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Part 1.

Table of Contents for Part 1

MIDDLE POMERANIAN SCIENTIFIC SOCIETY OF THE ENVIRONMENT PROTECTION

Rocznik Ochrona Środowiska

Volume 21. Year 2019 ISSN 1506-218X 14-28

Global Assessment of Industrial Expansion for Minimizing Environmental Impacts Utilizing the Principles of Mining and Logistics

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1. Introduction

The environmental aspects of mining and quarrying are a focus of experts worldwide. They are well aware of the need for compatibility between the extractive industries and the environment. Appropriate solutions and methods are sought to ensure a sufficient supply of raw materials, but there is also focus on the restoration and conservation of nature, natural resources and the environment.

The impacts of mining industry on the landscape are examined in the article "Experiences of voluntary early participation in Environmental Impact Assessments in Chilean mining" (Ocampo-Melgar et al. 2018).

The document "Knowledge coproduction in environmental impact assessment: Lessons from the mining industry in Panama" an explores issues related to the mining sector and environmental impact assessment for the proposed copper and gold mine in Panama (Mitchell & Leach 2019) and with the homogeneous production processes, simulation of production in manufacturing systems and approaches to their management deal authors Malindzak et al. 2017 and Trebuna et al. 2014.

The conference paper "Ensuring the Environmental and Industrial Safety in Solid Mineral Deposit Surface Mining" deals with the mining of raw materials in terms of safety and efficiency (Trubetskoy et al. 2017). A similar topic "The impact of mining changes on surrounding lands and ecosystem service value in the Southern Slope of Qilian Mountains" has been addressed by Qian et al. 2018.

The main environmental challenges of the gold mining sector in Colombia are the topic of "Gold mining as a potential driver of development in Colombia: Challenges and opportunities" (Betancur-Corredor et al. 2018).

Solutions to these issues are sought by Kozioł et al. 2016 in the study "Mining of aggregates in Poland – Opportunities and threats", Sajinkumar et al. 2014 examines the effect of quarrying in Banasuramala, and the expert Bergstrom in his paper "The curious case of Cuyuna: Re-Envisioning former extractive sites to stimulate local communities" focuses on ecological revitalization (Bergstrom 2017), and the natural process of revitalization following extraction is also examining by Gawałkiewicz 2018 and ecological innovation approach is examining by Loučanová & Olšiaková 2019.

Failure to maintain an ecological balance in an industry area is also the topic addressed by Pohrebennyk and Dzhumelia in the chapter of their book "Environmental assessment of the impact of tars on the territory of the Rozdil state mining and chemical enterprise "Sirka" (Pohrebennyk & Dzhumelia 2020).

Environmental impacts of raw materials are examined by the article "Temporally explicit life cycle assessment as an environmental performance decision making tool in rare earth project development" (Pell, Wall et al. 2019).

A further study on "A hybrid semi-quantitative approach for impact assessment of mining activities on sustainable development indexes" was prepared to develop a general impact assessment process for certain environmental indicators in mining (Amirshenava & Osanloo 2019).

The influence of mining on the environment was also of interest to Parviainen and Loukola-Ruskeenia in the article "Environmental impact of mineralised black shales" (Parviainen & Loukola-Ruskeeniemi 2019).

Reducing the negative environmental impact of mining activities is also the topic of "Energy storage in underground coal mines in NW Spain: Assessment of an underground lower water reservoir and preliminary energy balance" (Menéndez et al. 2019). Other interesting publications in this area are "Technical quality of fauna monitoring programs in the environmental impact assessments of large mining projects in south-eastern Brazil" (Dias et al. 2019) and "Evaluation of the environmental impact assessment (EIA) of Chinese EIA in Myanmar: Myitsone Dam, the Lappadaung Copper Mine and the Sino-Myanmar oil and gas pipelines" (Aung 2019).

