H–2	36.45; 34,30	31.92*	0.88; 0.93
I–1; I–2	23.84; 23.78	23.78*	1.00; 1.00
J–1; J–2	18.52; 17.44	18.08*	0.98; 1.04
F–1; F–2	17.48; 17.62	16.07**	0.92; 0.91

* – according to (Henager & Doherty, 1976)
** – as per Eurocode 2 (EN-1992-1-1, 2008)

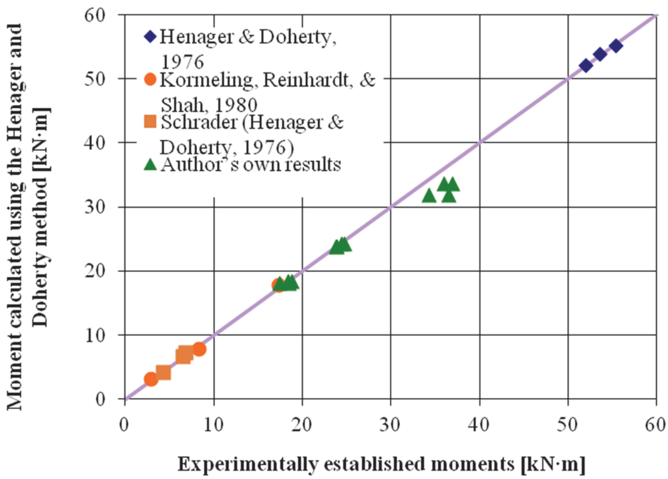

Fig. 6. The diagram of calculation of the carrying capacity of beams containing steel fibres according to (Henager & Doherty, 1976)

It appears from the above comparison that the method of calculation of the load carrying capacity of beams containing steel fibres applied by American Concrete Institute (ACI-544.4R-88, 1994) reflects well the test results for the wide scope of the tested elements. The mean differences between the calculated moment value and that obtained in tests do not exceed in the described experiments 3.1%. The analysis of beams made of plain concrete (F) showed that the breaking moment values calculated by application of the method used in the Eurocode 2 (EN-1992-1-1, 2008) are on average lower by 8.4% than those obtained in the tests.

4. Summary

The results of load carrying capacity of the tested beams containing steel fibres and the values calculated by application of the method proposed by (Henager & Doherty, 1976) show high correlation. The achieved spread (3.1%) falls well within the test spread obtained by the method authors i.e. from 2.8% to 6.3%. Such good consistency of results indicates that the calculation model applied was correct, however, it should be borne in mind that the model does not take into account the reinforcement within the compressed zone. The values of above method must be underlined here i.e. taking into account the influence of steel fibres within the cross-section stretched zone onto element load carrying capacity.

Having analysed the breaking moments achieved for beams containing steel fibres (B and J) and plain concrete beams (F) one can see that the load carrying capacity of the former is on average higher by 2.4% for beams (J) containing 30/0.55 steel fibres and 5.7% for beams (B) containing 50/0.80 fibres and the applied content of steel fibres by volume was: 0.43% and 0.42% respectively. At higher level of fibre reinforcement the load carrying capacity can increase even by 26% (Henager & Doherty, 1976).

The method indicated in the Eurocode 2 (EN-1992-1-1, 2008) can also be applied for calculation of the load carrying capacity of the waste fine aggregate concrete beams containing steel fibres but this method gives too low values for the breaking moments. The difference for the described experiments was on average 11.9% for the beams (J) containing 30/0.55 steel fibres and 15.8% for the beams (B) containing 50/0.80 steel fibres respectively.

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Abstract

This report presents the results of laboratory experiments of bending moment for fourteen concrete beams with steel bars. Twelve of the beams were made of waste fine aggregate concrete containing steel fibres: six with steel fibres 30/0.55 and six with steel fibres 50/0.80. The next two beams were made of plain concrete. The results of the experiments were compared with theoretical calculations based on a Eurocode 2 and also with the method suggested by Henager and Doherty.

Keywords:
waste sand, fine aggregate, composite, steel fibres

Moment zginający belek żelbetowych z drobnego kruszywa odpadowego

Streszczenie

Artykuł przedstawia wyniki laboratoryjnych badań momentu zginającego czternastu belek żelbetowych. Dwanaście z nich wykonano na bazie piasku odpadowego wzbogaconego włóknami stalowymi tj.: sześć z włóknami 30/0.55 i sześć z włóknami 50/0.80. Pozostałe dwie belki wykonano z betonu zwykłego. Wyniki badań eksperymentalnych zostały porównane z obliczeniami przeprowadzonymi na podstawie Eurocode 2 i metody zaproponowanej przez Henager i Doherty.

Słowa kluczowe:
piasek odpadowy, drobne kruszywo, kompozyt, włókna stalowe

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Phosphorus and its Fractionation in Bottom Sediments of Selected Lakes of Wielkopolskie Lakeland in Central and Western Poland

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1. Introduction

Over the last century, many Polish lakes have undergone degradation, usually caused by eutrophication. Eutrophication is a natural process but a very slow one in normal conditions. Anthropogenic pressure drastically accelerated this process, particularly in the lakes located in economically developed, highly urbanized or intensively farmed areas. Eutrophication disturbs homeostasis of these ecosystems by rapidly quickening their senescence and, in extreme cases, causing even their disappearance. Also, deterioration of water quality prevents the lakes from being used for e.g. sports and recreation purposes or as backup source of drinking water (Smith & Schindler 2009).

Stopping these unfavorable processes and restoring good condition of lake water is one of the most important challenges for modern societies. This stems not only from our responsibility for the environment we live in but also from the obligation imposed by the EU Water Framework Directive that binded all member states to achieve good condition of lake water until 2015. In justified situations, this deadline might be extended until 2021 or even 2027. The water quality of 66% of all natural and 55% of all artificial lakes in Poland is below "good ecological status", as defined in the Water Framework Directive (Łopata et al. 2019). Liquidation of point and non-point sources of contamination is often insufficient for the lakes to return to good condition. This may only be achieved by reclamation treatments (Grochowska et al. 2017, Siwek et al. 2014).

Phosphorus is one of the basic nutrients. In natural conditions it usually limits primary production, and so it is directly responsible for phytoplankton blooms and thus deterioration of light conditions in the pelagic zone and formation of anoxic zones (Ross et al. 2008). High phosphorus concentrations cause a domination of blue-green algae (Paerl et al. 2011).

Most of the methods for lake restoration consist in limiting phosphorus bioavailability, as this efficiently reduces phytoplankton growth and restores natural conditions of an ecosystem functioning. Phosphorus compounds are relatively poorly soluble and they are usually accumulated in bottom sediments. They contain the largest share of phosphorus in the entire ecosystem. Under favorable conditions, this phosphorus may be re-released into water and incorporated into the biological cycle (Sobczyński 2009a, Søndergaard et al. 2003, Wang et al. 2003). In eutrophic lakes, the bottom sediments are so called internal source of phosphorus and they may supply pelagic zone with considerable amounts of this element, similarly to external sources. This is why limiting or even stopping external phosphorus supply is usually insufficient to improve the condition of a lake (Søndergaard et al. 2003). Therefore, the plans for a lake remediation should account not only for total load of phosphorus accumulated in the surface layer of bottom sediments that exchange components with surrounding water but also for the potential of phosphorus re-release into the pelagic zone depending on its physical and chemical conditions (Kleeberg et al. 2013, Sobczyński 2009b) and the bioavailability (Kostecki 2017a,b). One of the most important solution is a labor and time-consuming fractionation of phosphorus in sediment samples, e.g. according to the method proposed by Psenner (Psenner et al. 1988). This is the only way of identifying the potential risk posed by phosphorus accumulated in the bottom sediments. The aim of the study was to investigate individual fractions of phosphorus differing in their re-release potential in the total pool of phosphorus accumulated in the bottom sediments of selected lakes in Wielkopolskie Lakeland. Four of the eight lakes (Wolsztyńskie, Jelonek, Winary, Góreckie) were subjected of reclamation work, consisting of chemical phosphorus blocking in bottom sediments with iron salts.

2. Materials and methods

The study included bottom sediments of eight eutrophicated lakes in which reclamation treatment was planned or already implemented (Table 1) (Berleć et al. 2013, Bernaciak & Mudrak 2014, Bryl & Wiśniewski 2015, Bryl et. al. 2017, Celewicz-Gołdyn & Klimko 2008, Sobczyński & Joniak 2008, 2009a, 2009b). All the investigated lakes are located within Wielkopolska region, in Wielkopolskie Lakeland that is the southernmost late glacial area (Fig. 1). Compared with other lake districts, Wielkopolskie Lakeland comprises much lower number of lakes. It is a macroregion located in central-western Poland, bordered by important rivers of this region: the Lower Warta Valley and Middle Noteć Valley on the north, the Wisła on the east, the Obra on the west, and the Obra and

Middle Warta on the south (Choiński 2006, Jańczak 1996). Annual precipitation is low and amounts to 450-550 mm.

Table 1. Morphometric data of the investigated lakes (Jańczak 1996)

No.	Lake	Water table area [ha]	Height [m a.s.l.]	Volume [m^3, k]	Mean depth [m]	Max. depth [m]
1.	Wolsztyńskie	124.2	59.8	2522.6	2.0	4.2
2.	Winiary	14.4	104.5	302.4	2.1	4.2
3.	Jelonek	14.4	104.8	172.8	1.2	2.4
4.	Siekiera	12.2	62.0	329.4	2.7	5.6
5.	Pniewskie	59.7	94.1	898.8	1.5	3.3
6.	Umultowskie*	3.0	91.0	59.5	2.0	3.8
7.	Strykowskie	305.3	73.7	13637.4	4.5	7.7
8.	Góreckie	97.4	66.3	6136.2	6.3	15.5

* (Gołdyn et al. 1996)

The investigated reservoirs are glacial lakes, usually shallow and characterized by large variations in water level. Lake Wolsztyńskie (52°07.6'N 16°06.9'E) is a polymictic, non-stratified, flow-through lake supplied mostly by the Dojca river. It is located in the northern part of Wolsztyn. Winiay (52°32.9'N 17°36.8'E) and Jelonek (52°32.1'N 17°35.5'E) are small, shallow, polymictic lakes with limited possibilities of water exchange. They are located in the central part of the city of Gniezno. Jelonek is supplied by the Struga Gnieźnieńska (Berleć et al. 2013). Winiary, the greatest reservoir in Gniezno, is connected via a canal with Lake Wełnickie and a small reservoir Koszyk. Lake Siekiera (53°01.6'N 17°06.5'E) is located in the western part of Szamocin, near the Struga Młyńska, within the river basin of the Warta and the Noteć. It is very popular for recreational activities, particularly fishing. It discharges into the Młynówka Szamocińska. Pniewskie (52°30.8'N 16°14.6'E) is a moraine lake of low mean depth. It is supplied by waters from Lubosz Wielki Lake, and its waters are discharged into the Mogilnica. The lake contains large amount of organic deposits distributed all over its area. It is located in the western part of the city of Pniewy. Lake Umultowskie (52°28.3'N 16°56.2'E) is a small (ca. 0.3 ha) postglacial, moraine reservoir located in the north of Poznań. Its maximum depth is ca. 4.0 m. It is a flow-through lake with some eutrophic features. It is supplied by and discharges into the Umultowski Stream. Strykowskie (52°15.9'N 16°36.5'E), the largest of the investigated lakes (305 ha), is a relatively shallow, polymictic, ribbon lake (maximum depth 7.7 m, 4.5 m on average). It is supplied by a few small watercourses and drainage ditches (Sobczyński & Joniak 2009a). The lake is located west of the city of Stęszew. Góreckie (52°15.9'N 16°47.9'E) is an example of a non-flow through, dimictic, ribbon lake. It is characterized by considerable depth and is located in Wielkopolski National Park (Sobczyński & Joniak 2008, 2009b).

Of all the studies lakes, only Wolsztyńskie, Winiary and Jelonek were subjected of reclamation work by means of the innovative Prote-fos method involving chemical inactivation (blocking) of phosphorus directly in bottom sediments with iron salts (PIX preparation). The innovative approach of this metod is based on the use of two-module veessel named Proteus, with surface and underwater unit, which is responsible for triggering and controlling all process of chemical reclamation work (Wiśniewski et al. 2010). Prote-fos metod is a modified Riplox method (Ripl 1976). Works were performed on the entire surface of the reclaimed lakes. Góreckie Lake was recultivate in 2010 with use of mobile pulverizing aeration technology with precise phosphorus inactivation by iron salts (Rybak et al. 2015, Sobczyński et al. 2012).

Physical and chemical analyses of bottom sediments from Lake Wolsztyńskie were conducted in the years 2012-2014. Bottom sediments samples were collected on 12 dates from four monitoring points. In the years 2012-2013, the lake was reclaimed. Control monitoring was performed in 2014. The fractions of phosphorus of bottom sediments from lakes Winiary and Jelonek was investigated in 2011, after the reclamation works that were conducted in the years 2009-2010. The analysis included data from one monitoring point per lake. Studies in Siekiera were carried out in the years 2014-2015 (three sampling dates) for two monitoring points. The data for Lake Pniewskie were obtained in May 2011 and the sediments were collected from four monitoring points. Samples of bottom sediment from the remaining lakes were collected at once (Góreckie in 2008, before reclamation works, Strykowskie in 2008, Umultowskie in 2015) from several points (Góreckie: 9 points, Strykowskie: 1 point, Umultowskie: 6 points).

The samples of bottom sediments were collected from profundal zone with a tube probe from the surface layer of 10 cm thickness, i.e. the layer that exchanges matter with the surrounding water. The collected sediments were placed in sealed, plastic containers to their full capacity to minimize its contact with atmospheric air. The samples were kept in a refrigerator at 4°C until the analysis. The samples of bottom sediments were collected in various amounts from the studied lakes. If the number of samples was larger, they constituted an element of a detailed research for the purpose of ongoing reclamation works.

After opening the containers, the sediments were thoroughly homogenized. Moist material was used to prepare two analytical samples of 4 g each. First of them was dried at 105°C to the constant mass. After drying hydration was calculated (Bolałek 2010). Organic matter content was determined as ignition losses at 550°C.

Residue after ignition was digested with diluted hydrochloric acid. The extract was used to determine total phosphorus content using a molybdate method with ascorbic acid as a reducing agent (Bolałek 2010, Hermanowicz et al. 1999).

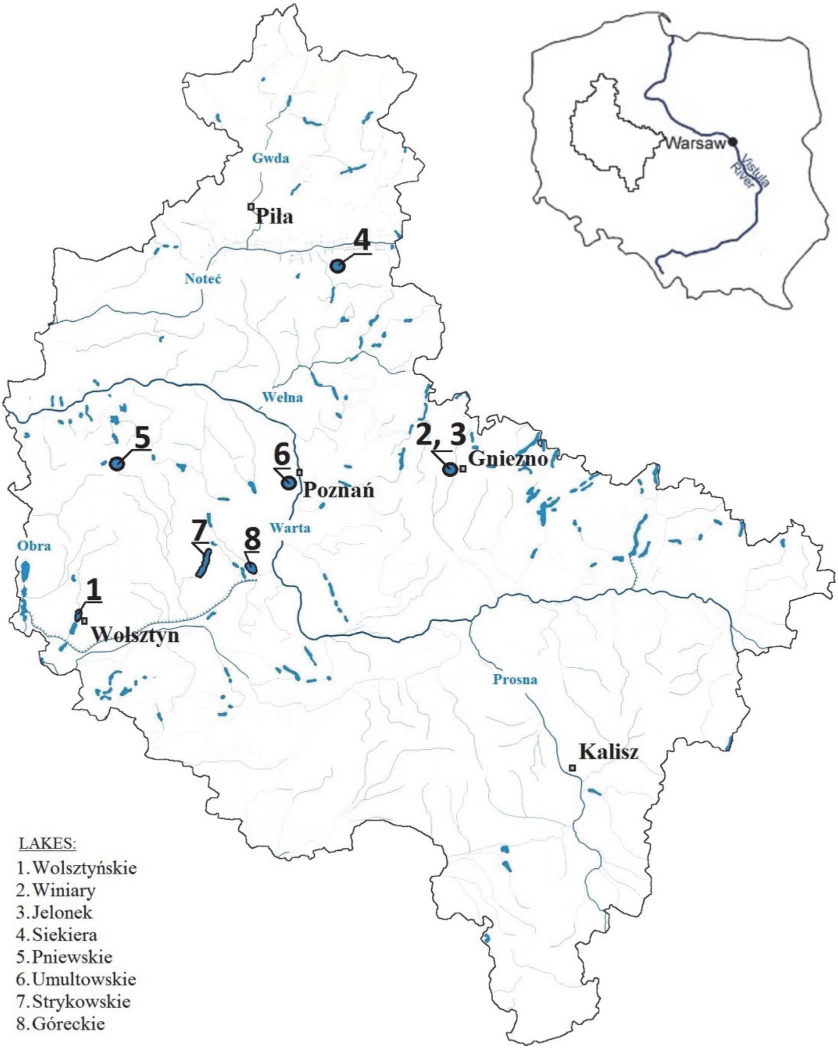

Fig. 1. Location of the investigated lakes on the map of Wielkopolska Province

Second sample of wet sediments was placed in 50 ml polyethylene screw-top tubes for phosphorus fractionation by means of sequential extraction as described by Psenner (Psenner et al. 1988). Five phosphorus fractions differing in their potential to be released into water were distinguished: fraction I (NH_4Cl-P)

– mobile, exchangeable phosphorus – extracted for 2 h with aqueous solution of NH_4Cl; fraction II (BD-P) – iron-bound phosphorus – extracted for 2 h with the solutions of 0.11 M $Na_2S_2O_4$ and 0.11 M $NaHCO_3$ mixed in 1:1 ratio; fraction III (NaOH-P) – phosphorus bound to organic matter and aluminium – extracted for 18 h with 1 M NaOH; fraction IV (HCl-P) – calcium-bound phosphorus – extracted for 18 h with 0.5 M HCl; fraction V (res-P) – residual phosphorus – the remains of the first four fractions were calcinated at 500°C, cooled and then digested with diluted hydrochloric acid.

Extraction was performed at room temperature on a rotary shaker. The samples were centrifuged after each stage and the extract was removed. The remaining sediment was treated with another extraction solvent. Phosphorus contained in the extracts was determined using molybdate method. The extracts that were colorful, were evaporated to dryness, calcinated at 550°C and again digested in diluted HCl.

For determination of calcium, iron and aluminium the samples were digested or wet mineralized with aqua regia (Sobczyński et al. 1996) and then the metal content was recorded with atomic absorption spectrometry (AAS). The results were statistically analyzed in the program Statistica 6 PL.

3. Results

Phosphorus in bottom sediments is bound mainly to organic matter and such metals as iron, aluminium and calcium, which is why their higher content is desired from the ecological perspective (Lampert & Sommer 2001). Total content of phosphorus in the bottom sediments of the investigated lakes was similar (Table 3) and analogous to that determined in bottom sediments of other eutrophic lakes of Wielkopolskie Lakeland: 0,86 – 1,82 g P kg^{-1} d.w. (Sobczyński et al. 1996) and 0,13 – 3,43 g P kg^{-1} d.w. (Karwacka et al. 2015) and also other lakes of Poland (Bojakowska 2016). Phosphorus content was the highest in Siekiera and the lowest in Lake Umultowskie (Table 3). The content of iron, aluminium, calcium and organic matter were much more variable (Table 2).