The importance of planned and managed raw material extraction with regard to environmental protection is also addressed in the publication "Environmental optimisation of mine scheduling through life cycle assessment integration" (Pell, Tijsseling et al. 2019), while Polish experts focus on mining waste in their contribution "Screening Life Cycle Assessment of beneficiation processes for Rare Earth Elements recovery from secondary sources" (Grzesik et al. 2019), Czech specialists focus on raw materials evaluation criteria in their contribution "Determination of importance of ore raw materials evaluation criteria" (Haverland & Besta 2018, Vilamova et al. 2016).

The effects of mining on the health of the population were collated by experts Nkyekyer and Dannenberg in the report “Use and effectiveness of health impact assessment in the energy and natural resources sector in the United States, 2007–2016” (Nkyekyer & Dannenberg 2019) and in the contribution “Asbestos exposure and minimization of risks at its disposal by applying the principles of logistics” (Straka et al. 2016).

The case study “Environmental impact assessment studies for mining area in Goa, India, using the new approach” deals with human activities in mining, which have the most disruptive and catastrophic environmental impacts, while greatly affecting the environmental, economic and social elements of the area (Sarupria et al. 2019).

2. Theoretical base

2.1. Remediation as a means of environmental protection

For this article, remediation can be defined is a set of technical remedies designed to reduce or eliminate pollution of soil, rock, groundwater and surface water resulting from inappropriate disposal of waste from extraction, or to prevent the further spread of pollution or threats to human health.

Remediation ensures the removal or fixing of hazardous substances that leak or have the potential to leak into the environment outside the structure of the repository or to reduce their concentration to an acceptable level. Remediation is always where work is done to remove or reduce the contamination of the natural environment, including its safe and long-term isolation in a limited area.

It is important to define the significance of recultivation for this article. This term refers to the treatment of a site affected by a repository that allows the resumption of a satisfactory state with particular emphasis on soil quality, wild flora and fauna, natural habitats, freshwater ecosystems, landscapes and suitable land use.

It is necessary to realize the main difference between remediation and recultivation. The problems that are most often encountered in extractive industry need to be prevented by recultivation, but if they are already present, they need to be removed through remediation.

As we know recultivation technology must always be designed with regard to future land use. However, in our case, it is industrial activity in the mining sector and the extension of mining in the mining area Košice IV – Hradová, therefore we are dealing with a remediation process, as during the extraction processes problems have occurred which were not envisaged and therefore not addressed by the recultivation plan.

The location of the discussed area, the stone quarry in Košice IV – Hradová for the extraction of granodiorite building stone, is determined by the local accumulation of mineral resources in sufficient quality and quantity for extraction. The projected maximum annual production capacity by 2021 is 290 000 tons/year.

The deposit is part of the resource base of the eastern edge of the Slovak Ore Mountains and its wider surroundings. Remediation of the steep slope above national road III/3390 is conditioned by the morphology of the terrain at the intersection of the Hornád River through "Black Mountain" and the route of the national road Košice-Sever to Kostoľany nad Hornádom, where the slopes of the granodiorite body of Hradová (the massif of the Black Mountain in the Vepor zone) are steep and unstable in terms of slope movements and rock rubble.

2.2. Defining the requirements of industrial activity

In 2011, an extraordinary situation was declared in Eastern Slovakia due to the active landslides on the Kostoľany road in Košice. The operation of the quarry located near the affected site ensured that the slope was remediated.

On the left side of the road there is a steep slope, which was strongly disturbed by landslides. Frequent slope landslides on the steep slope resulted in the rocks and rocky blocks falling from the highest and steepest slopes, weighing up to several tons.

We can ascribe the cause of these events to strong erosive activity, especially the intense alternation of positive and negative temperatures. The heavily eroded steep slope can cause direct threats to the health and life of passers-by. In order to increase safety, in 2012, traffic was reduced to only one lane controlled by traffic lights (Dilský 2012).

2.3. Defining environmental requirements

Important factors in terms of environmental requirements include safety, stability, biotope, logistics and the emissions factor. In terms of the further utilization of the quarry, the emissions factor is particularly important. The total annual emissions of the site under consideration are 4 167.6 kg or 2.0838 kg/h (Table 1).

3. Case study

3.1. Project to expand industrial activity in the particular region – capacity of deposit

The subject of the geological task was the verification of new deposits of building stone west of the existing area of extraction at Košice IV – Hradová. The goal of the geological task is to verify 5 million m^3 of building stone deposits.

Table 1. Emissions of pollutants from the quarry

Source	Pollutant	Emissions (kg/h)	
		Short-term	Long-term
Diesel mechanisms	CO	0.0413	0.0138
	NO_x	0.2583	0.0861
	SO_2	0.0517	0.0172
	PM (particulate matter)	0.0734	0.0245
	TOC (total organic compounds)	0.0059	0.0020
Stone extraction and processing	PM	2.0838	0.6946

The solution of the geological task did not result in permanent interference with the environment. Boreholes were made on existing forest roads. After geological mapping (Fig. 1), geophysical profiles with respect to borehole localization were also identified. Boreholes were made after the completion and operational evaluation of geophysical works. This ensured optimum deployment of the exploration boreholes. In order to demonstrate the quality of building stone, a survey is the only way to verify building stone deposits, with the exception of extraction (EUROVIA – Kameňolomy, s.r.o. Košice 2010).

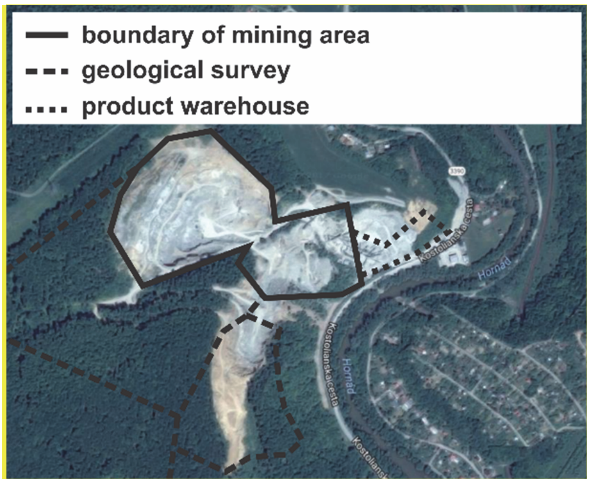

Fig. 1. Map of boundary of mining area and geological survey of Hradová quarry (EUROVIA – Kameňolomy, s.r.o. Košice 2017)

3.2. Possibilities of extending industrial activities – stabilization of deposits

The actual purpose of the activities under consideration is to expand the Košice IV – Hradová quarry and provide sufficient reserves of a mineral resource, namely granodiorite building stone, within the existing extraction area at Košice IV – Hradová, and especially outside it.

As mentioned earlier, for the expansion of extraction, it is necessary to focus on the proposal for stabilization of the slope, which consists of reducing the slope inclination by building terraces with a height of approx. 24 m on the slope at approx. 70°. The terraces are designed with a slope of 2.0% and a width of 23 to 40 m. A recultivation project has been prepared for this purpose. The work is being carried out in two stages.

In the first stage, the surface of the slope has been straightened so that it will be possible to build a protective barrier (Fig. 2), which is 2.0 m high, and will be able to capture loose boulders.

In the second stage, definitive recultivation of the slope will be performed, consisting of excavation work on the terraces from top to bottom. After the excavation is completed, recultivation will be carried out (Dilský 2012).