The presence of these macroelements in the lakes depends on the formation and use of the catchment, hydrogeological conditions and anthropopressure. Their migration occurs as a result of complex physico-chemical processes due to water and wind erosion. The highest mean content of Al in bottom sediments of the studied lakes was observed in Winiary Lake (20,6 g Al kg^{-1} d.w.) and the lowest in Umultowskie (2,03 g Al kg^{-1} d.w.) and Wolsztyńskie (2,44 g Al kg^{-1} d.w.) lakes. The highest mean content of Ca was in Wolsztyńskie Lake (243 g Ca kg^{-1} d.w.), but the lowest in Strykowskie Lake (19.8 g Ca kg^{-1} d.w.). The lowest mean content of Fe was detected in Umultowskie Lake (1,86 g Fe kg^{-1} d.w.) and the highest in

Wolsztyńskie (10,3 g Fe kg^{-1} d.w.), Winiary (32,9 g Fe kg^{-1} d.w.), and Jelonek (17,0 g Fe kg^{-1} d.w.) lakes (Table 2).

The organic matter content of the studied bottom sediments ranged from 13% d.w. (Lake Wolsztyńskie) to 70,4% d.w. (Lake Umultowskie). The largest amount of organic matter was found in the sediments from Umultowskie Lake, on average: 63,8% d.w. and Pniewskie Lake, on average: 40,7%. The lowest amount in the sediments of the lakes Winiary and Jelonek, on average: 17,8-20,4% d.w. (Table 2).

Almost in all analized cases (except Jelonek Lake) the fraction bound with organic matter and aluminium (NaOH-P) had the largest participation in bottom sediments, on average: 35,1-45,3% TP. The largest participation of mobile fractons (NH4Cl-P and BD-P) was observed on the lakes: Wolszyńskie (total 25%), Siekiera (total 27,7%) Strykowskie (total 18%) (Table 3).

Average annual phosphorus content decreased from year to year: from 1.077 g P kg^{-1} d.w. to 1,000 g P kg^{-1} d.w. In the case of stable, permanently bound forms, i.e. phosphorus bound to calcium and phosphorus in residual form, the average annual phosphorus values were at the level of 0.11-0.12 (res-P) and 0.22 (HCl-P) g P kg^{-1} d.w. The share of the fraction related to organic matter and aluminum (NaOH-P) was the largest but also decreased each year: from 0.54 to 0.39 g P kg^{-1} d.w. In 2014, a slight increase in the share of fraction NH_4Cl-P was observed (Fig. 2).

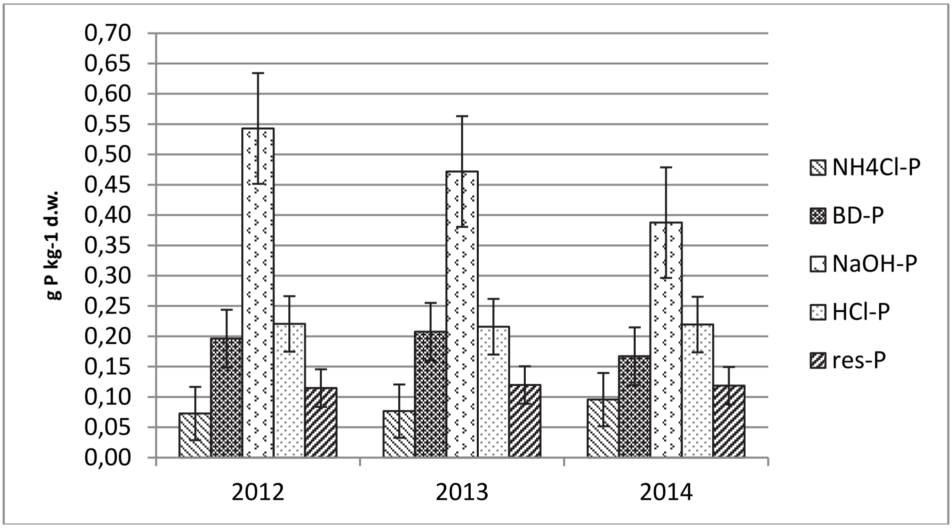

Fig. 2. Average annual phosphorus content in each fraction on the example of Wolsztyńskie Lake

Analysis of vertical changes of phosphorus fractions concentrations in the bottom sediments of Wolsztyńskie Lake (Fig. 3) showed that only in the case of the samples taken at monitoirng point no. 3 (the deepest place in the lake) the sum of the bioavailable phosphate fractions (NH4Cl-P and BD-P) sometimes exceeded 30% of the overall content. However, the mean for all other monitoirng points was usually around 25% (Tab. 3). Despite the fact that biologically less accessible fractions (HCl-P, res-P) constituted a much larger share in the total phosphorus pool, intense phytoplankton blooms are observed on this lake. This situation proves that there is big the problem of the external supply of nutrients to the lake from the catchment.

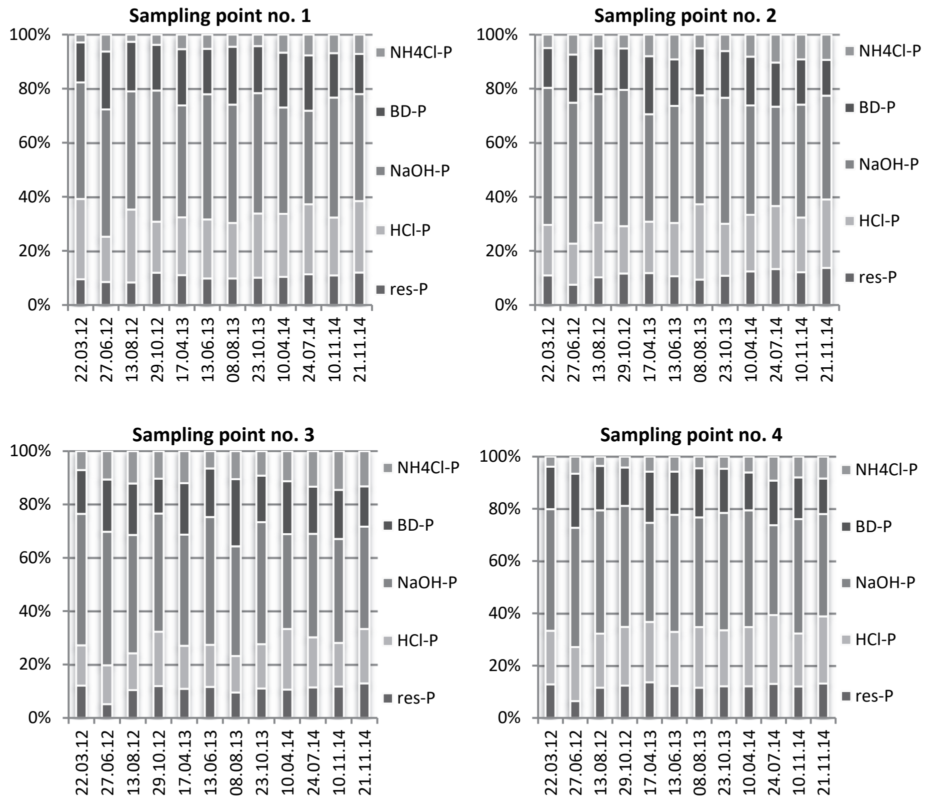

Fig. 3. Vertical changes of phosphorus fractions concentrations in bottom sediments of Wolsztyńskie Lake

Table 2. The content of iron, aluminium, calcium and organic matter in the dry weight of bottom sediments samples of the studied lakes

Lake (name)		Ignition losses (organic matter)	Iron	Aluminium	Calcium
		% d.w.	g Fe kg^{-1} d.w.	g Al kg^{-1} d.w.	g Ca kg^{-1} d.w.
Wolsztyńskie (n=48)	a	21.1	10.3 ±0.52	2.44 ±0.12	243 ±12.2
	b	21.4	9.68 ±0.48	2.41 ±0.12	229 ±11.5
	c	13.0-28.5	5.19±0.26-18.0±0.90	0.98±0.05-4.35±0.22	188±9.40-417±20.9
Winiary * (n=5)	a	17.8	32.9 ±1.65	20.6 ±1.03	127 ±6.35
	b		31.7 ±1.59	7.58 ±0.38	134 ±6.70
	c		30.9±1.55-35.8±1.79	6.94±0.35-72.0±3.60	95.0±4.75-149±7.45
Jelonek * (n=5)	a	20.4	17.0 ±0.85	8.91 ±0.45	145 ±7.25
	b		16.5 ±0.83	6.71 ±0.34	138 ±6.90
	c		11.8±0.59-22.5±1.13	5.28±0.26-18.5±0.93	136±6.8-169±8.45
Siekiera (n=6)	a	34.2	7.43 ±0.37	3.25 ±0.16	145 ±7.25
	b	35.9	7.28 ±0.36	3.12 ±0.16	141 ±7.05
	c	27.0-38.6	1.05±0.05-12.6±0.63	1.91±0.10-4.86±0.24	78.9±3.95-206±10.3
Pniewskie (n=4)	a	40.7	6.61 ±0.33	no data	91.8 ±4.59
	b	41.4	6.74 ±0.34	no data	92.2 ±4.61
	c	34.5-45.5	4.95±0.25-8.03±0.40	no data	87.1±4.35-95.8±4.79
Umultowskie (n=6)	a	63.8	1.86 ±0.09	2.03 ±0.10	97.7 ±4.90
	b	62.8	1.88 ±0.06	2.06 ±0.10	108 ±5.40
	c	58.4-70.4	0.78±0.04-3.41±0.17	1.53±0.08-2.50±0.13	5.98±0.30-204±10.2
Strykowskie* (n=1)	a	25.0	5.92 ±0.30	3.05 ±0.15	19.8 ±0.99
	b				
	c				
Góreckie (n=9)	a	27.0	7.27 ±0.36	4.59 ±0.23	101 ±5.05
	b	27.1	6.53 ±0.33	4.37 ±0.22	112 ±5.60
	c	26.2-28.1	3.56±0.18-11.5±0.58	3.02±0.15-6.88±0.34	71.0±3.55-128±6.40

a – mean, b – median, c – range,
* – Ignition losses was performed only for one sample of the bottom sediments

Table 3. Phosphorus content in samples of bottom sediments of studied lakes and its distribution between each individual fractions

Lake (name)		Total P content	NH_4Cl-P	BD-P	NaOH-P	HCl-P	res-P
		g P kg^{-1} d.w.	Share of specific fractions [% TP]				
Wolsztyńskie (n=48)	a	1.08 ±0.04	7.4	17.6	43.3	20.7	11.0
	b	1.04 ±0.04	6.8	17.3	43.8	20.6	11.5
	c	0.66±0.03-1.56±0.06	2.7-14.5	13.1-25.2	34.4-52.1	13.7-29.7	5.1-13.7
Winiary * (n=5)	a	1.01 ±0.04	0.3	7.0	45.9	30.1	16.7
	b						
	c						
Jelonek * (n=5)	a	0.98 ±0,04	4.8	8.6	25.4	44.8	16.4
	b						
	c						
Siekiera (n=6)	a	1.36 ±0.05	15.1	12.6	35.1	20.8	16.4
	b	1.32 ±0.05	15.7	12.5	34.7	19.0	15.6
	c	0.99±0.04-1.76±0.07	6.9-19.7	6.7-17.8	32.7-38.6	17.0-32.1	12.5-20.8
Pniewskie (n=4)	a	1.03 ±0.04	7.4	9.9	39.0	31.3	12.4
	b	0.98 ±0.04	7.8	9.9	40.2	29.5	12.5
	c	0.89±0.04-1.27±0.05	5.9-8.2	8.6-11.2	30.9-44.7	25.1-40.9	11.4-13.4
Umultowskie (n=6)	a	0.74 ±0.03	10.2	6.2	44.1	26.3	13.2
	b	0.73 ±0.03	9.7	6.3	45.0	24.5	12.9
	c	0.61±0.02-0.86±0.03	6.6-14.7	4.8-7.4	38.7-47.3	20.0-35.8	12.4-14.5
Strykowskie (n=1)	a	1.23 ±0.05	9.5	8.5	38.2	29.8	14.0
	b						
	c						
Góreckie (n=9)	a	1.14 ±0.05	7.2	11.1	45.3	23.3	13.1
	b	1.15 ±0.05	7.1	11.1	46.8	22.8	13.6
	c	1.01±0.04-1.27±0.05	4.1-12.1	6.4-18.0	38.4-50.6	17.6-29.4	11.9-14.5

a – mean, b – median, c – range,
* – total P content and P-fractions were performed only for one sample of the bottom sediments

4. Discussion

Only three reservoirs (Wolsztyńskie, Jelonek and Winiary) were subjected to reclamation treatment with Prote-fos method that involves binding phosphates in bottom sediments by means of iron ions. This procedure resulted in ecologically favorable increase in iron concentration in the surface layer of the sediments. The reclamation effects were particularly noticeable for Lake Wolsztyńskie, where the share of iron-bound phosphorus (BD-P) was high as compared with the other lakes and amounted to 17.6% TP. Despite high iron content in Winiary and Jelonek lakes, the share of BD-P was not substantial, even in comparison with the lakes in which phosphorus inactivation was not implemented. This may be explained by low content of NH_4Cl-P, i.e. the mobile phosphorus bound to and inactivated by iron ions in the sediments. Supplying the sediments with iron ions caused sequestration of the mobile phosphorus and its conversion into a less available fraction (Katsev & Dittrich 2013, Kleeberg et al. 2013). Iron surplus introduced during reclamation should protect the pelagic zone against phosphorus released from the other fractions, particularly NaOH-P in which it is bound to organic matter and aluminium and may be released into water in the course of organic matter mineralization. The surface layer of the sediments, artificially enriched with iron, should then bound and immobilize the released phosphorus ions. This process is enhanced by aerobic conditions, as iron(III) forms a poorly soluble salt with phosphate ion (Grochowska & Gawrońska 2004, Sobczyński 2009b). This was confirmed in the lakes in which anoxic conditions (reducing conditions) occur in the deepest parts, where phosphorus release from bottom sediments to the pelagic zone was greater than in shallow zones where oxygen reaches the bottom and oxidizing conditions prevail (Kowalczewska-Madura et al. 2010a,b, Łukawska-Matuszewska & Burska 2011). All this caused that although the relationship between the content of iron in the bottom sediment and the percentage share of the BD-P in the total pool was observed, this relationship was not too strong, it was significantly weaker than the one described in the literature (Siwek 2010). The total share of the first two fractions, i.e. exchangeable phosphorus and iron-bound phosphorus that are most readily released into the pelagic zones was almost 28% TP for Lake Siekiera and 25% TP for Lake Wolsztyńskie. In other lakes, this share was much lower, even by several percent, which was also enough for phytoplankton bloom to occur in these lakes (Bartoszek 2007).

The sediments from Lake Umultowskie were typical organic sediments, as their mean share of organic matter was nearly 64% d.w. High content of organic matter was also detected in the sediments form Pniewskie and Siekiera lakes. The other lakes contained lower amounts of organic matter (Table 2). This was not clearly reflected in percentage share of NaOH-P, i.e. phosphorus bound to organic matter and aluminium. It should be mentioned that aluminium content in the sediments from both Umultowskie and Siekiera lakes was relatively low and this may explain why the share of NaOH-P was not significantly different from its content in the other lakes. The bottom sediments from both these lakes were rich in phosphorus from NH_4Cl-P that is mobile phosphorus. This was probably due to the fact that organic sediments contain considerably greater amounts of interstitial water than mineral sediments and phosphorus from NH_4Cl-P is the most abundant in this water (Czerwieniec 2003, Gnauck et al. 2002, Kentzner 2001, Wiśniewski 1995). Aluminium content in Lake Pniewskie was not determined for technical reasons. High amounts of NaOH-P were reported for Wolsztyńskie, Jelonek and Góreckie lakes, which was not justified by high contents of organic matter or aluminium (except for Lake Winiary where the sediments contained significant amount of aluminium). Therefore, no strong relationship was observed between the content of organic matter and aluminium in the bottom sediments and the share of NaOH-P bound with organic matter and aluminium in total phosphorus content as well as the absolute content of this phosphorus fraction. Phosphorus bound to organic matter is transformed into mineral form during organic matter mineralization. Studies on bottom sediment cores featuring layers differing in their accumulation time (age) demonstrated that phosphates released during organic matter mineralization were to a high degree bound to calcium present in the sediments, thus increasing the share of HCl-P (Sobczyński & Joniak 2009a).

There was also no relationship between calcium content in the sediments and the share of HCl-P (Ca-bound phosphorus) in the total pool of phosphorus as well as the absolute content of this fraction. This was probably due to substantial surplus of calcium in relation to phosphorus that could be bound with it, which was why further increase in calcium content would not increase the share of HCl-P in total phosphorus pool.

Lack of clear, described in the literature (Siwek 2010), relationship between the sediment content of iron, calcium and aluminium and distribution of sediment phosphorus between BD-P, NaOH-P and HCl-P, i.e. the fractions in which phosphorus is bound to these metals is probably due to the fact that there are various mechanisms of metal precipitation in a lake ecosystem apart from binding to phosphorus (Sobczyński et al. 2004, Zerbe et al. 1995).

Residual-P that contains phosphorus practically non bioavailable in normal environmental conditions was relatively small. This is not favorable from ecological perspective, as phosphorus bound in this fraction is considered to be completely withdrawn from the biological cycle.

In seven out of eight investigated lakes, the most abundant fraction of phosphorus was NaOH-P bound with aluminium and organic matter. The only exception was Jelonek lake, where the bottom sediment contained mostly phosphorus from HCl-P bound with calcium. The share of HCl-P was also high in the other lakes, and together with NaOH-P they accounted for 55.9% TP of phosphorus in Siekiera and 76.0% TP in Winiary. The sum of these two fractions in the bottom sediments from the investigated lakes was considerably higher than the sum of NH_4Cl-P and BD-P comprising easily bioavailable phosphorus. A significant but smaller proportion of phosphorus was contained in the residual fraction V that did not participate in the biological cycle of the lake ecosystems. Its share ranged from 11% TP in Lake Wolsztyńskie to 16.7% TP in Winiary. Nevertheless, all the eight lakes are classified as eutrophic or nearly eutrophic and they experience phytoplankton blooms.

In reclaimed lakes, in the composition of bottom sediments, some differences can be observed in relation to non-reclaimed lakes, resulting for example from of the reclamation methods used. The treated lakes are usually characterized by a lower share of mobile fractions, as in the case of the Gniezno lakes, which show the effect of using bentonite clay enriched with lanthanum (a large percentage of bio-available fractions). In the case of Wolsztyn Lake, the situation is different. Of all the studied lakes, despite the remediation carried out in 2005-2006 by means of introducing aluminum salt into the water column (Gawrońska et al. 2007), the bottom sediments of the Wolsztyńskie Lake were characterized by the lowest concentration of aluminum and a large amount of iron, as a result of feeding iron salts directly to the bottom sediments in 2012-2013. As a consequence, phosphorus has been blocked in mobile forms, which gets into the water column in specific anaerobic conditions. The share of these fractions was higher compared to other lakes. The average annual phosphorus content for stable, permanently bound forms, i.e. phosphorus associated with calcium (HCl-P) and phosphorus in the residual form (res-P) practically does not change. Only the content of mobile forms, that are sensitive to changes in various physico-chemical conditions prevailing in water, are change. In the case of Góreckie Lake, the reclamation was carried out at a later date than the collection of sediments.

5. Conclusions

Phosphorus present in bottom sediments of eight investigated lakes located within Wielkopolskie Lakeland was mostly bound within not readily bioavailable fractions, i.e. those involving organic matter, aluminium and calcium, in total mean 55,9 – 76,0%. The share of residual fraction comprising virtually non bioavailable phosphorus was low and ranged from 5,1 to 20,8% of the phosphorus content in a given sample. Total share of these three fractions was higher than that of two mobile fractions readily released into the pelagic zone but despite this seemingly favorable ratio the lakes were eutrophic and required reclamation treatments. Reclamation work involving the iron salt dosage to bottom sediments of lakes (Wolsztyńskie, Jelonek, Winiary) causes a reduction of the mobile fraction NH_4Cl-P in the total pool.