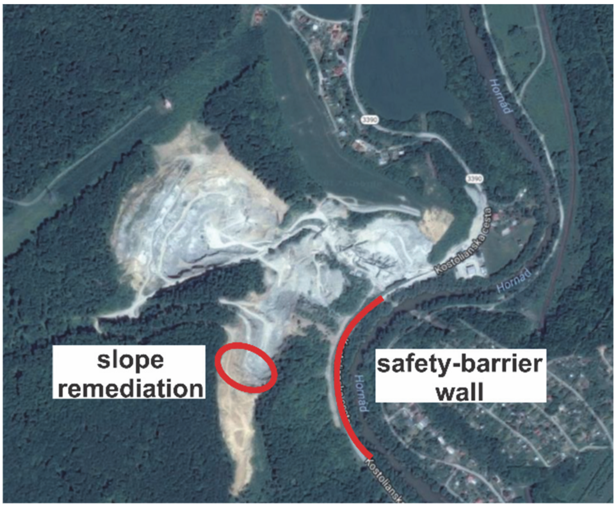

Fig. 2. Schematic representation of the slope remediation and safety-barrier wall (EUROVIA – Kameňolomy, s.r.o. Košice 2017)

Drainage on the site is solved with a single camber inclination towards the Hornád side of the road, as it is today. The plain was drained by the downward slope towards the Hornád River, then the area behind the protective-safety barrier, which is closer to the slope, is drained along the compacted slope of the barrier to the nearest passage. Earthworks on the building site consist of:

- Removal of soil from the slope on which the remediation was carried out, however, it was first necessary to deforest the slope.
- Tipping of earth to form the safety barrier.
- Excavating the slope to the level of the terraces
- Adding soil to the terraces based on the recultivation project, recultivation will be carried out in the future.
- Waste arising during the remediation of the slope will be collected in the area of the Hradová quarry together with the waste generated during the operation of the quarry.

Upon completion of the remediation of the slope, recultivation will be carried out, which will include the following parts based on the recultivation project:

- Adding soil.
- Planting forest stands – trees.
- Caring for tree stands for 3 years.
- Planting more trees.
- Recultivation will be carried out in two stages, as will the slope remediation itself.
- Total land area for recultivation is 80 500 m^2.

3.3. The benefits of increasing production

Based on the geological survey, a total calculation of geological reserves, including overburden, was carried out in the explored area. In the area or areas where the geological survey of deposits was carried out, the body of the deposit was divided using 12 sections into vertical blocks, the volume of which was calculated by the product of the average content of the adjacent sections and their distance. If the sections were less than 10° between each other, the following relationship (1) was used to calculate the section distances.

$$v = (h1 + h2) / 2 \tag{1}$$

where:
h1, h2 – the lengths of the perpendiculars defined at the centre of gravity of the respective profiles.

The method of parallel cuts can be justified by the simple and precise construction of the surfaces of the block of reserves in individual sections, where the accuracy of the calculation is proportional to the density of cuts, which is in the range of 50 m.

Formulas used to calculate reserves:

$$Q = \frac{(P1+P2)}{2} \text{ x } V \text{ (m}^3\text{)} \tag{2}$$

$$Q = \frac{(\text{P1+P2+}\sqrt{(P1\ x\ P2)})}{3} \text{ x } V \text{ (m}^3\text{)} \tag{3}$$

$$Q = \frac{P1 \text{ x } V}{2} \text{ (m}^3\text{)} \tag{4}$$

where:
Q – volume (m^3),
P1, P2 – area of block in adjacent sections (m^2),
V – distance between sections (m).

The equation from (2) above is used when the sectional area difference is less than 40%, equation (3) is used if the difference in sectional area is greater than 40% and equation (4) is used if the bearing body is in a single line.

3.4. Overall results and evaluation of calculations of reserves in the exploration area

During the geological survey, after extensive calculations and evaluation of the area, a total of 28 501 850 m^3 of mineral resources were verified. The exploration area of raw material of quality category I (block I / area I) contains 21 539 703 m^3. The exploration area also contains lower quality raw material in category II (block II / area II) with 6 962 147 m^3 of reserves (Gallo et al. 2016).

4. Results and discussion

4.1. Impacts on the environment, including in terms of long-term and other possibilities of expansion and liquidation of activities

The quarry has a negative impact due to the relatively high dust content that exceeds limit values. Near the quarry there is an about 60 m wide belt of forest, lining the river Hornád. The forest acts as a filter against the spreading of dust, reducing it by more than 50%. That is why we can assume that the quarry has a reduced impact on the environment from dust.

The actual operation of the quarry is static source of noise, which is related to the performance of surface extraction of stone, namely blasting and granulometric treatment of stone in the quarry. A permanent source of operating noise is the stone crushing line located in the current mining area. Another source of noise is traffic from road I/68. However, it should be emphasized, in particular, that damage to the health of the population around the site due to excessive noise is not likely.

The operation of the quarry affects the well-being and quality of life especially for several houses in the north-eastern part and for the gardens in the south-eastern part on the other side of the Hornád. Fig. 3 illustrates the situation indicating the distance to settlements, including the gardens, from the nearest place of extraction.

Fig. 3. Distance of settlements from the nearest place of extraction (EUROVIA – Kameňolomy, s.r.o. Košice 2017)

The transport of aggregates is performed along the I/68 road, which is the largest source of air pollution in the vicinity of the quarry at present. It is assumed that 2/3 of the stone transport goes towards Košice and 1/3 towards Kostoľany nad Hornádom. A total of 3,327 cars passed through the Košice – okolie road section per year, which is part of the quarry underway. It follows from the above facts that the workers in the quarry and the population in the vicinity are not at risk of health damage from air pollution.

Harm to the health of the population around the activity under consideration due to water contamination is not likely.

Harm to the health of the population around the activity dues to soil contamination and the penetration of pollutants emitted from equipment into the food chain is not likely.

Harm to the health of residents around the proposed activity due to excessive noise from quarrying is not likely. Impulse noise due to detonations or blasting work is the impact most subjectively perceived by the population. However, blasting works are rare over time, and therefore, noise limits do not apply to this activity.

The area in question has quite varied natural conditions, the terrain is rugged with a rich representation of original and natural forest, meadow and wetland communities, agricultural cultures and garden areas. There is also a variety of animal species (reptiles, mammals and birds). The quarry, plans to expand extraction of building stone adjacent to the existing extraction area. When assessing the effects on the natural environment, it is necessary to start with the species composition and structural properties of vegetation stands, which are high in the area concerned. The forests are of the highest biotic quality. The locations of existing local biocentres have lower levels of biotic quality. In the evaluated area, there are no endangered habitats of animals and plants that will be disturbed by the expansion of the quarry. The occurrence of protected species of plants and animals has not been recorded directly on the site. No significant negative impact on nature is expected.

The operation of the quarry or the extraction and treatment of stone (crushing, sorting) and handling of aggregates is a source of air pollution. The proposed activity is a medium source of air pollution. The operator of the air pollution source must comply with all the obligations arising from the applicable legislation in the field of air protection. In order to reduce dust in the quarry, crushed material is sprinkled with an aqueous film, the roads with a water cannon and vehicles leaving the quarry are cleaned in the washing plant to eliminate the effects on the quarry's surroundings as much as possible.

4.2. Evaluations and analysis of impacts by relevance

In order to ensure the ecological stability of the area, it is necessary to respect and protect the elements of the national network of protected areas. The solution of the Hradová quarry itself is located outside protected areas. For this reason, no impact on large-scale or small-scale protected areas or protective zones is expected. There is only one stage of effects on the individual components of the environment over the period of the proposed activity, the extension of the quarry. In this case it is the extraction stage, which is a continuation of the current activity. Table 2 summarizes the impacts of the quarry's operations.

Table 2. Overview of impacts related to quarry operations (EUROVIA – Kameňolomy, s.r.o. Košice 2017)

Impact type	Positive Impact	No change to current status	Negative impact	Type of impact
Landscape		X		The proposed activity is a continuation of the existing activity, and there will be no change from the landscape point of view
Flora and fauna		X		There will be no change in terms of flora and fauna

Table 2. cont.