Reclamation of eutrophic lakes should account for the bottom sediments as an internal source of phosphorus. To identify the risk of phosphorus release into water it is not enough to simply determine its total sediment content but it is also necessary to figure out its distribution among the fractions differing in their potential of phosphorus release and incorporating it into the biological cycle. Even though these fractions are defined as phosphorus combinations with such metals as iron, aluminium or calcium or with organic matter, the knowledge on the content of these components in the sediments is not enough to confirm what amount of total phosphorus is bound to them and how the conditions prevailing in the pelagic zone may affect phosphorus release.

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Abstract

The role of phosphorus contained in bottom sediments of water reservoirs is crucial in the whole eutrophication process. It is an element responsible for the proper functioning of aquatic ecosystems, and its excess leads to deterioration of water quality. The release of phosphorus from bottom sediments directly into the water depends on many factors. This process is particularly intensified at the moment of anaerobic conditions occurring in the bottom layer, or the phenomenon of resuspension of sediments due to external factors, such as intense waving. The persistence of phosphorus deposition in sediments also depends on the nature of chemical connections and changing oxidation-reduction conditions, temperature and pH.

Bottom sediments from eight selected lakes of Wielkopolskie Lakeland were investigated for their total phosphorus content and the possibility of its re-release into water. The subject of the study were the following lakes: Wolsztyńskie, Winiary, Jelonek, Siekiera, Pniewskie, Umultowskie, Góreckie, Strykowskie. The investigated water reservoirs are glacial lakes, usually shallow and characterized by large variations in water level.

The samples of bottom sediments were collected from profundal zone with a tube probe from the surface layer of 10 cm thickness, i.e. the layer that exchanges matter with the surrounding water. The collected sediments were placed in sealed, plastic containers to their full capacity. Before proceeding to carry out detailed laboratory analyzes, samples were prepared accordingly. First, the bottom sediments were thoroughly homogenized. Then, they were dried and subjected to further testing. The obtained results were statistically analyzed in the program Statistica 6 PL.

Phosphorus was fractionated by means of a sequential extraction described by Psenner. The sediments were also analyzed for the content of phosphorus binding components such as organic matter, iron, aluminium and calcium. Phosphorus was found to be bound mostly to organic matter, aluminium and calcium – the fractions from which it was difficult to release into water. The share of exchangeable and most mobile and bioavailable iron-bound fraction of phosphorus was the lowest but it was still high enough to cause phytoplankton blooms. No clear relationships between the content of individual phosphorus-binding components and the share of phosphorus fractions related to them in total phosphorus pool were identified. Total content of phosphorus in the sediments of the investigated lakes was analogue and similar to that determined in bottom sediments of other eutrophic lakes of Wielkopolskie Lakeland. The content of aluminium, calcium, iron and organic matter were much more variable.

Keywords:
lake, bottom sediments, phosphorus, fractionation of phosphorus, organic matter, iron, aluminium, calcium

Fosfor i jego frakcje w osadach dennych wybranych jezior Pojezierza Wielkopolskiego w środkowej i zachodniej Polsce

Streszczenie

Rola fosforu zawartego w osadach dennych zbiorników wodnych jest kluczowa w całym procesie ich eutrofizacji. Jest pierwiastkiem odpowiedzialnym za prawidłowe funkcjonowanie ekosystemów wodnych, a jego nadmiar prowadzi do pogorszenia się jakości wody. Uwalnianie się fosforu z osadów dennych bezpośrednio do toni wodnej zależy od wielu faktorów. Szczególnie proces ten intensyfikuje się w momencie pojawienia się w warstwie naddennej warunków beztlenowych, czy też zjawiska resuspensji osadów na skutek oddziaływania czynników zewnętrznych, np. intensywnego falowania. Trwałość deopozycji fosforu w osadach zależy również od charakteru połączeń chemicznych oraz zmiennych warunków oksydacyjno-redukcyjnych, tempe-ratury, a także pH.

Badano osady denne z ośmiu wybranych jezior Pojezierza Wielkopolsko-Kujawskiego pod kątem całkowitej zawartości fosforu i potencjalnej możliwości jego ponownego uwalniania do toni. Przedmiotem badań były następujące jeziora: Wolsztyńskie, Winiary, Jelonek, Siekiera, Pniewskie, Umultowskie, Strykowskie, Góreckie. Badane zbiorniki wodne to jeziora polodowcowe, zwykle płytkie, charakteryzujące się dużymi wahaniami poziomu wody.

Próbki osadów dennych pobierano za pomocą sondy rurowej z powierzchniowej warstwy osadu o miąższości 10 cm, czyli warstwy, która uczestniczy w wymianie materii z tonią. Pobrany osad umieszczano w szczelnych, plastikowych pojemnikach napełniając je do pełna. Przed przystąpieniem do przeprowadzania szczegółowych analiz laboratoryjnych próbki zostały odpowiednio przygotowane. W pierwszej kolejności osady denne dokładnie zhomogenizowano. Następnie wysuszono oraz przeprowadzono kolejne analizy. Uzyskane wyniki badań poddano analizie statystycznej w programie Statistica 6 PL.

Frakcjonowanie fosforu realizowano na drodze ekstrakcji sekwencyjnej wg schematu zaproponowanego przez Psennera. Dodatkowo w osadach oznaczano materię organiczną oraz żelazo, glin i wapń, czyli składniki osadu wiążące fosfor. Stwierdzono, że w ogólnej puli fosforu poszczególnych osadów największy udział miały frakcje związane z materią organiczną i glinem oraz z wapniem, czyli stosunkowo trudniej uwalniane do toni. Udział frakcji wymiennej i związanej z żelazem, czyli frakcji najbardziej mobilnych, biodostępnych, był mniejszy co jednak było wystarczające, aby w wodach tych jezior występowały zakwity fitoplanktonu. Nie zaobserwowano natomiast wyraźnych zależności pomiędzy zawartością w osadach poszczególnych składników wiążących fosforany, a udziałem frakcji fosforu z nimi związanych w ogólnej jego puli. Łączna zawartość fosforu w osadach badanych jezior była analogiczna i podobna do tej stwierdzonej w osadach dennych innych eutroficznych jezior Pojezierza Wielkopolskiego. Zawartość glinu, wapnia, żelaza i materii organicznej była znacznie bardziej zmienna.

Słowa kluczowe:
jezioro, osady denne, fosfor, frakcjonowanie fosforu, materia organiczna, żelazo, glin, wapń

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Occurrence of Oribatid Mites During the Revitalization of Bare Root Forest Nursery

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1. Introduction

Every year in Polish forestry there are huge requirements for fresh seedlings of forest trees because about 90% of forests are artificially regenerated (Walczyk and Tylek 2012). In Poland in 92% production of seedlings is conducted in field conditions (bare root forest nurseries). In these forest nurseries that produce bare root seedlings may sometimes experience disturbances in their soil biological balance. A direct effect of these disturbances is deteriorated quality of the seedlings. In-ground forest nurseries are usually established on forest soils where the stand was cut down. However, using agricultural models for the management of a forest nursery and production of tree seedlings causes gradual degradation of the nurseries. Major cause of this degradation is markedly reduced amount of organic matter resulting in limited microbiological activity and insufficient presence of ectomycorrhizal fungi (ECM) (Kropp and Langlois 1990; Aučina et al. 2014). To curb these processes and to restore biological balance of the forest soil, various enrichment procedures are introduced, involving fertilization with organic composts, peat, tree bark, or green fertilization (forecrop). Mulching the mineral surface of the soil with edaphon-rich raw humus is a technique particularly useful from the ecological point of view, and it directly improves soil environment revitalization. This treatment restores natural layered structure of forest soils (Leski et al. 2009; Aučina et al. 2014). Moreover, spreading forest litter allows for reintroduction of multiple microorganisms and small animals, such as oribatid mites (Oribatida). Oribatid mites are one of the most abundant and species-rich group of arthropods in forest soils. A single site may often harbor even up to a few hundred thousand individuals per square meter and from 20 to 50 species per research site (Norton1990; Behan-Pelletier 1999). Oribatid mites play many important environmental functions, they improve pedogenic processes and propagation of bacteria and fungi, and they indirectly affect the formation of endo- and ectomycorrhizas (Klironomos and Kendrick 1996; Schneider et al. 2005; Remén et al. 2010). They are also good bioindicators of soil biological activity (Behan-Pelletier 1999, 2003; Gulvik 2007). Our earlier studies showed that intensive cultivation practices in in-ground forest nurseries drastically reduced the abundance and species diversity of oribatid mites, down to only 3-4 species and 670-1,050 individuals per m^2 (Klimek et al. 2013a). The aim of this study was to analyze the prevalence of Oribatida during a 3-year cycle of revitalization conducted in in-ground nursery of Białe Błota near Bydgoszcz. Revitalization practices implemented in the nurseries of Scots pine (*Pinus sylvestris* L.), beech (*Fagus sylvatica* L.), and small-leaved linden (*Tilia cordata* Mill.) involved fertilization with bark-enriched compost and mulching with raw humus.

2. Material and methods

The study was conducted in the years 2008-2010 in Białe Błota nursery belonging to Bydgoszcz Forest District (53°06'12.3"N 17°55'41.5"E). The soil cover was brunic arenosol formed from alluvial sands. The surface layer had a texture of fine-grained slightly loamy sand and contained 6-7% of clay fraction (<0.002 mm). In terms of organic matter content the surface layer may be classified as mineral and humus one, as it contained from 35.7 to 38.4 $g \cdot kg^{-1}$ of organic carbon. Soil pH in 1M KCl ranged from 6.9 to 7.0.

The experiments were established in the spring of 2008, in the nurseries producing Scots pine, beech and small-leaved linden. Each nursery included 16 experimental plots (4 variants x 4 repetitions) with the area of 2 m^2 each. The experiments included the following variants: C – control, O – organic fertilization, M – mulching with raw humus, OM – organic fertilization and mulching with raw humus.

The organic fertilizer (compost) included sanitized sewage sludge (60%) and pine bark (40%). It was applied in the spring of 2008 at a dose of 100 t ha^{-1} and mixed with surface soil layer (to the depth of 10 cm) before sowing the seeds. Mulching with raw humus was carried out on 15 September 2008, and the dose was 100 m^3 ha^{-1}. The control variant was an in-ground nursery attended to as per recommended standard practices.

The experimental plots were irrigated by periodically operating stationary sprinkling machine. Irrigation doses and times were determined according to the recommendations for open area forest nurseries. Plants grown in the areas around Bydgoszcz, as well as in entire central Poland, need intense irrigation (Żarski 2011). In 2008, total precipitation rate in the vegetative period was 281.5 mm (Table 1). In 2009, it was two times lower, and in 2010 no irrigation was necessary as the natural precipitation was high enough. In 2008, total amount of precipitation was lower than normal, and especially low rainfall was recorded in May, June, and September. In 2009, the precipitation was lower than normal in April, August and September. In a generally wet vegetative period of 2010, low rainfall was recorded in June and October (30% and 78% of normal range, respectively). Soil samples for acarological studies were collected six times in the years 2008-2010, in the last ten days of May and October. In total, 720 soil samples were collected, i.e. 10 samples (two or three from each plot) per each experimental variant on each collection date. The soil was sampled from the area of 17 cm^2 and up to 3 cm deep. The mites were extracted over 7 days using Tullgren funnels, fixed in 70% ethanol, prepared and classified into species or genera. A total of 3,586 juvenile and adult oribatid mites were classified. Their mean density (N) was given per 1 m^2 of soil. Oribatida communities in each variant were described using a domination ratio D (%), total number of species (S), average number of species per sample (s) for a series of 60 samples, and Shannon's diversity index (H') (Magurran 1988). Prior to statistical analysis, the numerical data were subjected to a logarithmic transformation - ln (x+1) (Berthet and Gerard 1965).

Table 1. Rainfall (P) and irrigation (I) in the Białe Błota forest nursery during the vegetation period of the years 2008-2010 (mm)

Year		Months							Total IV-IX
		IV	V	VI	VII	VIII	IX	X	
2008	P	38.7	11.5	15.5	58.7	95.5	20.2	80.0	320.1
	I	57.4	63.7	74.9	53.9	24.8	6.8	0	281.5
2009	P	0.4	85.3	57.4	118	1.6	34.4	66.2	379.3
	I	16.6	30.3	35.6	32.9	19.3	6.3	0	141.0
2010	P	33.8	92.6	18.1	107	151	74.7	2.3	479.6
	I	0	0	0	0	0	0	0	0
Norm (long-term average)		29.8	60.6	47.3	83.1	62.8	44.1	40.2	367.9

The statistical analysis was performed using Statistica 10,0, and a compliance of the measurable parameters with the normal distribution was assessed using Kolmogorov-Smirnov test. As the normal distribution was not confirmed, a non-parametric analysis of variance (Kruskal-Wallis) was performed. For statistically significant differences ($p < 0.05$) an analysis for each pair was carried out (Mann-Whitney U test) to identify significantly different means.

3. Results

On the first sample collection date in mid-May 2008, the density of oribatid mites in the nurseries producing pine, beech and linden was extremely low for all experimental plots and did not exceed 200 individuals m^{-2} (Fig. 1). Mean density of the mites assessed over the 3-year study cycle on the control plots managed according to the standard nursery practices was low and amounted to 110-240 individuals m^{-2} (Table 2). The number of the mites slightly but significantly increased after fertilization with the compost (variant O) on the plots with deciduous seedlings. Mulching was the soil revitalization method that markedly improved the density of Oribatida. The greatest mean density of the mites (8,630 individuals m^{-2}) was observed in linden nursery, on the plots mulched with raw humus and fertilized with the compost (OM).

Shortly after mulching, in autumn 2008, the density of oribatid mites in all nurseries was high and ranged from 4,210 to 19,140 individuals m^{-2} (Fig. 1). In pine nursery, this high density lasted only until the spring of 2009 and then declined. High number of the mites in this nursery (4,270-23,540 individuals m^{-2}) was observed only at the end of the 3-year study cycle. In beech nursery, significant decrease in the density of the mites was recorded in May 2010, but a substantial spike in their numbers was observed as soon as the next season. Particularly high oribatid mite density (17,220 individuals m^{-2}) was noticed in linden nursery (variant M) in October 2009. In 2010, their number in this variant was much lower. Very high initial density of oribatid mites in linden nursery mulched with raw humus and fertilized with the compost (19,140 individuals m^{-2}) rapidly declined in May 2009. However, in October 2009, a huge increase in Oribatida count was found, and at the end of the study cycle it rose again to 12,820 individuals per m^2. In total, 37 Oribatida species were found in the investigated pine, beech, and linden nurseries. Depending on the tree species, the number of Oribatida species on the control plots (C) ranged from 3 to 5 (Table 3). A few more species (5-7) were observed on organically fertilized plots. Significantly more species were recorded on the mulched plots, i.e. 15-23 in M variant and 16-24 in OM variant.

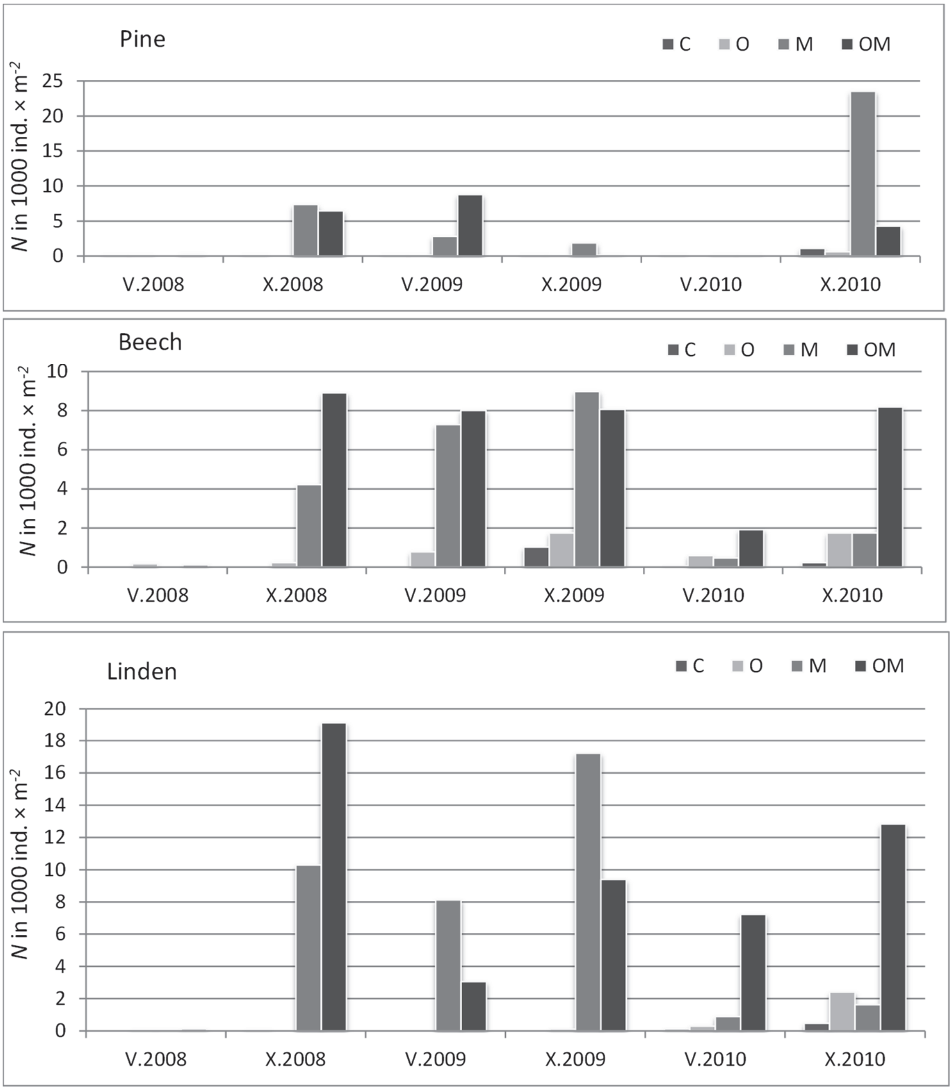

Fig. 1. Density (*N*) of oribatid mites in a three-year period of the study (2008-2010) in the variants of the experiment in the Białe Błota forest nursery

Table 2. The density of oribatid mites (N in 10^3 individuals m^{-2}) in the variants of the experiment for the forest nurseries: pine (P), beech (B) and linden (L) in Białe Błota

Taxon	Species of seed-lings	Experiment variant				Kruskal-Wallis test	
		C	O	M	OM	*H*	*p*
Eremaeus oblongus C.L. Koch, 1836	P	0	0	0.10^{Aa}	0.45^{Ba}	64.53	0.0000
	B	0	0	0.06^{Aa}	0.17^{Ba}		
	L	0	0	0.17^{Aa}	0.26^{Ba}		
Lauroppia neerlandica (Oudemans, 1900)	P	0	0	0	0.25^{a}	38.55	0.0001
	B	0	0	0.01^{Aa}	0.04^{Aa}		
	L	0	0	0.14^{a}	0		
Liochthonius sp.	P	0	0	0.02^{Aa}	0.02^{Aa}	38.53	0.0001
	B	0	0	0.02^{Aa}	0.07^{Aa}		
	L	0	0	0.09^{Aa}	0.29^{Bb}		
Oppiella nova (Oudemans, 1902)	P	0.21^{ACa}	0.05^{Ba}	4.20^{Ca}	0.60^{ABa}	75.08	0.0000
	B	0.05^{ABa}	0.01^{Aa}	0.17^{Ba}	0.49^{Ca}		
	L	0.03^{Aa}	0.05^{Aa}	0.28^{Aa}	0.94^{Ba}		

Table 2. cont.

Taxon	Species of seed-lings	Experiment variant				Kruskal-Wallis test	
		C	O	M	OM	*H*	*p*
Oribatula tibialis (Nicolet, 1855)	P	0.01^{Aa}	0.01^{Aa}	0.11^{Aa}	0.12^{Ba}	84.65	0.0000
	B	0.02^{Aa}	0.03^{Aa}	0.33^{Ba}	0.38^{Cb}		
	L	0.01^{Aa}	0.01^{Aa}	0.24^{Ba}	0.19^{Ba}		
Pergalumna nervosa (Berlese, 1914)	P	0	0	0.02^{Aa}	0.37^{Aa}	24.03	0.0126
	B	0	0	0.01^{Aa}	0.06^{Aa}		
	L	0	0	0.04^{Aa}	0.05^{Aa}		
Scutovertex sculptus (Michael, 1879)	P	0	0	0.03^{Aa}	0.05^{Aa}	45.77	0.0000
	B	0	0	0.30^{Aa}	0.10^{Ba}		
	L	0	0.01	0.04^{Aa}	0.02^{Aa}		
Suctobelba sp.	P	0	0	0.07^{Aa}	0.10^{Aa}	39.50	0.0000
	B	0	0	0.04^{Aa}	0.24^{Ba}		
	L	0	0	0.14^{Aa}	0.28^{Ba}		

Table 2. cont.

Taxon	Species of seed-lings	Experiment variant				Kruskal-Wallis test	
		C	O	M	OM	H	p
Tectocepheus velatus (Michael, 1880)	P	0.02^{Aa}	0.07^{Aa}	1.21^{Ba}	1.15^{Ba}	210.50	0.0000
	B	0.13^{Aa}	0.74^{Ba}	2.61^{Cb}	3.79^{Db}		
	L	0.07^{Aa}	0.40^{Ba}	4.78^{Cc}	6.07^{Dc}		
# Other species of Oribatida	P	0	0.02	0.23	0.86	-	-
	B	0.02	0.08	0.55	0.72		
	L	0	0.02	0.67	0.59		
Oribatida total	P	0.24^{Aa}	0.15^{Aa}	5.95^{Ba}	3.31^{Ca}	225.81	0.0000
	B	0.22^{Aa}	0.86^{Ba}	3.78^{Cb}	5.87^{Db}		
	L	0.11^{Aa}	0.48^{Ba}	6.37^{Ca}	8.63^{Db}		

Other species of Oribatida ($N < 200$ individuals m^{-2}): *Brachychthonius* sp. – L: M, OM; *Camisia biurus* (C.L. Koch, 1839) – L: M, OM; *Carabodes forsslundi* Sellnick, 1953 – P: M, OM, B: M, OM, L: M; *C. minusculus* Berlese, 1923 – L: M; *C. subarcticus* Trägardh, 1902 – P: M, OM, B: OM, L: M, OM; *Ceratozetella sellnicki* (Rajski, 1958) – B: M; *Chamobates schuetzi* (Oudemans, 1902) – B: O, M, OM; *Eupelops torulosus* (C.L. Koch, 1840) – B: O, M, OM; *Hemileius initialis* (Berlese, 1908) – P: M; *Hemi-nothrus peltifer* (C.L. Koch, 1839) – B: M; *Licneremaeus licnophorus* (Michael, 1882) – L: M, OM; *Metabelba pulverulenta* (C.L. Koch, 1839) – P: M, OM, B: M, OM, L: M, OM; *Micreremus brevipes* (Michael, 1888) – B: M, OM, L: OM; *Microppia minus* (Paoli, 1908) – P: O, L: M; *Microtritia minima* (Berlese, 1904) – B: M, L: M; *Nothrus silvestris* Nicolet, 1855 – B: OM; *Odonto-cepheus elongatus* (Michael, 1879) – L: OM; *Oppia denticulata* (Canestrini, 1882) – B: OM; *Phthiracarus longulus* (C.L. Koch, 1841) – B: M, OM, L: M, OM; *Punctoribates* sp. – B: M, OM, L: M, OM; *Quadroppia quadricarinata* (Michael, 1885) – L: M, OM; *Ramusella mihelcici* (Pérez-Íñigo, 1965) – P: O, OM, B: O, OM, L: O; *Rhysotritia duplicata* (Grandjean, 1953) – P: M, OM, B: C, OM, L: M, OM; *Scheloribates latipes* (C.L. Koch, 1844) – L: OM; *S. pallidulus* (C.L. Koch, 1841) – L: OM; *Steganacarus carinatus* (C. L. Koch, 1841) – P: OM, B: M, OM, L: M, OM; *Trhypochthonius tectorum* (Berlese, 1896) – P: M; *Trichoribates trimaculatus* (C. L. Koch, 1836) – P: M, OM, B: M, OM, L: OM.

[ABC] – the same letter for a seedling species means lack of significant differences among the variants of the experiment – a the Mann-Whitney U test at $p < 0.05$)

[abc] – the same letter for a single variant of the experiment means lack of significant differences among the species of the seedlings – a the Mann-Whitney U test at $p < 0.05$)

Table 3. Number of oribatid mite species (*S*), average number of species (*s*) and Shannon index (*H'*) in the variants of the experiment for the forest nurseries: pine (P), beech (B) and linden (L) in Białe Błota

Index	Species of plant	Experiment variant				Kruskal-Wallis test	
		C	O	M	OM	*H*	*p*
S	P	3	5	15	16	–	–
	B	5	7	20	22	–	–
	L	3	5	23	24	–	–
s	P	0.15^{Aa}	0.17^{Aa}	1.53^{Ba}	1.40^{Ba}	220.51	0.0000
	B	0.18^{Aa}	0.50^{Ba}	1.73^{Ca}	2.18^{Db}		
	L	0.12^{Aa}	0.28^{Ba}	1.83^{Ca}	2.33^{Db}		
H'	P	0.46	1.26	0.99	1.98	–	–
	B	1.15	0.64	1.28	1.52	–	–
	L	0.86	0.63	1.22	1.27	–	–

^{ABC} – the same letter for a seedling species means lack of significant differences among the variants of the experiment – a the Mann-Whitney U test at $p < 0.05$)
^{abc} – the same letter for a single variant of the experiment means lack of significant differences among the species of the seedlings – a the Mann-Whitney U test at $p < 0.05$)

Average number of species per sample (*s*) was always the lowest on the control plots (0.12-0.18), and its highest range was recorded in deciduous tree nurseries in OM variant (1.40-2.33), and in pine nursery in M variant (1.53). In pine nursery, both types of mulched plots harbored significantly more species than the non-mulched ones. In deciduous tree nurseries, *s* index was gradually increasing in consecutive variants (C, O, M, OM) and the differences between individual variants were significant. This shows positive effects of not only mulching but even organic fertilization alone on the occurrence of oribatid mites. No significant differences in the mean number of Oribatida species were found between individual tree species in C, O, and M variants. Significant differences were only found in OM variant between pine and deciduous trees, with improved mite species count in beech and linden nurseries. Shannon's diversity index (*H'*) was always the highest in OM variant and it ranged from 1.27 to 1.98. Average number of species per sample (*s*) in C and O variants usually slightly increased over the 3-year course of the study (Fig. 2). Only in compost-enriched beech and linden nurseries this increase was larger and *s* index was 2-3 times higher than in pine nursery. The highest values of this index (3.1-6.8) on the mulched plots were reported in the autumn of 2008, one month after mulching. Over the next seasons, the average number of species per sample *s* decreased, and in the last season it was between 0.9 and 2.8 for all the nurseries. From all Oribatida species native to the investigated area, three species were present in all variants: *Oppiella nova* (mean *D* 25%), *Oribatula tibialis* (mean *D* 5.1%), and *Tectocepheus velatus* (mean *D* 56.8%) (Table 2). The most abundant oribatid mite was *T. velatus* that dominated on all the plots in beech and linden nurseries and in O and OM variants in pine nursery. The other plots were dominated by *Oppiella nova*.

Mean density of the most common mite *Tectocepheus velatus* ranged from 20 to 6,070 individuals m^{-2}. In non-mulched pine nursery its count was low, and mulching caused a significant improvement in *T. velatus* abundance. At the control plots in deciduous trees and pine nurseries, the density of this mite was low and ranged from 70 to 130 individuals m^{-2}. The density of *T. velatus* in beech and linden nurseries was significantly higher in O variant than in control. This indicated a positive effect of compost fertilization on the occurrence of this mite over the 3-year course of the study. The dynamics of Oribatida count indicated a substantial increase in the number of the mites in the second year of the study for beech, and only at the end of the study (October 2010) for linden (Table 4). Positive effect of mulching on the count of *T. velatus* was clearly greater in beech and linden than in pine nursery (Table 2). In both deciduous tree nurseries, the highest density of this mite was observed at the plots that were both mulched and fertilized with the compost. The highest counts for M and OM variants were recorded for linden nursery (4,780 and 6,070 individuals m^{-2}, respectively), which demonstrated a highly positive effect of this tree species on the occurrence of *T. velatus*. This effect was also confirmed by an analysis of dynamic changes in this mite density that at the last evaluation stage was even higher than immediately after reintroduction (Table 4). The highest mean density of *Oppiella nova* (4,200 individuals m^{-2}) was observed in M variant in pine nursery (Table 2). Changes in this mite density indicated intense growth of its population in the autumn of 2010, resulting in 21,790 individuals m^{-2} (Table 4). No positive correlations were observed between compost fertilization and *O. nova* density (Table 2). The effect of mulching was not as clear as in the case of *Tectocepheus velatus*. The highest density of *Oppiella nova* in beech and linden nurseries was observed when the plots were both mulched and compost-fertilized, and the differences between C and OM variants were significant. Mean density of *Oribatula tibialis* on the investigated plots ranged from 10 to 380 individuals m^{-2}. Low density of this mite

(10-120 individuals m^{-2}) was observed in all variants in pine nursery and on non-mulched plots in beech and linden nurseries. On mulched plots in beech and linden nurseries this population was a bit larger (190-380 individuals m^{-2}).

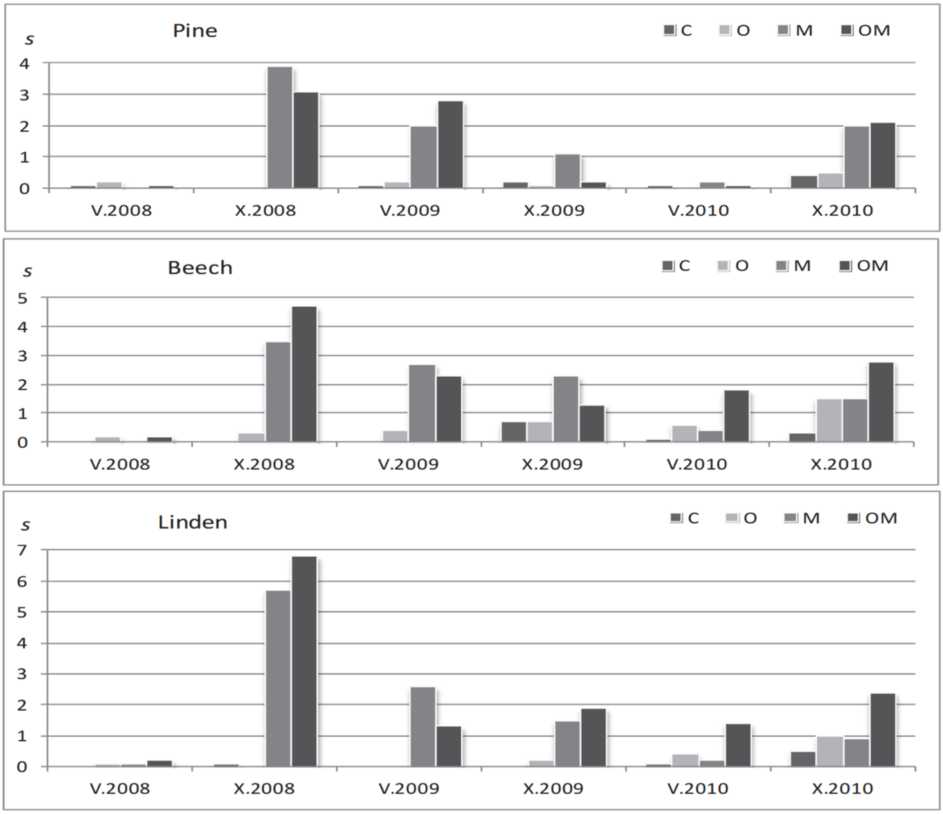

Fig. 2. Average number of Oribatida species per a sample (*s*) over the 3-year course of the study (2008-2010) in the variants of the experiment in the Białe Błota forest nursery

4. Discussion

Apart from their bioindicative role, the presence of Oribatida in in-ground forest nurseries has a strong practical aspect. Forest nurserymen believe that the most important soil organisms, directly affecting the quality of nursery material, are ECM fungi. Microorganisms, including ECM fungi present in nursery soils serve as a source of food for numerous Acari species (Schneider et al. 2005; Remén et al.2010). The presence of mites is also beneficial for the microorganisms, as the soil fauna feeding on mycorrhizas may stimulate their growth (Hanlon and Anderson1979, 1980) and inoculate the soil with fungal spores and hyphae via defecation or by transferring them to new substrates on their bodies (Lussenhop1992; Renker et al.2005).

Table 4. The dynamic changes in the density of *Oppiella nova* and *Tectocepheus velatus* (*N* in 10^3 individuals per m^2) over the 3-year course of the study in the variants of the experiment for the forest nurseries: pine (P), beech (B) and linden (L) in Białe Błota

Species of Oribatida	Species of seedlings	Variant	Research data					
			V. 2008	X. 2008	V. 2009	X. 2009	V. 2010	X. 2010
Oppiella nova	Pine	C	0	0	0	0.12	0.06	1.08
		O	0.06	0	0	0	0	0.24
		M	0	1.51	0.24	1.57	0.12	21.8
		OM	0	0.60	0.06	0	0.06	2.89
	Beech	C	0	0	0	0.12	0.06	0.12
		O	0	0	0	0	0	0.30
		M	0	0.42	0.12	0.18	0	0.30
		OM	0	1.51	0	0	0.30	1.14
	Linden	C	0	0	0	0	0.12	0.06
		O	0.06	0	0	0.06	0.12	0.06
		M	0.06	1.02	0.30	0.12	0	0.18
		OM	0	3.73	0	0.30	0.24	1.38

Table 4. cont.

Species of Oribatida	Species of seedlings	Variant	Research data					
			V. 2008	X. 2008	V. 2009	X. 2009	V. 2010	X. 2010
Tectocepheus velatus	Pine	C	0.06	0.06	0	0	0	0
		O	0	0	0.06	0	0	0.36
		M	0	3.61	1.93	0.12	0	1.63
		OM	0.18	2.95	2.53	0.12	0	1.14
	Beech	C	0	0	0	0.72	0	0.06
		O	0.06	0.12	0.78	1.75	0.36	1.14
		M	0	1.51	6.08	6.56	0.36	1.14
		OM	0.06	2.17	6.56	7.46	0.84	5.66
	Linden	C	0	0	0	0	0	0.42
		O	0	0	0	0	0.18	2.23
		M	0	4.21	5.60	16.6	0.90	1.38
		OM	0.06	8.55	2.41	7.95	6.86	10.6

The experiments carried out in Białe Błota nursery were aimed at soil revitalization. Organic fertilization with bark-enriched compost produced from municipal sewage sludge enhanced organic matter content and mulching with raw humus improved the soil structure and restored its natural layers. Moreover, the soil was inoculated with typical forest edaphon. The use of sewage sludge, and especially taking advantage of its fertilizing and pedogenic properties, is a very good idea from the environmental perspective. This is the simplest and cheapest method of disposing the waste harmful to people and environment.

Earlier studies confirmed positive effects of the practices implemented in this experiment on the quality of linden seedlings. Both treatments improved this plant growth and leaf number and area (Klimek et al. 2013b). The greatest diameter of root collar, and number and area of leaves were observed in 3-year old linden seedlings grown on the plots mulched and fertilized with the compost. Compost fertilization alone positively affected the density of oribatid mites, as significant increase in the count and average number of species per sample (*s*) were noticed in beech and linden nurseries (Table 2 and 3). Another experiment carried out for two years in the same nursery on the plots with pine and birch did not show any effect of compost fertilization on the density of oribatid mites (Klimek et al. 2008, 2009, 2013a).

An analysis of the abundance and species diversity of Oribatida revealed the most effective soil revitalization in deciduous tree nurseries where mulching was combined with organic fertilization (Table 2). Successful attempts at soil inoculation with mesofauna by spreading raw humus have been reported in numerous publications (Klimek et al.2008, 2009, 2011, 2012). Good revitalization results were achieved in birch nursery (Klimek et al. 2009), and the treatment was more successful than in pine (Klimek et al. 2008), and larch nursery (Klimek et al. 2012). The seedlings of deciduous trees grow faster and provide edaphon with better protection against harmful solar radiation than coniferous seedlings. Moreover, they enrich the soil with organic matter in the form of leaves falling down in the autumn. Poor effectiveness of edaphon inoculation may therefore be due to excessive drying of the exposed soil surface. Sensitivity of soil mesofauna, and particularly Oribatida to low moisture has been reported in the literature (Lindberg and Bengtsson 2005). When natural precipitation is too low, forest nurseries are irrigated. However, the amount of water provided as per irrigation standards for seedlings may be too small to make up for soil surface drying, especially on sunny spring and summer days. The effect of Oribatida on the quality of seedlings produced in forest nurseries is obviously indirect. It consists mainly in improving the activity of soil microorganisms (Wallwork 1983) and accelerating the processes of organic matter decomposition by its disintegration. By constant reduction of fungi and bacteria population, these small arthropods are capable of maintaining the organic matter in the growth phase (so called compensatory growth). Some researchers claim oribatid mites feed mainly on mycelium (Lindberg and Bengtsson 2005), and the environmental conditions facilitating mycelium development are also beneficial for Oribatida populations (Blakley et al. 2002; Pollierer et al.2007). It may be therefore assumed that abundant presence of oribatid mites indicates proper course of soil revitalization processes (bioindicative role) and occurrence of microorganisms typical for forest soils, especially fungi. This hypothesis was confirmed by abundant presence of two fungivorous mites *Oppiella nova* and *Tectocepheus velatus* on the mulched plots (Table 2 and 4). *T. velatus*, the species common in various biotopes, turned out to be a good bioindicator and was especially responsive to the implemented revitalization treatments. It is a par-thenogenetic species, characterized by short reproduction cycle, high reproduction rate and high ability to colonize new environments (Siepel 1994, Skubała and Gulvik 2005; Gulvik 2007). It belongs to fungivores (Luxton 1972; Ponge 1991) feeding on ectomycorrhizal fungi (Schneider, et al. 2005; Remén et al. 2010), and spreading them in the process, which makes it a good stimulant of the revitalization of nurseries.

4. Conclusion

Fertilization with bark-enriched compost prepared from sanitized municipal sewage sludge carried out in the in-ground nursery in Białe Błota positively affected the density and species diversity of oribatid mites in beech and linden nurseries. Substantial increase in the abundance and number of Oribatida species following mulching with raw humus and organic fertilization, particularly clear in deciduous tree nurseries, made this experimental variant stand out as the most effective soil revitalization treatment. The most effective bioindicator and stimulant of soil revitalization was a common fungivorous species *Tectocepheus velatus*.