Impact type	Positive Impact	No change to current status	Negative impact	Type of impact
Transport			X	In connection with the increase in mining capacity, the traffic burden will increase
Land		X		The proposed activity does not impose any demands on land use, no impact on the soil is expected
Air quality		X		New stationary technological sources of air pollution will not arise in connection with the proposed activity. Increased dustiness will occur with the passage of motor vehicles, we do not expect a significant change from the current state
Public health		X		There will be no significant changes to the current situation
Job opportunities	X			Positive impact on the creation of new jobs – about two employees
Noise		X		There will be no significant change compared to the current situation
Water		X		There will be no change compared to the current situation
Waste		X		An increase in waste compared to the current state is not expected

5. Conclusions

The recovery of free reserves in the quarry is irreversible over time, so it is necessary to consider expanding the quarry so that the demands of customers can be met in the future. Importing stone from a greater distance or opening a completely new quarry would not only be economically disadvantageous, but it would also place a greater burden on the environment. The expansion of the currently prepared and running quarry therefore appears to be the most advantageous solution.

Currently, during live quarrying the quarry undoubtedly has a disruptive effect on the function of the biocentre. The mentioned remediation of the steep slope above the Kostoľany road extends into the biocentre. However, the remediation is motivated by the protection of the life and health of road users on the Kostoľany road and therefore there is no alternative solution. In the medium and long term, the territory under consideration has the potential to be integrated into the natural area, or even to become a gene fund location.

Provided that all approved operational procedures and relevant legislative regulations are strictly adhered to on the basis of the public health impact assessment carried out, the expansion of mining operations of Hradová quarry can be objectively evaluated as acceptable on a whole society basis without serious impact on the health of workers and residents living in the area under consideration.

It is possible to envisage two interesting alternatives for the use of quarry operations for non-mining purposes:

- The first alternative is to use the quarry area under consideration as a cultural monument of open-cast mining. The proposal is based on the fact that near the quarry field there is a hiking trail which is part of the Vihorlat Protected Landscape Area and is slightly frequented. It is for this reason that this alternative would suitably fit into the environment. If this option were implemented, it would be necessary to propose a process of forest reclamation in combination with recreational reclamation.
- The second alternative is to use the quarry area as a waste repository. However, this is not the most appropriate way of land use from the environmental and ecological point of view. The advantage of this project is that it is the cheapest way to reclaim land. The disadvantage, however, is the level of soil contamination in the area and the possible contamination of surrounding waters. In this variant of land use, reclamation works take into account the protection of the surface against leakage of chemical elements from waste and the solution of the drainage system. In such a case, however, the revitalization work will not be subject to the liquidation and quarry operation plan.

The quarry does not affect protected areas and is not expected to have a direct negative impact on rare communities or protected areas in the wider area during quarry operations.

The assessed activity does not directly interfere with the urbanized area. The quarry is to be integrated into the forest land after extraction and recultivation. Freight traffic from the Hradová quarry is about 5% of the total traffic on the Kostoľany road, all predictions associated with dust and noise on the Kostoľany road, due to traffic on the Kostoľany road, are beyond the control of the proposer.

The submitted paper is a part of the project "Research and development of new smart solutions based on principles of the Industry 4.0, logistics, 3D modelling and simulation for production streamline in the mining and building industry." VEGA 1/0317/19.