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Abstract

The study was conducted in the years 2008-2010 in the bare root nursery Białe Błota that produced pine, beech and linden, and belonged to Bydgoszcz Forest District. The experiments included the following variants: C – control, O – organic fertilization, M – mulching with raw humus, OM – organic fertilization and mulching with raw humus. Relatively small but significant increase in the number and diversity of Oribatida species was observed in O variant for the deciduous trees. Mulching was the soil revitalization method that clearly improved the density and biodiversity of Oribatida species. In total, the investigated area harbored 37 species of oribatid mites. The most effective bioindicator and stimulant of soil revitalization was a common fungivorous species *Tectocepheus velatus*.

Keywords:
organic fertilization, mulching, tree seedlings, bioindication, oribatid mites.

Występowanie mechowców podczas rewitalizacji szkółek leśnych

Streszczenie

Badania były prowadzone w latach 2008-2010 w należącej do Nadleśnictwa Bydgoszcz, szkółce leśnej Białe Błota produkującej sosnę, buk oraz lipę. Badania prowadzone były w następujących wariantach: C – kontrola, O – nawożenie organiczne, M – mulczowanie świeżym humusem, OM – nawożenie organiczne i mulczowanie świeżym humusem. Stosunkowo mały, ale znaczący wzrost liczby i zróżnicowania gatunkowego mechowców zaobserwowano w wariancie O dla drzew liściastych. Mulczowanie było metodą rewitalizacji gleb, która wyraźnie wpłynęła na intensywność i zróżnicowanie gatunkowe mechowców. Na badanej powierzchni stwierdzono ogółem 37 gatunków mechowców. Najskuteczniejszym bioindykatorem i stymulatorem rewitalizacji gleby był powszechnie występujący gatunek grzybożerny *Tectocepheus velatus*.

Słowa kluczowe:
nawóz organiczny, mulczowanie, sadzonki drzew, bioindykacja, mechowce

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Concept of Near-Autonomous Passive House

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1. Introduction

The definition of passive house was created in 1988 by Wolfgang Feist (the founder of the Passive House Institute). According to Feist, passive house is a building with extremely low energy requirements for interior heating (15 kWh/m^2 per year), for which thermal comfort can be achieved solely through passive heat sources (e.g. residents, electrical appliances, solar heat, heat recovered from ventilation) and by post-heating or post-cooling of the fresh air mass, which is required to achieve sufficient indoor air quality conditions – without the need for active heating system (Feist 1988).

The definition above is just the basis for what a passive house is – it's not a trademark or brand name, but an idea, a construction concept. A building standard that is truly energy efficient, comfortable, affordable and ecological at the same time. Research and development of passive housing is led by The Passive House Institute (ger. *Passivhaus Institut*). The Institute's tasks include setting standards and assigning certificates to passive houses. In order to obtain a certificate, the building must meet a number of criteria for energy consumption. The basis is to obtain the aforementioned energy demand for heating the interior of the building at 15 kWh/m^2 per year, Which corresponds to the consumption of 1.5 l of fuel oil per square meter per year. Demand for primary energy used for all home appliances (electrical appliances, heating, hot water heating) cannot exceed 120 kWh/m^2 per year. Another condition is air tightness n_{50} of the building – by using a constant output pressure, the software calculates the amount of air exchange at a pressure difference in one hour. At a pressure of 50 Pa, the object can reach a maximum of 0.6 air changes per hour. The tightness of passive building must go hand in hand with excellent thermal insulation, in moderate climate, the heat transfer coefficient (U-value) of a building cannot exceed 0.15 W/m^{2}K. The ultimate condition is to achieve thermal comfort both in summer and in winter, throughout the usable area of the building, by achieving a temperature not higher than 25ºC for 90% of the year (*www.passivehouse.com*, 2017.05.07).

2. Methodology

Due to the data validity (being the key aspect), the basis of a cost analysis of necessary installations and additional elements of the project was information included in the websites of the companies dealing with passive and energy-efficient buildings, operating in Poland. Characteristics of installations increasing the autonomy of an exemplary passive house and the criteria for the construction of passive houses were backed up by a thorough analysis of the subject literature. Based on the literature, nine design criteria are presented, seven of which are necessary. Ultimately, on the basis of the existing project, a model passive house was created, supplemented by the latest energy-efficient technologies. In order to estimate the general average solar conditions of Poland, Photovoltaic Geographical Information System was used. The gathered information allowed to assess usability of the concept of near-autonomous passive house.

3. Passive house criteria and use of renewable energy sources

Passive houses effectively use solar energy, internal heat sources and ventilation with heat recovery, so conventional heating systems are no longer necessary even during winter frosts. Ventilation system, the basis of the passive house, unobtrusively ensures constant access to fresh air without drafts. The use of an efficient ventilation system allows to give up the standard, uncontrolled way of building ventilation – opening windows (or involuntary ventilation due to leaks). Passive house criteria are achieved through smart building design and a number of rules (Feist 2006, Wnuk 2007, Piotrowski 2009, Costa Duran 2012, Piotrowski, Dominiak 2012, Wnuk 2012, Steinmüller 2014, Stram 2016).

Building setting in relation to the directions of the world – for optimal passive use of sunlight to warm the interior, the back of the building should be oriented south. By designing large windows on the southern façade of the building, solar thermal energy will become the passive heating system of the building (unlike active systems, which require mechanical circulation of heat). During the day, sunlight is absorbed through uncovered windows by the inner walls, the ceiling and floor, thus accumulating heat in the building. Absorption capacity can be further increased by painting it to dark colour (up to 75%). A greenhouse effect is created – the room is heated by the sunlight retained by the glass.

Simplicity of structure – energy efficient architecture is characterized by the guarantee of thermal comfort without any additional heating systems. Compact construction requires less energy to heat, therefore it is necessary to minimize the length of walls and the number of corners – each of them threatens with the occurrence of thermal bridges.

Avoiding thermal bridges – the thermal bridge is an element of building construction with a higher thermal conductivity than the surroundings. It consists of any structural break through the insulation coating, as well as corners of the building and connections or contacts of materials with different thermal conductivity. Incorrect window placement or door fit can also lead to the formation of thermal bridges, and as a result cause heat loss and reduce the energy balance, by creating the temperature difference inside and outside of the building. In order to limit the occurrence of thermal bridges, it is essential not to break the insulation layer of the building.

Proper layout of the utility and residential rooms – proper setting of rooms is an important part of designing a passive house, the building location requirements and the way the sunlight is used must be reflected in the planning of the rooms. For this reason, living rooms should be located on the south side of the building. Well-isolated northern part of the building (with a small number of window openings) should be distributed with bathroom and utility room. Bedrooms should be located in the east or west of the building.

Air tightness of the building structure – passive building envelopes are characterized by exceptionally high thermal insulation. For this reason, traditional foundations cannot be used in construction. Instead, the building must be placed on a well-isolated plate, and all insulating elements should be made continuously (preferably prepared in one piece). Thermally insulated bearing walls are an important element of the structure, omission in insulation continuity can cause thermal bridges and thus allow heat to escape. Thick and heavy construction components constitute as an additional energy store, and contribute to the accumulation of heat in the building. Quality of exterior windows and doors are an important element of a passive house. It must meet high insulation requirements, it is therefore important to use doors and window frames made of materials with good thermal performance (e.g. pine wood) and reduce heat loss through windows (e.g. by using insulated glazing). All means of achieving adequate thermal insulation are designed to achieve nearly full tightness of the building, which is a key element of passive house construction. Achieving almost full tightness prevents heat loss by air convection and it is necessary for proper operation of heat recovery ventilation.

Heat recovery ventilation – the heart of the passive house. Properly designed ventilation system continuously removes contaminated and „used" air (from kitchen or bathroom), replacing it with fresh air coming from the outside. Standard ventilation system causes energy losses by also removing heated air, therefore the passive house ventilation system is supplemented with a heat recovery system. Heat exchanger (recuperator) absorbs heat from removed, warm air, and then returns it to the fresh air. To improve the performance of the recuperator (the efficiency right now is 75-95%) and to minimize the consumption of electricity, the system can be supplemented by a ground heat exchanger. Through a tube network buried in the ground (usually at a depth of 2 m) the air can be heated up to 20 degrees or cooled down by 10 degrees. This is possible due to the relatively constant temperature at this depth (which is no more than 10°C during the summer and no less than 4°C during the winter). An additional antibacterial layer prevents unpleasant odours. It is possible to use an integrated heating system with a recuperator, a ground heat exchanger and an electric heater powered by solar collectors.

Use of renewable energy sources – necessary factor for the use of passive houses. Sunlight can be used in passive manner (as explained previously) and in active manner – by using photovoltaic cells. Solar energy can be used: to improve the performance of the recuperator (by charging additional immersion heater for warming fresh air), to heat up utility water and to supply power to the lighting system and other electrical equipment in the passive house. The construction of a wind farm is associated with high investment costs and its power definitely exceeds the energy requirements of a single building – therefore, in order to supply the passive house with electricity the so-called small wind turbines (with rated power up to 100 kW) can be used. Low investment costs, simple construction and setup, as well as low wind power requirements, makes it available for individual customers. The use of solar and wind power is not determined by exceptional spatial conditions (only the lack of high structures in the vicinity is required, due to the sunlight blocking and wind-insulation). In case of using hydropower requirements are higher – the building plot must adjacent to the river. Small hydropower plant (with rated power up to 500 kW), as in the case of a small wind power plant, does not require a lot of investment costs, therefore it can be an alternative source of electricity in passive house placed in the immediate vicinity of the river. Regardless of the origin, the energy that drives electrical appliances from renewable sources, is a necessary complement to the environmentally friendly passive house. In an ecologically designed home (beyond the requirements of a passive house) in order to save utility water, home water supply system can be complemented with rainwater tank and household sewage treatment plant. The first system collects rainwater from the gutter network, purifies it with the filtering system and transmits it to the sanitary appliances. And the second system, after cleaning, distributes used water for reuse, e.g. in the garden or in the toilet.

Proper arrangement of the building plot – an aspect helpful but not necessary for passive house building. Due to the different behavior of different types of trees during different seasons, deciduous trees should be located on the southern side of the passive house, while coniferous trees on the north side. Deciduous trees protect the south façade of the house from intense sunlight in the summer and during winter lose leaves and do not block the sunrays, necessary to operate the passive heating system. Conifers, while preserving their form throughout the year, provide good insulation against the wind.

Use of energy efficient household appliances – to meet the energy requirements of the building with renewable energy sources, it's necessary to minimize its consumption as much as possible without limiting the usability. For this purpose, despite higher initial investment costs, passive house should be equipped with energy-efficient electrical appliances, to reduce electricity consumption by up to 60%.

4. Passive housing in the world

Passive House Database is an official register and review of existing passive houses (investments confirmed with Passive House Institute Certificate) and energy efficient buildings with the attributes of passive house. The database is the result of cooperation of Passive House Institute, Passivhaus Service Ltd. (*ger. Passivhaus Dienstleistung GmbH*), German Passive Buildings Information Society (*ger. IG Passivhaus Deutschland*) and International Passive House Association. At the moment of writing this article, Passive House Database contained information on 4 149 buildings built up to year 2017 (of which 1 147 is a certified passive house), however there are certainly more uncertified passive houses worldwide. The database also contained information about 55 energy efficient buildings with the attributes of passive house and 16 certified passive houses built already in 2017. However, due to the time remaining until the end of the year, these investments will not be included in the analysis. In addition, some entries contain no information about the year of investment (this applies to 87 buildings). Data from Passive House Database were used to create Table 1, portraying the development of energy efficient buildings with the attributes of passive house and passive houses in the world (Passive House Database, *www.passivhausprojekte.de*, 2017.09.20).

Based on the data, graphs showing number of energy efficient buildings with the attributes of passive house and certified passive houses were created (Figure 1 and Figure 2).

Figure 1 shows an almost constant upward trend in the number of energy efficient buildings with the attributes of passive house build in the years 1996-2011, with periods of slight decline in 2001, 2006 and 2010, and Figure 2 shows a dramatic increase in the number of passive houses built between 2006 and 2012. Increased interest in passive houses from 2006 may be related to the release of the first version of computer Passive House Planning Package – toolset to help designers create, verify and optimize passive house projects. Passive House Planning Package by Passive House Institute has created the possibility of more accurate analysis of the construction project and opened the way to passive construction for a wider number of designers. A growth in 2006 may also be the result of the launch of annual International Passive House Days, held by International Passive House

Association, in 2004. This initiative once a year brings together experts, owners and residents of passive houses and ecological building enthusiasts. Passive House Association, in cooperation with its national subsidiaries, creates the basis for the development of an energy sustainable future, promoting new ideas and technical solutions for the construction of passive houses. International Passive House Days are held continuously every year, raising awareness of the public in the field of environmentally friendly but affordable construction solutions (*www.passivehouse.com*, 2017.09.14, *www.passivehouse-international.org*, 2017.09.14).

Table 1. Number of energy efficient buildings with the attributes of passive house and passive houses in the world (years 1991-2016)

Year	Number of energy efficient buildings with the attributes of passive house	Number of passive houses
1991	1	1
1992	0	0
1993	0	0
1994	0	0
1995	0	0
1996	1	0
1997	11	0
1998	39	9
1999	75	12
2000	128	32
2001	101	22
2002	140	17
2003	178	27
2004	228	32
2005	229	32
2006	213	19
2007	233	32
2008	262	47
2009	329	58
2010	285	83
2011	340	121
2012	325	145
2013	288	122
2014	269	130
2015	220	115
2016	167	70
Overall	4062	1126

Source: own elaboration, based on Passive House Database

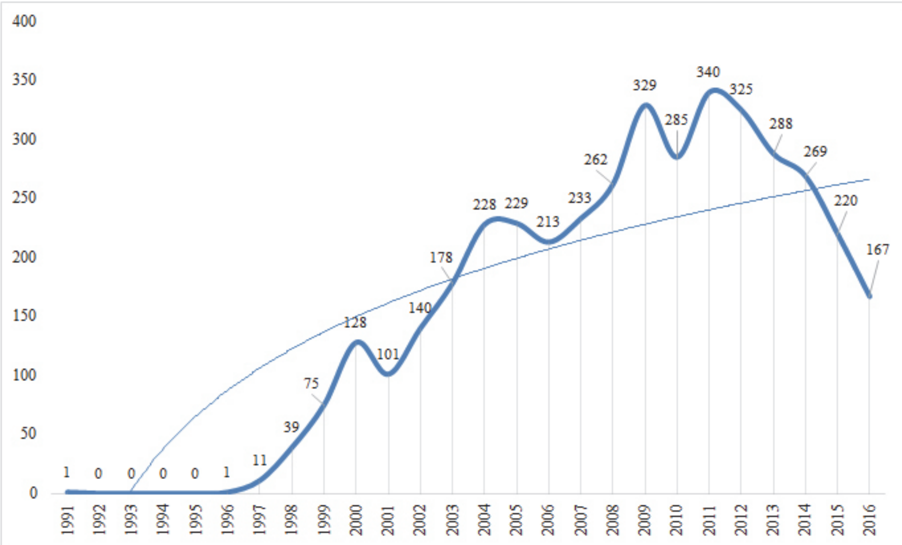

Fig. 1. Number of energy efficient buildings with the attributes of passive house in the world (years 1991-2016)
Source: own elaboration, based on Passive House Database

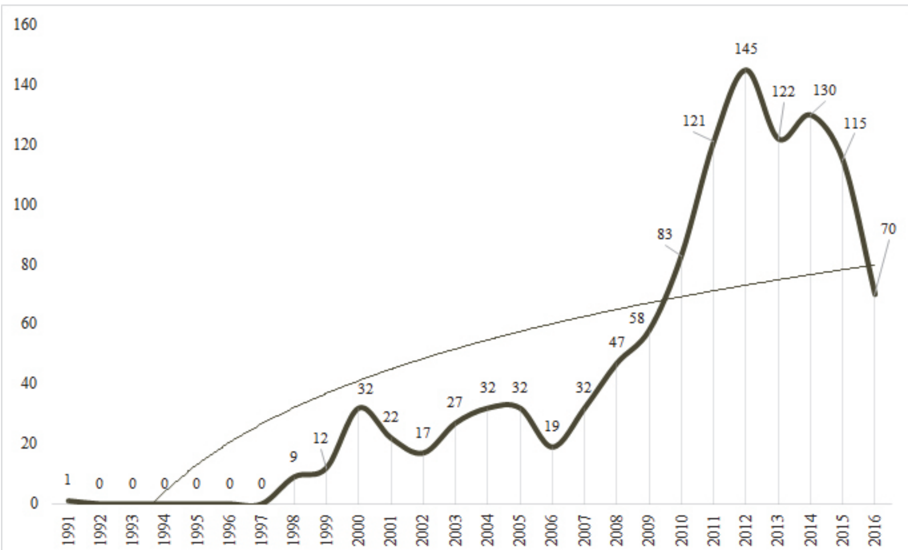

Fig. 2. Number of certified passive houses in the world (years 1991-2016)
Source: own elaboration, based on Passive House Database

The Passive House Database grows slowly, but constantly – the theoretical downward trend may be due to the detail of the certification process, and in the next few years, the upward trend will stabilize. Despite the downward trend in the number of passive houses being built since 2012, this type of construction is still developing, just as people's awareness of the need to save energy in every area of their lives.

5. Exemplary passive house model

Requirements for land development for passive housing differs from requirements for standard construction. By setting the goal for the highest energy autonomy of the object, additional requirements appear – for example, space should be allocated for equipment using renewable energy sources. The exemplary model was based on the 163 P2 project by design agency "Bravo Passive Houses" (pol. Brawo Domy Pasywne) located in Stawiguda, Poland (Bravo Passive Houses, project 163 P2, www.grupabrawo.pl/domy/6/brawo-163-p2, 2017.05.07). The model house is a single-family detached house, with attic and without basement, with a total usable floor area of 178.36 m^2 (of which 94 m^2 on the ground floor and 84.36 m^2 on the first floor) and 8 m high. The horizontal projection (plan view) of the building has a rectangular shape, measuring 12.24 x 9.86 m, with a protruding southern part of the living room, measuring 4.76 x 1.20 m, and the total built-up area equals 126.40 m^2. The model provides the following layout of rooms on the ground floor of the building: anteroom of 16.97 m^2 area, kitchen of 15.24 m^2 area, dining / living room of 35.22 m^2 area, office room of 13.23 m^2 area, bathroom of 2.98 m^2 area and utility room of 10.36 m^2 area. Fan-shaped stairs lead from the anteroom on the first floor, which includes: corridor of 8.45 m^2 area, two bedrooms of 15.12 m^2 area each, main bathroom of 15.13 m^2 area and main bedroom of 30.54 m^2 area. The base project was complemented with a detached garage with a usable area of 42 m^2. Figure 3 is a visualization of a passive house model, with the area of every room.

The foundations of the house consist of a compacted aggregate layer, 100 mm concrete C12/15 plate, PE insulation film, 300 mm thick Styrofoam with thermal conductivity (k-value) of 0,031 W/mK and screed of 80 mm thickness. For the floor, used insulating elements made possible to reach the heat transfer coefficient (U-value) of 0,1 W/m^2K. The exterior walls of the building were made of 12.5 mm thick plasterboard, Insulating mineral wool of 50 mm thickness, vapour barrier film, 12 mm MFP construction board, mineral wool layer of 180 mm thickness and thermal conductivity (k-value) of 0,036 W/mK, wooden poles 45 mm thick, another 12 mm MFP construction board, windproof film, façade wool layer of 250 mm thickness and thermal conductivity (k-value) of 0,036 W/mK, metal grate and "Ceresit" CT 174 silicate-silicone plaster. The total thickness of the outer baffle equals 600 mm, and heat transfer coefficient (U-value) equals 0.073 W/m^2K.

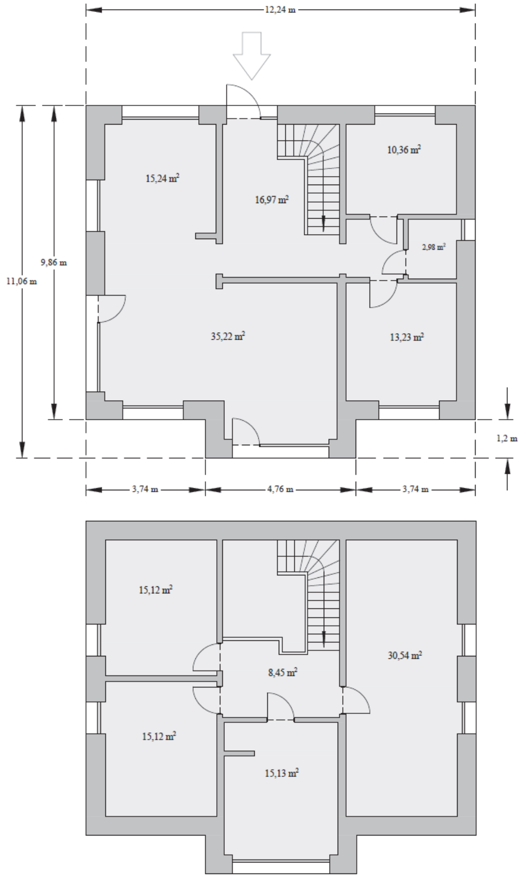

Fig. 3. Passive house model
Source: own elaboration based on project 163 P2

Figure 4 shows the cross section of the external wall of the model passive house, detailing the materials used.

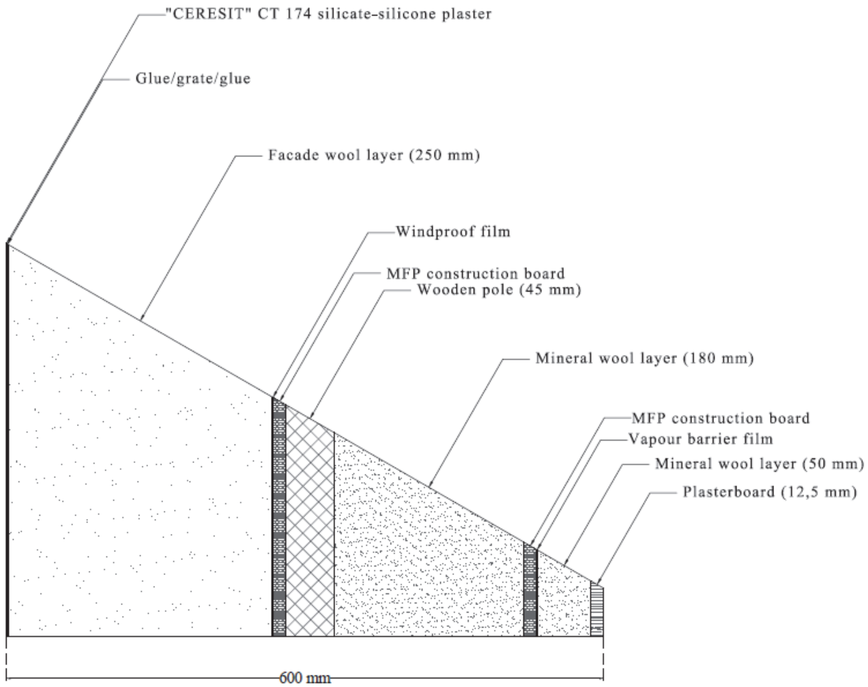

Fig. 4. External wall cross section
Source: own elaboration

The building has a gable roof with a 40º angle, which is covered with tile and made of: 12.5 mm thick plasterboard, vapour barrier film, metal grate, mineral wool layer of 550 mm thickness and thermal conductivity (k-value) of 0,033 W/mK, 60 x 180 mm rafters, 15 mm MFP construction board and waterproof roofing film with a density of 160 g/m^2. Heat transfer coefficient (U-value) of the roof equals 0,059 W/m^{2}K.

The model passive house was equipped with an exterior door from the company "Cal", from the "Alaska" collection, with a thickness of 90 mm and heat transfer coefficient (U-value) of 0,71 W/m^{2}K; and insulated glazing "IDEAL 8000" from the "Aluplast" company with a thickness of 85 mm and heat transfer coefficient (U-value) of 0,50 W/m^{2}K (*www.drzwi-cal.pl*, 2017.05.07, *www.aluplast.com.pl*, 2017.05.07).

An exemplary passive house model was equipped in the central ventilation unit with heat recovery "Zehnder ComfoAir 550 Luxe VV ERV R". A compact unit consists of: recuperator with automatic by-pass system (workaround for exhaust air, bypassing the heat exchanger and not heating up the fresh air) and integrated electric preheater. The cross-flow exchanger allows for 95% heat recovery, with the use of DC motors, low power consumption was achieved (13-350 W). Airflow volume stream is in the range of 50-550 m^3/h, at a noise level of 28-35 dB (comfortable for the human ear). The system is controlled with touch panels and its operation is simple and easy. The price of the system is 16 800 PLN (*www.zehnder.pl*, 2017.05.07).

The ComfoAir 550 Luxe system can be directly connected to the ground heat exchanger – in exemplary passive house "GEOSTRONG 1400" from the company "GLOBAL-TECH" was used. Almost 100% efficiency of heat exchange can be achieved, which is unusual in other types of ground heat exchangers. Because of the exceptional endurance of the system (460 t/m^2) the "GEOSTRONG 1400" can be placed at a greater depth than other models. During winter measurements (at air temperature -20°C), air at the outlet of the exchanger never exceeded 0°C. Meanwhile, during the summer measurements (air temperature to 35°C) system reached 17°C. Used humidity reduction system in summer and humidifying the air in winter definitely improves thermal comfort inside the building. Model 1400 placed in the ground at a depth of 5 m, requires an area of 7.10 x 10.80 m. Due to complete synchronization with the "ComfoAir" ventilation system "GEOSTRONG" ground heat exchanger does not require any additional electricity. The cost of purchasing this installation is 19 200 PLN (*www.gruntowe-wymienniki.pl/geostrong*, 2017.05.07).

"ComfoAir" electricity demand can be fully covered by the use of renewable energy sources. Wind energy can be converted into electricity using a small VAWT (Vertical Axis Wind Turbine) wind farm. The use of vertical Darrieus turbines reduces the noise and vibration level, at the expense of reduced capacity of the power plant (estimated at 40%). Additional advantages of vertical wind turbines are less sensitivity to swirling and change of the wind direction. In exemplary passive house model the use of solar home power plant "VAWT-2kW Solta" was established – it allows to generate 1 800-15 600 kWh of electricity per year with a minimum level of momentary power of 353 W (for wind speed at 4 m/s). The cost of this installation is 24 000 PLN. In the case of investment in a more powerful power plant with power of 20 kW (price - 50 000 PLN), 6 600-133 200 kWh of power can be generated per year (www.solta.info.pl, 2017.05.07, Tytko 2011).

Planned "Selfa SV60P-240 PVCWU-10" photovoltaic modules consists of an autonomous system of using solar energy to heat up utility water in the tank, the system does not require connection to the power grid. Comprised of 10 photovoltaic modules, it can reach power of 3 400 watts (depending on the sun exposure). The system completely covers the needs of a family of four in hot water, its cost is 6,800 PLN. The installation of additional modules can support the operation of the hot water heating system or can be used to power home electrical appliances (*www.selfa-pv.com*, 2017.05.07).

In order to make passive house independent of the supply of running water, rainwater harvesting system was used – complete Professional Set with "Diamant 4800" underground tank with "GRAF Minimax" internal filter kit. This set is a comprehensive and professional solution for home and garden. Rainwater harvesting systems reduce the consumption of drinking water by replacing it with rainwater, e.g. for garden watering, washing, toilet flushing or floor cleaning. In total, it saves about 60% of drinking water. Rainwater is collected from the roof through a set of gutters and transported to an underground tank. A 4 800 l tank provides the optimum volume for a family of four. The filter unit (with 95% efficiency) is integrated into the tank and acts in a self-cleaning manner. The cost of the set is 13 000 PLN. Additionally, the rainwater harvesting system can be complemented by the household sewage treatment plant – "SEDYMENT BIO 2000 OB3K" was used in exemplary passive house. It is characterized by approximately 96% reduction of contamination, with a power consumption of only 29 W. Waste generated in the purification process is discharged into the soil, therefore a distance of at least 3 m from the building, 2 m from the boundary of land plot and 30 m from the drinking water intake is required. The household sewage treatment plant has a capacity of 2 300 l and its price is 8 500 PLN (*www.powode.pl*, 2017.05.07., *www.sedyment.com.pl*, 2017.05.07).

The base 163 P2 project was characterized by tightness n_{50} of 0.6/h, primary energy demand of 101 kWh/m^2 per year and energy requirements for interior heating of 14 kWh/m^2 per year. Due to the use of more modern components and materials, the energy performance of the building should be even lower. In total, the cost of installations that helps to achieve partial autonomy and the cost of ventilation to reduce the energy demand for heating the building, amounted to 88 300 PLN (approximately 19 000 £, 21 000 € or 25 000 $). The amount of extra investment costs is high, but it allows you to forget the monthly home use fees. Table 2 shows the total cost list for additional installations (currency rates from *www.bankier.pl*, 2017.08.30).

All controls for additional technical installations will be placed on the ground floor in the utility room. The main element in the utility room will be Central ventilation unit with heat recovery "ComfoAir 550 Luxe" measuring 0.73 x 0.57 m and an area of 0.41 m^2. At a distance of 1 m to the outside wall at the utility room "Diamant" rainwater tank will be located, measuring 1.70 x 1.70 m and an area of 2.89 m^2. Ground heat exchanger "GEOSTRONG 1400" measuring 7.10 x 10.80 m and an area of 76.68 m^2 has sufficient load capacity, therefore a detached garage with an area of 53 m^2 was designed in the place over it. The ground heat exchanger will be located at a maximum distance of 7 m from the building. On the roof of the building, 10 photovoltaic modules will be installed, of 1.69 m^2 area each. In the further part of the building plot, in order to avoid possible energy losses, the location of the VAWT wind farm is planned, measuring 9.00 x 9.00 m and an area of 81 m^2. A small wind farm should be placed at least 20 m from the building. Due to the disposal of waste from "SEDYMENT BIO" sewage treatment plant to the soil, it should be located at a considerable distance from the building. Sewage treatment plant measuring 1.80 x 1.60 m and an area of 2.88 m^2 is planned approximately 35 m from the house.

Table 2. Cost of additional installations

Installation type	Cost [PLN]	Cost [GBP]	Cost [EUR]	Cost [USD]
Central ventilation unit with heat recovery	16 800	3 645,44	3 942,74	4 708,78
Ground heat exchanger	19 200	4 166,21	4 505,98	5 381,47
Small wind turbine	24 000	5 207,77	5 632,48	6 726,83
Photovoltaic modules	6 800	1 475,53	1 595,87	1 905,94
Rainwater harvesting system	13 000	2 820,87	3 050,93	3 643,70
Household sewage treatment plant	8 500	1 844,42	1 994,84	2 382,42
Sum	88 300	19 160,25	20 722,84	24 749,15

Source: own elaboration

According to earlier guidelines, the passive house was located in the north-south line. To maximize the passive use of sunlight, eliminating all possibilities of shading by neighbouring buildings, the side boundaries of the plot have been determined at a distance of 19 m from the exterior walls, and southern border – 49 m. Front of the building is planned 11 m from the border of the plot. Ultimately, the example building plot has dimensions of 70.00 x 50.00 m and area of 3,500 m^2.

6. Achievement of partial energy autonomy of the building

Photovoltaic Geographical Information System (PVGIS) may be the source of information on the levels of sunlight. It is part of the SOLAREC action, contributing to the efficient use of renewable energy in the European Union. The system itself operates at the Institute for Energy and Transport from Joint Research Centre under the authority of the European Commission. To determine country's energy potential interactive map can be used – after selecting the location and entering basic data (e.g. power and angle of installed photovoltaic cells) the system provides, e.g.: estimated losses due to temperature and low irradiance (using local ambient temperature), estimated loss due to angular reflectance effects, other losses (cables, inverter etc.) and combined PV system losses. Additionally, gives information about optimal angle of the photovoltaic panel with the division into months. It is also possible to simulate the operation of a single photovoltaic panel, with full freedom of input data. Using the PVGIS site, the average energy potential in terms of solar energy for Poland was calculated (based on 20 samples). Assuming the technical characteristics of the photovoltaic modules installed in exemplary passive house, as well as the shape of the roof of the building, system estimated losses due to temperature and low irradiance at 12.6%. Amount of produced energy from a photovoltaic system installed (nominal power of 2 500 W) was average 178.66 kWh per month, 59.67 kWh for the winter months and 266.67 kWh for the summer months, and for the whole year it reached 2 322.60 kWh. For maximum power (3 400 W) the average was 242.98 kWh per month, 81.03 kWh for the winter months and 362.67 kWh for the summer months, and for the whole year it reached 3 158.70 kWh. Due to the achieved level of energy requirements for heating the building at 14 kWh/ m^2 per year, for the usable floor area of 178,36 m^2, the annual energy requirement for interior heating would be 2497.04 kWh. Additionally installed photovoltaic module system for the nominal power level will meet the energy needs for interior heating at 93%, while at maximum power – at 126%. (Photovoltaic GIS – Interactive Maps, *re.jrc.ec.europa. eu/pvgis*, 2017.05.07; Suri, Huld, Cebecauer, Dunlop 2008).

7. Summary

Passive housing, an idea born in the minds of German engineers, brought energy efficiency to a higher level, by providing thermal comfort with minimum energy consumption, precisely sealing the building and protecting it with a thick layer of insulation while not suffocating the inhabitants. The use of renewable energy sources combined with the idea of passive houses with assumption to reach the highest level of independence from traditional technical infrastructure networks, seems to be the only effective and (most importantly) long-term solution to the existing energy crisis.

The purpose of the article was verification of the possibilities of creating such a near-autonomous passive house. After a thorough analysis of installations available on the Polish market and by calculating additional costs, comforting vision of such project was presented, along with the estimation of meeting the primary needs of the residents.

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Abstract

The global energy crisis has created the need for implementing energy-efficient solutions in the case of spatial planning and architecture. Raised energy prices encourage energy saving and implementation of new technologies (eco-friendly technologies). These aspirations are met by introducing appropriate technological solutions, to ensure the highest self-sufficiency of buildings, and by using renewable energy sources to cover the remaining energy needs. The concept of passive housing has become the answer to all these needs – it features thermal comfort with minimum energy requirements. Additional implementation with the use of renewable energy sources was proposed in this article, in order to achieve partial independence from traditional technical infrastructure.

Keywords:
passive house, energy-efficient building, eco-friendly technologies, spatial planning

Koncepcja niemal autonomicznego domu pasywnego

Streszczenie

Światowy kryzys energetyczny zrodził potrzebę wprowadzania energooszczędnych rozwiązań również w przypadku planowania przestrzennego i architektury. Rosnące ceny energii zmuszają nas do oszczędzania oraz wdrażania nowych technologii (technologii przyjaznych środowisku). Dążenia te spełniane są poprzez wprowadzanie odpowiednich rozwiązań technologicznych, służących zapewnieniu jak największej samowystarczalności energetycznej budynków oraz poprzez wykorzystanie odnawialnych źródeł energii do pokrywania pozostałego zapotrzebowania energetycznego. Odpowiedzią na te potrzeby stała się koncepcja budownictwa pasywnego – charakteryzującego się komfortem cieplnym przy minimalnym zapotrzebowaniu na energię. W artykule zaproponowano dodatkowe uzupełnienie o użycie odnawialnych źródeł energii, w celu osiągnięcia częściowej niezależności od tradycyjnych sieci infrastruktury technicznej.

Słowa kluczowe:
dom pasywny, budownictwo energooszczędne, technologie przyjazne środowisku, planowanie przestrzenne

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Transformation of Density Hydrographic Network in Headwaters of Piwonia River

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1. Introduction

Transformations of terrain significantly affect biodiversity, energy flow, biochemical cycles and climate both on the regional and local scale. In the context of spatial processes transforming the landscape, urbanization is classified as a process of perforation or abrasion (Fortin & Dale 2005). Hydrogenic landscapes are characterised by particular nature richness. At the same time they are of key importance for the stability of ecological relations of individual regions. Aquatic, wetland, peatbog and grassland ecosystems are dominant in hydrogenic landscapes (Choiński & Ptak 2009).

Poland is a country with the lowest European ratio of natural water resources per capita. On the other hand, it has 7081 water bodies larger than 1 ha (Choiński 2007, Choiński et al. 2011). The majority of natural lakes are found in the northern part of the country, with young, diverse post-glacial landscape. Remaining regions are characterised by the low number of standing water bodies. The unequal spatial distribution of lake areas is an important fact, as lakes are considered to be significant factor in sustainable development, biodiversity and economic growth (Walsh et al. 2003, Davies et al. 2008, Parparov & Gal 2012). Their role is understood more and more not only among scientist, but also among society (Skiwierawski 2018).

The scale of landscape and land use transformation is usually based on archive spatial materials, i.e. aerial photographs and maps serving as evidences of natural and anthropogenic changes (Suchożebrska & Chabudziński 2007, Myga-Piatek 2010, Nieścioruk 2013, Ignatius & Jones 2014). In recent years, the importance and popularity of spatiotemporal presentation of landscape changes and geographical background of historical facts increases significantly (Holdsworth 2003, Mościcka 2009, Withers 2009, Chabudziński et al. 2018). The role of Geographic Information System (GIS) tools in the process of verification of historical cartographic representations is not to be underestimated (Hawthorne 2011, Nita & Myga-Piątek 2012).

Lakes, as young elements of the landscape, are a subject to dramatic and rapid changes, which can be traced with the use of mentioned spatial materials and GIS tools. For example, the water surface area of Lake Udzierz decreased from 148.87 to 69.60 ha in the last century and that of Lake Mątasek from 29.5 to 0.64 ha. Such drastic morphometric changes in the case of mentioned lakes are, on the one hand, mainly due to poorly conducted drainage and, on the other hand, the eutrophication of water intensified by the anthropogenic impact (Fabich & Kwidzyńska 2012). The other example is the examination of the area of 25 lakes in the Mazurian and Pomeranian Lake District that decreased by 5.6%, while their volume has decreased by 9.9% in a period of over 50 years (Choiński & Ptak 2009). The processes of lake disappearance are responsible for parallel processes related to shallowing of lake bowls, and not only to shrinking of the shoreline. Reducing the volume of lake troughs adversely affects the natural resistance of lakes to degradation. The disappearance of lakes also contributes to the physiographic changes of the area (Marszalewski & Adamczyk 2004; Marszelewski 2005, Ptak 2013). Another hydrographic case is a drainage density in Tuchola Forest which has increased from 0.7 to 1.95 $km \cdot km^{-2}$, while the area of lakes share has increased from 1.81 to 1.93% only. However, the number of reservoirs has increased from 36 to 675 in a period of 110 years (Szumińska & Absalon 2012).

The study aims at analysing the changes in the arrangement and density of the hydrographic network of the headwaters of Piwonia river. The work contains a comparison of a pre-war state of hydrographic network with a current one, seriously modified during the hydrotechnical works in 1960s. The analysis of river network density was conducted using ArcGIS on the base of maps. The paper presents changes in river network density as a function of distance increasing from the central point. The study results in development of methodology of melioration activities assessment based on cartographic materials. The analyzes were carried out for the period 1938-2011 (73 years).

2. Material and methods

Hydrographic network in Poland was formed mainly as a result of the landforms development in the Tertiary and Quaternary. Its main elements are: rivers, lakes, ponds, wetlands, groundwater, springs, artificially constructed canals and reservoirs. One of the indicators characterizing the river network is its density. There are many different methods for calculating the density of river network. The study uses the Neumann method, which has the widest scope of applications among all other methods. The density according to the Neumann method is measured by the total length of rivers in kilometres per square kilometre (Gibson et al. 2004).

The analysed catchment is located approximately 30 km north-east from the city of Lublin. It is an area of the headwaters of Piwonia river catchment of 24.5 km^2, located near Uściwierskie Lakes in Western Polesie. There are five lakes within studied area: Bikcze, Nadrybie, Uściwierz, Uściwierzek, and Ciesacin with a total area of 3.83 km^2 and 11.23 km^2 of direct catchment (Czarnecka 2005, Grzywna 2013).

The surface geological layer is dominated by sandy and silty sediments of last two glacial periods when the analysed area was beyond the glaciation extent. The holocene organogenic sediments in a form of vast peatlands and by-lake plains also play an important role. The height differences are not big with a dominant role of erosional and depositional plains. Low slope values causing a slow outflow and a low permeability are reasons for shallow groundwater (Harasimiuk et al. 1998).

The analysis of river network density was conducted using ArcGIS and information gathered from cartographic materials. The study was based on topographic maps in a uniform scale of 1: 000 from 50 years in 1938 and 2011. The statistical analysis used the full study period (73 years), for short periods of little change.The past state was vectorised using the 1:50 000 topographic map of 1938 by Military Geographical Institute (WIG). The modern one was based on the visualisation of VMap L2 topographic database of 2011. Both materials were georeferenced into the WGS. The course of river lines was transferred to numerical maps and their lengths were measured and saved as attributes of objects. The next step was to create equidistant from the research area central point (φ = 51°22'04'' N, λ = 23°04'23'' E). The zones covered 4 kilometres in diameter with step every 250 meters and with limitation to the catchments area. Lakes areas were subtracted from the zones. Centroids representing specific properties were used for statistical calculations. The river was fragmented with the help of the centroid line. Then, in separated 250 m wide belts, the length of rivers was determined and their density was calculated.The river network was then intersected with the zones resulting in lengths values in every zone. They were used to calculate river network density and create a choropleth map showing the density in square fields of 250 m side. It can also be illustrated by means of variogram, presenting a change of network density with growing distance from the given centre point.

Three different spatial statistics were calculated next to assess changes in network of watercourses in the examined region. They were used to compare patterns in structure of river network density. For these tests, area of catchment was divided by criss-cross net on square fields of 250 m side. The results are illustrated by means of variogram.

Pearson's test (Verburg et al. 2006) was used to analyse the similarity level of watercourses distribution in years 1938 and 2011. CRH procedure was applied for testing significance correlation of spatial data (Clifford et al. 1989).

Ripley's K test (Dale 1999, Próchnicki 2011) was used for analysing concentration of watercourses in function of distance. It was compared to a hypothetical, ideally random sample with Poisson distribution. Regarding shape of catchment, confidence areas were obtained by means of 999 permutation of distribution of watercourses.

3. Results

3.1. Transformation area

The hydrographic phenomena in Poland are formed above all under the influence of climate, geological structure, topography and evaporation of surface water (Wilgat 1954).

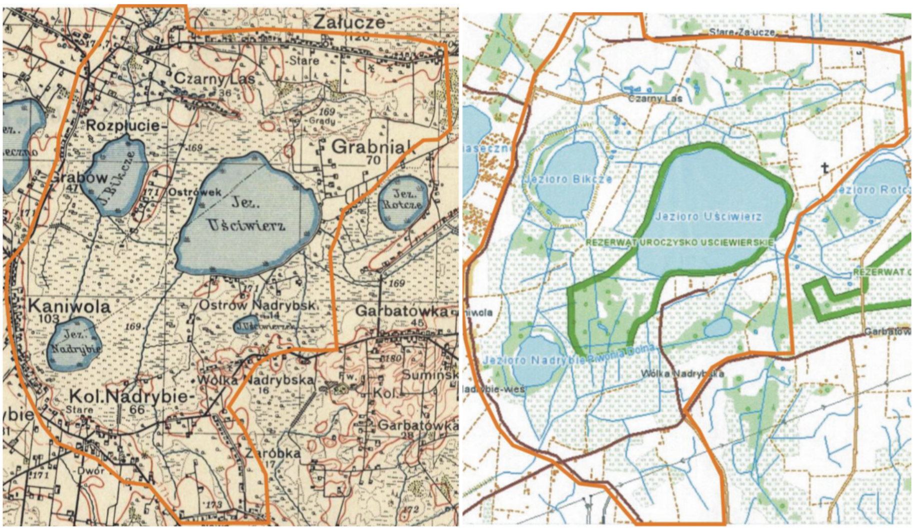

Fig. 1. The hydrographic network of the research area (1938, 2011), —— basin

In 1938, Piwonia river flew across the lakes (according to WIG map). In the 1960s, the water canal being a beginning of Piwonia Dolna river was traced, passing Nadrybie to the north and Bikcze and Łukie lakes to the west. As a result of hydro-technical works, the length of the river increased by 5.3 km, from 57.4 km to 62.7 km, and the springs were moved from Nadrybie Lake to

Uściwierzek Lake (Fig. 1). Reshaping of hydrographic system and construction of Wieprz-Krzna canal in 1954-61 resulted in burying 3 km of watercourses, including 1 km of canal built in the early 20th century, which formed part of Piwonia river. In addition, Bikcze lake was surrounded with dike and all lakes were surrounded by a network of peripheral canals. In the 1950s of the twentieth century, Bikcze Lake was surrounded with dike, its water surface was elevated and the lake was converted into a retention reservoir, while the river bed was risen (Michalczyk et al. 2011).

The largest transformations of hydrographic network in Poland took place in the 60s of the 20th century and were associated with the construction of water canals, river regulations and drainage of wetland areas (Miller 2005, Solon 2009). The construction of Wieprz-Krzna drainage system contributed to the negative changes in water conditions, causing a decrease in water level in lakes and in soil, as well as increased the rate of outflow, reduction of natural retention and introduction of external, highly eutrophic waters (Janiec 1993, Chmielewski 2009). It also caused an increase in the length of watercourses and ditches almost triply in this area. The mentioned contribution is also confirmed by very large changes in the hydrographic network in the catchment area of Uściwierskie lakes. The size of water reservoirs has slightly changed (Grzywna & Nieścioruk 2016). Some of them have completely changed the shape of the shoreline. The consequence was the reduction in water surface of lakes.

The melioration works changed the course of the river completely. The water ditch being the beginning of Piwonia river was traced near Bikcze and Nadrybie lakes and further into Uściwierzek Lake. As a result of this work, the 7.3 km section of the river was created within the analyzed catchment.

In addition to Piwonia river bed regulation, 40 km of new melioration ditches were built. Moreover, construction of Bogdanka – Wola Wereszczyńska Canal (KBWW) was completed in 1973. At present, this canal is heavily vandalized and even filled with rubble in some sections. Due to the lack of a proper exploitation and maintenance of water facilities, especially within the catchment, the secondary periodic flooding of the area occurs. The canal performs an emergency function of water supply during peat bog fires.

In the early 1990s, attempts to restoration both the river bed and drainage facilities were undertaken. Changing the environmental law in the year 2000 made it impossible to continue the implementation of the harmonization of nature and economy (Chmielewski 2009). In 2007, the whole group of Uściwierskie Lakes was classified as Nature 2000.

The analysis of the use of direct catchment of Uściwierskie Lakes reveals that the largest area (40%) is covered by grasslands. The high share of the water surface of up to 34% of the total catchment area also draws some attention. However, the area of studied lakes was gradually decreased from 4.25 km^2 in 1938 to

3.68 km^2 in 2011. The biggest absolute decrease can be observed for the largest Uściwierz lake. Its area decreased by 30.1 ha during 63 years. The most significant change in the environment occurred in case of Ciesacin lake. Its areas decreased by 90%. In 2011 it was only 0.2 ha of plant-covered water. Although the analysed area is characterized by the occurrence of poorly fertile brown and black soils developed from sandy and silty forms, 15% of it are arable lands (Wilgat 1954, Harasimiuk et al. 1998, Chmielewski 2009).

Length of the hydrographic network visible on maps increased from 19.7 km in 1938 to 55.8 km in 2011 year (without 5.5 km of KBWW), being the result of the construction of a drainage ditches system in the late 60s of the 20^{th} century. When analysing changes in the land-use structure of the catchment, it was found that the area of lakes decreased by 16.5% during 1938-2011. The open water surface of Ciesacin lake completely disappeared as a result of hydro-technical works. The history of changes in water relations in past 200 years in the analysed area (Radwan et al. 2002, Kowalewski 2012, Michalczyk et al. 2012, Grzywna 2013, Mięsiak-Wójcik et al. 2014, Grzywna & Nieścioruk 2016, Kowalewski & Żurek 2016, Michalczyk et al. 2017).

3.2. Statistical analysis

As a result of fragmentation in centroid belts, river sections were obtained for which the hydrographic network density was calculated (Fig. 2). In 1938 were identified: 11 fragments were identified with a density below 1 $km \cdot km^{-2}$, 18 with a density 1-2, 34 with a density 2-3, 42 with a density 3-5 and 5 with a density above 5 $km \cdot km^{-2}$. In 2011, 90 fragments with a density of 1-2 $km \cdot km^{-2}$, 46 with a density of 2-3, 36 with a density of 3-5 and 13 with a density of over 5 $km \cdot km^{-2}$. The density of hydrographic network increased from 0.98 $km \cdot km^{-2}$ in 1938 to 2.77 $km \cdot km^{-2}$ in 2011 year. The number of river fragments increased from 110 to 185. Obtained density of watercourses in function of distance from catchment centre shows an increase of its values in year 2011. Nowadays its values hardly ever go below 2000 meters per square kilometres, while the density for 1938 is lower than 1200 in all zones with no observation in first two zones. The general spatial character of density changes is similar, with low values in first zones preceding areas of the highest values and slow decrease of density towards edges of the research area (Fig. 3). The difference, beside values themselves, is about 2500 meters shift of both diagrams, as the 1938 peaks slightly at 1.5 km diameter zone (with 1.2 $km \cdot km^{-2}$) and the modern one at 2.75 km (with 3.7 $km \cdot km^{-2}$). In both cases, the density of the water network has similar values – density clusters in 1938 and 2011 were similarly distributed. The tendencies described are also observable at the visual assessment of source maps.

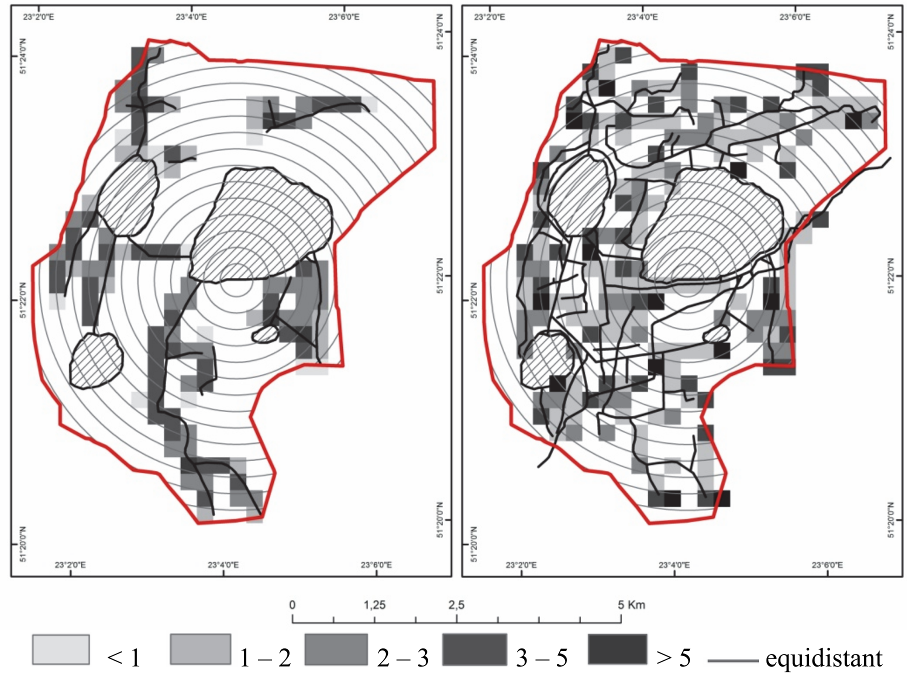

Fig. 2. River network density in 1938 and 2011 [km·km^{-2}]

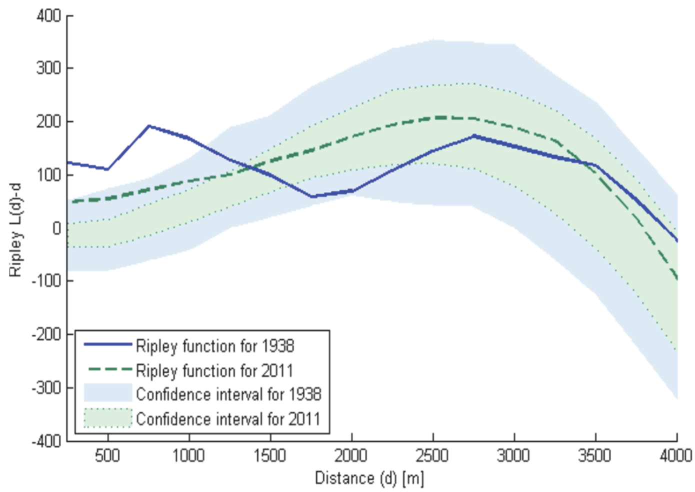

Fig. 3. Variogram as an outcome of Ripley's K test

Spatial distribution of river network in successive time pairs was analysed with the Pearson's test. Pearson's correlation coefficient *r* in Uściwierskie Lake for the pair 1938-2011 was significant (p-value < 0.05) amounted to 0.5. A significant correlation is a result of the development of the existing water network. Not very high value of Pearson's correlation coefficient indicates the development of existing watercourses and the emergence of new ditches.

Ripley's K test was performed on the map of watercourses intersected by criss-cross network with squares of 250 m side. In examined catchment, Ripley's K test for both years shows existence of watercourses clusters (statistically significant test values at the distance up to 1250 meters). Due to fewer number of watercourses there is a wider confidence area for test values for year 1938.

4. Conclusions

The usefulness of both maps in environmental management is unquestionable, and their complementary use guarantees comprehensive survey of issues connected with natural environment of a given area. The implications of density factor change is often a subject of research on local and regional scale, with focusing on lakes drainage, anthropogenic eutrophication, lowering the water level, land use or renaturalization of river network (Querner et al. 2004, Sidle et al. 2007, Du et al. 2011).

Length of the analysed hydrographic network increased from 19.7 km in 1938 to 55.8 km in 2011 year according to maps. The area of studied lakes was gradually decreased from 4.25 km^2 to 3.68 km^2. When analysing changes in the catchment land-use structure, it was found that the area during 1938-2011 decreased by 16.5%. It justify describing the spatial network structure in both districts as clusters of regular size and distribution. Pearson's correlation coefficient for the pair 1938-2011 was significant and amounted to 0.5 pointing emergency of additional ditches.

Generally, lakes in Poland show the tendency to decrease both in area and number. Lake basins are subject to constant evolution. Causes of changes are both natural and human activity. Among natural factors the most important role play: water level fluctuation, climate changes, depth of lake basin, hydrographic network etc. The most important anthropogenic factors are: hydrotechnical works, deforestration and agriculture.

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Abstract

The analysis of river network density was conducted using ArcGIS and information gathered from cartographic materials. The past state was vectorised using the 1:50 000 topographic map of 1938 by Military Geographical Institute. The modern one was based on the visualisation of VMap L2 topographic database of 2011. Both materials were georeferenced into the WGS. The next step was to create equidistant from the research area central point. The zones covered 4 kilometres in diameter with step every 250 meters and with limitation to the catchments area. Lakes areas were subtracted from the zones. The river network was then intersected with the zones resulting in lengths values in every zone. They were used to calculate river network density. It can be illustrated by means of variogram, presenting a change of network density with growing distance from the given centre point. The largest transformations of hydrographic network took place in the 1960s of the 20th century due to the construction of Wieprz-Krzna Canal, Piwonia regulation, and wetlands drainage. The river length increased by 5.3 km, and its headwater was transferred from Nadrybie Lake to Uściwierzek Lake. Density of hydrographic network increased from 0.98 km·km^{-2} in 1938 to 2.77 km·km^{-2} in 2011 with the decrease of area of lakes by 16.5%. On the basis of spatial statistics, the spatial network structure in examined area in both years can be described as clusters of regular size and random distribution. Pearson's correlation coefficient for the 1938 and 2011 is significant and amounts to 0.5 which is the result of new watercourses emergence. Ripley's K test shows the most significant growth of clusters at the distance of about 2.75 km from the centre of the region.

Keywords:
river network, lakes drainage, Ripley's K test, Pearson's test

Przekształcenia gęstości sieci hydrograficznej w zlewni górnej Piwonii

Streszczenie

Analizę gęstości sieci rzeki przeprowadzono przy użyciu ArcGIS i informacji zebranych z materiałów kartograficznych. Materiał historyczny został wektoryzowany za pomocą mapy topograficznej Wojskowego Instytutu Geograficznego w skali 1:50 000 z 1938 roku. Materiał współczesny opierał się na wizualizacji topograficznej bazy danych VMap L2 z 2011 roku. Oba materiały zostały przekształcone do układu WGS. Następnym krokiem było utworzenie punktu centralnego obszaru badawczego. Następnie, z ograniczeniem do obszaru zlewni, wyznaczono strefy do 4 kilometrów średnicy, z krokiem co 250 metrów. Obszary jezior zostały wycięte ze stref. Wówczas sieć hydrograficzna została przecięta strefami na oddzielne fragmenty. Wykorzystano je do obliczenia gęstości sieci rzecznej. Można to zobrazować za pomocą wariogramu, przedstawiając zmianę gęstości sieci z rosnącą odległością od wyznaczonego punktu środkowego. Największe przekształcenia sieci hydrograficznej miały miejsce w latach 60 XX wieku, ze względu na budowę Kanału Wieprz-Krzna, regulację Piwonii i odwadnianie terenów podmokłych. Długość rzeki wzrosła o 5,3 km, a jej początek został przeniesiony z jeziora Nadrybie do jeziora Uściwierzek. Gęstość sieci hydrograficznej wzrosła z 0,98 $km \cdot km^{-2}$ w 1938 roku do 2,77 $km \cdot km^{-2}$ w 2011 roku. W okresie 1938-2011 nastąpił spadek powierzchni jezior o 16,5%. Na podstawie statystyk przestrzennych strukturę sieci przestrzennej w badanym obszarze w obu okresach można określić jako klastry o regularnym rozmiarze i rozkładzie losowym. Współczynnik korelacji Pearsona dla lat 1938-2011 jest wysoki i wynosi 0,5, co jest wynikiem pojawienia się nowych cieków wodnych. Test Ripleya K pokazuje najbardziej znaczący wzrost skupisk w odległości około 2,75 km od centrum regionu.

Słowa kluczowe:
sieć rzeczna, odwodnienie jezior, test K Ripleya, test Pearsona

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Impact of Compression on Bed Porosity in Gravitational Filtration Process

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1. Introduction

Filtering layer makes the most important part of a filter and the device efficiency as well as filtrate parameters depend on its correct selection, therefore, it should well stop suspended solids and make little hydraulic resistance for filtrate stream. Permeability of such layers in the case of suspended matter liquid phase and its ability to stop the solid phase depends on the size and shape of grain comprising the filtering layer. Flow of the medium in the gravitational filtration process is a hydrodynamic phenomenon velocity of which is directly proportional to pressure difference occurring on both sides of the filtering layer and inversely proportional to the resistance that such medium meets during flow through, among other things, pores of the filtering layer. Filtration velocity rises more slowly than the pressure difference increase because in the case of increasing of the pressure difference, porosity of the filtering layer decreases and resistance increases (Ciborowski 1973, Piecuch 2007, Rup 2006). Process equations describe filtration in partly idealised conditions in which impact of the process distorting factors is eliminated. Also in practical considerations an assumption is being made that porous granular bed is not compressed during the filtration process accomplishment. However, thickness of the filtering layer decreases to a small degree under impact of various factors (e.g. flow, pressure difference), resulting in increase of compression coefficient and bed total resistance (Domski et al. 2017, Głodkowska et al. 2018). Bed porosity as well as filtration and permeability coefficients decrease. Therefore, the primary filtration equations cannot always be used without making proper corrections (Żużikow W. A. 1985, Piekarski 2009).

In this paper variation of values of selected parameters, i.e. bed porosity, filtration coefficient, total resistance and volumetric flow rate depending on the change of bed compression as a factor distorting the gravitational filtration process are presented in mathematical form.

2. Methodology of research

Quartz sand with a mass of 1000 g used in the tests was subjected to grain size analysis. The data from screening were entered into FILTRA software, which computed characteristic diameters and derived filtration bed grain size distribution graphs. The filtration bed was then put in a water-filled column of 5 cm diameter and subjected to backwashing. In the next stage bed height was corrected up to 30 cm. The initial difference between the water-table height in the filtration column and filtrate in overflow tank was 36 cm. The bed infiltration column was subjected to dynamic compacting, after each test series, obtaining various bed compression height values.

The independent variable parameter in the gravitational filtration process was the different bed height obtained in dynamic compaction, hence, the initial difference of water-table height in the filtration column and in the overflow tank as well as compression coefficient value. However, the main variable resulting parameter of the process was the average time of water-table lowering in the filtration column. The process parameters were entered into FILTRA software, which computed the filtration coefficient values based on the variable pressure method and through application of Hazen, Krüger, Seelheim and Slichter empirical formulas (Piekarski 2009). Numerical application based on the Krüger and Slichter formula provided bed porosity value. However, based on the values of filtration and dynamic viscosity coefficients as well as medium density, the software computed the filtration bed permeability coefficient value. Furthermore, the application derived the total bed resistance and volumetric flow rate values (Piekarski 2009).

3. Test results and interpretation

The grain size nonuniformity coefficient of the tested bed, computed from the grain size analysis (Figure 1), amounted to U=2.39. Grain reliable diameter d_M was 376 μm, modal diameter d_{MO} reflecting the maximum of mass share curve $f_N(d_i)$ was 250 μm. Medial diameter d_{ME} equal to 50% of mass share was 467 μm, whereas: d_{10}=220 μm, d_{20}=296 μm and d_{60}=525 μm.

The non-compressed bed filtration coefficient after intense backwashing (through the bottom of the bed) computed from laboratory tests through application of the variable pressure method was 3.53E-4 m/s. After taking into account of temperature value (T=22ºC) density of water directed to the filtration process was 997.79 kg/m^3 and the dynamic viscosity coefficient value was 9.55E-004 Pa·s. Hence, the computed value of the permeability coefficient was 3.44E-011 m^2. Based on the grain size nonuniformity coefficient amounting to U=2.39, empirical coefficient value C_H=463 was adopted, so the filtration coefficient value based on Hazen formula was 3.53E-004 m/s. However, the filtration coefficient value based on Seelheim formula was 1.06E-004 m/s, and according to Krüger – 3.44E-004 m/s. Based on Slichter empirical formula, the computed filtration coefficient value was 3.59E-004 m/s.

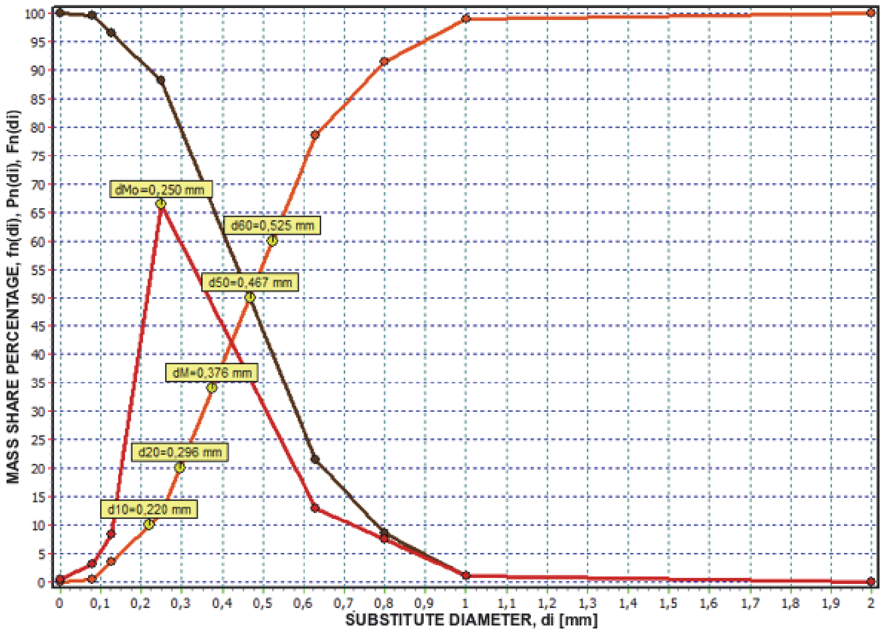

Fig. 1. Filtration bed granular composition analysis with indication of characteristic diameters

After transformation of Krüger and Slichter formulas the calculated value of bed porosity amounted to 0.44. The substitute diameter (taking into account bed porosity value 0.44 and equivalent diameter 288 μm) was 151 μm, hence, according to Kozeny-Carman empirical formula, the permeability coefficient value was 3.44E-11 m^2, being equivalent to the value computed through application of the variable pressure method amounting also to 3.44E-11 m^2. The filtration bed total resistance value was 4.24E9 $N{\cdot}s/m^5$, whereas the value of volumetric flow rate was 9.24E-7 m^3/s.

Table 1. Results of bed height H [mm] change impact on the values of average time of medium-table lowering t [s], porous filtration bed compression coefficient x [%], filtration coefficient K [m/s], permeability coefficient k [m/s], bed total resistance Rz [N·s/m^5], bed porosity ε [-] and volumetric flow rate qv [m^3/s] due to bed compression in gravitational filtration process

Parameter	Symbol	Unit	Bed height H [mm]				
			300	290	280	270	268
Surface lowering	L	[mm]	0	10	20	30	32
Bed compression	x	[%]	0.00	3.33	6.67	10.00	10.67
Average time of medium-table lowering	t	[s]	39	58	72	82	83
Bed porosity	ε	[-]	0.44	0.39	0.36	0.34	0.33
Filtration coefficient ($\cdot 10^{-4}$)	K	[m/s]	3.53	2.39	1.78	1.52	1.48
Permeability coefficient ($\cdot 10^{-11}$)	k	[m^2]	3.44	2.23	1.70	1.47	1.44
Bed total resistance ($\cdot 10^{9}$)	Rz	[N·s/m^5]	4.24	6.32	7.84	8.92	9.03
Volumetric flow rate ($\cdot 10^{-7}$)	qv	[m^3/s]	9.24	6.04	4.74	4.06	3.99

Due to dynamic compaction originating from 3.33% compression, bed surface height was decreased by 10 mm. This resulted in reduction of the filtration coefficient values by 1.14E-4 m/s and permeability coefficient by 1.21E-11 m^2. Porosity decreased by 5% (Figure 2). The total resistance value increased by 2.08E9 N·s/m^5, which finally caused reduction of the volumetric flow rate value by 3.20E-7 m^3/s (Figure 3). Following further compaction bed surface height was reduced, with relation to its initial value, by 20 mm. In this particular case the bed was compressed by 6.67%. Decrease of the filtration coefficient value by 1.75E-4 m/s and permeability coefficient by 1.74E-11 m^2 was found. Porosity decreased by 8%. The total resistance increased by 3.60E9 N·s/m^5, whereas the volumetric flow rate value decreased by 4.50E-7 m^3/s.

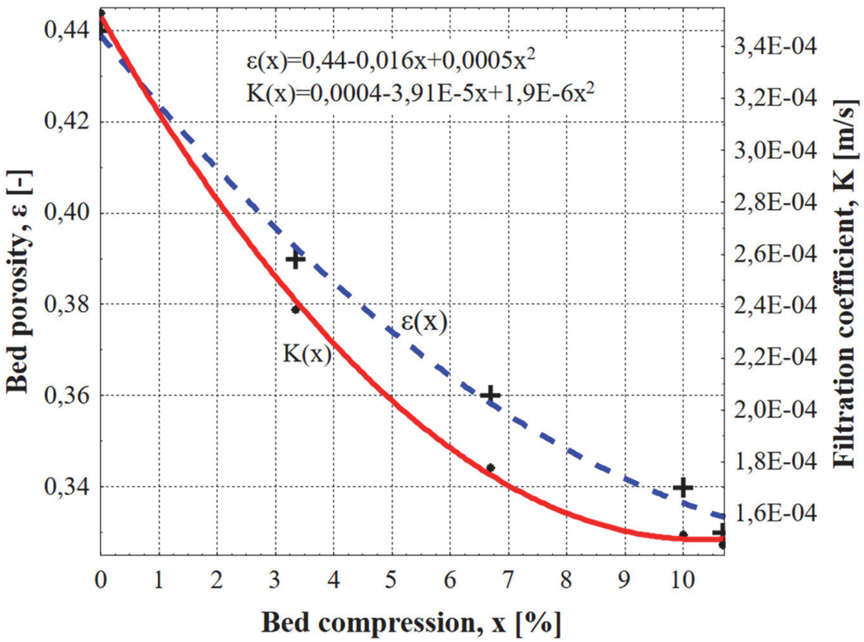

Fig. 2. Impact of bed compression value change x [%] on the change of filtration bed porosity value ε [-] and filtration coefficient K [m/s] in the gravitational filtration process

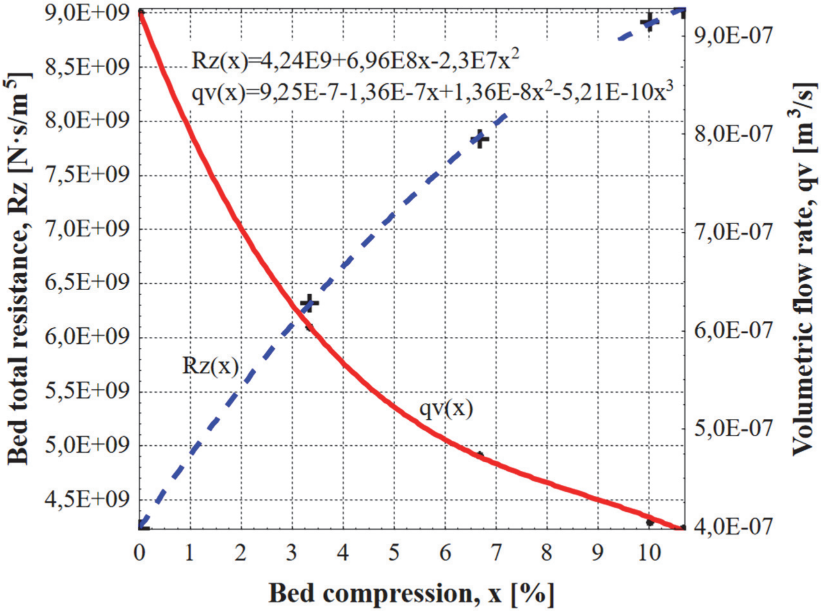

Fig. 3. Impact of bed compression value change x [%] on a) the change of bed total resistance value Rz [N·s/m^5] and volumetric flow rate qv [m^3/s] in the gravitational filtration process

In the subsequent stages of this research work, volume of free spaces in the filtering layer porous structure decreased due to further dynamic compaction (Table 1), which resulted in the bed surface lowering max. by 32 mm. This resulted, finally, in increase of compression by approximately 11% and total resistance by 4.79E9 N·s/m^5. Values of filtration coefficient decreased by 2.05E-4 m/s and permeability – by 2.00E-11 m^2. Porosity decreased by 11%. Finally, the volumetric flow rate decreased by 5.25E-7 m^3/s.

At the second stage of tests, empirical equations presented in Figures 2 and 3, were checked. To do that, the filtration bed was subjected again to intense backwashing (through the bottom of the bed) and tests for change of porosity and volumetric flow rate values, depending on the change of compression values in conditions different to those in the previous test part, were performed. FILTRA software computed bed porosity through Slichter formula transformation whereas the volumetric flow rate was computed based on Darcy equation. Bed total resistance occurring in the equation was computed by the application using the compression coefficient values variable. The test results are presented in Table 3.

Tab. 3. Test results for impact of bed compression change on bed porosity values change, total resistance and volumetric flow rate in the gravitational filtration process in model and real conditions

Bed compression	Bed porosity	Bed total resistance	Volumetric flow rate	
			Model conditions	Real conditions
x	ε	R_Z ($\cdot 10^9$)	q_v ($\cdot 10^{-7}$)	
%	-	$N\cdot s/m^5$	m^3/s	
0.00	0.44	4.24E+09	9.25	9.19
1.67	0.41	5.34E+09	7.33	7.17
5.00	0.37	7.15E+09	5.20	5.30
8.33	0.34	8.44E+09	4.35	4.21

Based on the graph presented in Figure 4 it can be stated that as compression values increased from 0 to 8.33, the volumetric flow rate calculated from the model decreased from 9.25E-7 m^3/s to 4.35E-7 m^3/s, e.g. by 4.9E-7 m^3/s (approximately 47%), whereas in laboratory tests similar change was noted within the range from 9.19E-7 m^3/s to 4.21 m^3/s, i.e. by approximately 4,98E-7 m^3/s (approximately 46%).

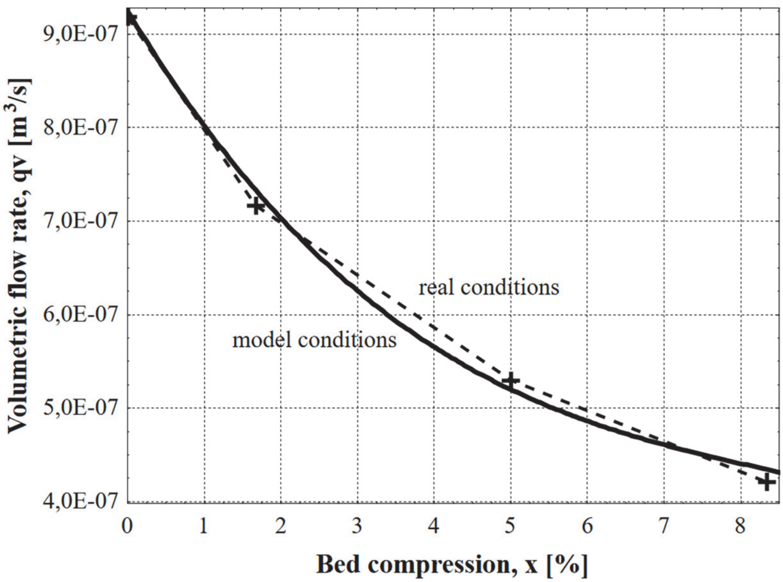

Fig. 4. Graph illustrating impact of bed compression values change x [%] on volumetric flow rate values change qv [m^3/s] in model and real conditions

4. Conclusions

Based on the research work performed it can be stated that:

1. Filtration bed gets, due to action of various factors, compressed to insignificant degree. Reduction of its thickness, causes, depending on the shape and size of grain making the filtering layer, decrease of porosity, therefore, decrease of filtration and permeability coefficients values and increase of bed resistance value.
2. Due to compression phenomenon within the range from 0% to approximately 11%, amount of free spaces in the filtering layer porous structure decreased, which is confirmed by decrease of porosity coefficient values within the range from 0.44 to 0.33. Consequently, decrease of values of filtration coefficient (from 3.53E-4 m/s to 1.48E-4 m/s) and permeability coefficient (from 3.44E-11 m^2 to 1.44E-11 m^2) and increase of total resistance values (from 4.24E9 $N \cdot s \cdot m^{-5}$ to 9.03E9 $N \cdot s \cdot m^{-5}$) was found.
3. It is well-founded to use in the equations pertaining to filtration bed porosity computation such parameter as bed compression. Furthermore, mathematical equations originating from polynomial regression describing change of resulting variable parameter values for porosity, filtration and permeability coefficients as well as total resistance depending on bed compression values change can be used with sufficient accuracy in description of the gravitational filtration phenomenon.
4. Analysis of bed porosity, depending on its compression in the gravitational filtration process, should be further developed to a broader extent, in particular, with relation to the impact of solid phase occurring in the medium directed to the process on bed compression because it has a significant impact on the filtration process type.

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Abstract

Gravitational filtration process velocity is directly proportional to the pressure difference occurring on both sides of the filtrating layer and inversely proportional to the resistance that the medium meets during its flow through filtering layer pores. Velocity of filtration increases at a smaller rate than the pressure difference increase because in the case of the pressure difference increasing, filtrating layer porosity decreases and resistance increases. Therefore, correct selection of the porous layer has impact on the filtration device efficiency and filtrate parameters, so, it should stop suspended solids and generate insignificant hydraulic resistance to the filtrate stream. Often an assumption is made in practical analyses that granular porous beds do not get compressed during filtration process. However, due to action of various factors, thickness of the filtrating layer reduces resulting in increase of compression and bed total resistance. Bed porosity and filtration, as well as permeability coefficients values, decrease. Change of bed porosity value can be determined through mathematical approach depending on, among other things, bed compression change as gravitational filtration process distorting factor.

Keywords:
gravitational filtration, bed porosity, bed compression, mathematical modelling

Wpływ kompresji na porowatość złoża w procesie filtracji grawitacyjnej

Streszczenie

Szybkość procesu filtracji grawitacyjnej jest wprost proporcjonalna do różnicy ciśnień powstającej po obu stronach warstwy filtrującej i odwrotnie proporcjonalna do oporu jaki napotyka medium w trakcie przepływu przez pory warstwy filtrującej. Szybkość filtracji wzrasta wolniej niż zwiększa się różnica ciśnień, ponieważ w przypadku zwiększania różnicy ciśnień maleje porowatość warstwy filtrującej i wzrasta opór. Od prawidłowego doboru warstwy porowatej zależy wydajność urządzenia filtracyjnego oraz parametry filtratu, dlatego powinna ona zatrzymywać cząstki stałe z zawiesiny oraz generować nieznaczny opór hydrauliczny strumieniowi filtratu. Często w analizach praktycznych zakłada się, że ziarniste złoża porowate w trakcie procesu filtracji nie ulegają kompresji. Jednak na skutek działania różnych czynników zmniejsza się grubość warstwy filtrującej, czego efektem jest wzrost kompresji oraz oporu ogólnego złoża. Zmniejsza się porowatość złoża oraz wartości współczynników filtracji i przepuszczalności. W ujęciu matematycznym zmianę wartości porowatości złoża można wyrazić między innymi w zależności od zmiany kompresji złoża jako czynnika zniekształcającego proces filtracji grawitacyjnej.

Słowa kluczowe:
filtracja grawitacyjna, porowatość złoża, kompresja złoża, modelowanie matematyczne