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Abstract

This article addresses research into the effective expansion of industrial activity, taking into account environmental needs. The aim is to analyse and assess the possibilities for further development of industrial activity in a particular region of Slovakia. The objective of the geological task is to verify 5 million m^3 of building stone of category Z-2. In terms of environmental requirements important factors include safety, stability, habitat, logistics and the emissions factor. In terms of further utilization, the emissions factor is particularly important. The emissions factor for drilling, loading, unloading and for aggregate moisture of 0-0.5% is 9.4 g of PM per tonne of aggregate, which for extraction of 300 000 tons per year gives an output of 2 820 kg/year and 1.41 kg/h. The emission factor for primary and secondary aggregate processing with aggregate moisture of 2-3% with application of water spray is 14.6 g of PM per ton of aggregate, giving emissions of 657 kg of PM per year and 0.3285 kg of PM per hour. For the tertiary aggregate processing, at aggregate moisture of 2-3%, the emission factor is 230.2 g of PM per tonne of aggregate, giving emissions of 690.6 kg of PM per year and 0.3453 kg of PM per hour. The total annual emissions are 4 167.6 kg of PM, i.e. 2.0838 kg/h. In order to secure the ecological stability of the land area, it is necessary to respect and protect the elements of the national network of protected areas. The solution for the Hradová quarry is located outside of protected areas. For this reason, no impact on large-scale or small-scale protected areas or protective zones is expected.

Keywords:
ecological aspects, remediation-reinstating of slope, recultivation, emissions, environmental impacts, mining, logistics

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The Investigation of the Applicability of Data-Driven Techniques in Hydrological Modeling: The Case of Seyhan Basin

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1. Introduction

Hydrology science is described as the life cycle of water. It is a fact that rainfall-runoff modeling and the other data-driven techniques are significant events in this cycle. Especially, estimation of missing the streamflow is an important process for designing and planning flood protection studies in the data-driven techniques. Drought is thought one of harmful natural phenomenon in terms of hydrology. Drought estimation methods should be investigated in detail. Furthermore, observational data in hydrological works have many errors due to gauging. These obtained data should be evaluated for applicability in some hydrological calculations. Therefore, this paper aims to research use of data-driven techniques in hydrology.

In the literature there are several studies that use ANN and data mining methods for hydrological studies such as rainfall-runoff modeling and drought analysis. The ANN methods is one of the most commonly used in rainfall-runoff relation modeling (Dawson & Wilby 1999, Alp & Cigizoglu 2005, Nourani et al. 2009, Machado et al. 2011, Gumus et al. 2013, Kumar et al. 2016, Turhan et al. 2016a, Loyeh & Jamnani 2017, Patel & Joshi 2017, Asadi et al. 2019, Lin et al. 2019). Feed Forward Back Propagation (FFBPNN) and Generalized Regression Neural Networks (GRNN) methods can be seen to be generally utilized for hydrological data estimation (Cigizoglu 2005, Turan & Yurdusev 2009, Turhan et al. 2016b, Tayyab et al. 2016, Gumus et al. 2018). Standardized Precipitation Index (SPI), Standardized Runoff Index (SRI), Streamflow Drought Index (SDI), De Martonne Index (DMI),...etc methods play a very important role in determining drought (Shukla & Wood 2008, Stachowski 2010, Sattari et al. 2011, Bartholy et al. 2013, Tabari et al. 2013, Turhan et al. 2016c, Gumus & Algin 2017, Gumus 2017, Myronidis et al. 2018, Tri et al. 2019). The studies conducted in the field of construction/civil engineering using data mining methods have been increasing in recent years. It is observed that the results are taken by using data mining methods in the studies including concrete compressive strength, leadership analysis, productivity determination, building material decision making process, rainfall estimation, streamflow estimation, occupational health and safety assessment, cost analysis, analysis of traffic accidents, project management,... etc. subjects (Caldas et al. 2002, Wilmot & Cheng 2003, Baykasoglu 2005, Liaoa & Perng 2008, Kaya et al. 2013, Keles & Kaya 2014, Ozel & Topsakal 2014, Keles 2016, Kaya Keles 2017, Kaya Keles & Keles 2017). Data mining techniques have been used for hydrological studies (Trafalis et al. 2002, Damle & Yalcin 2007, Terzi 2012, Yurekli et al. 2012, Kusiak et al. 2013, Keskin et al. 2013, Sattari et al. 2018, Hatami et al. 2018, Mishra et al. 2018, Sattari & Sureh 2019, Kaur & Sood 2019, Sezen et al. 2019).

In this paper, two data-driven techniques such as ANN and Data Mining were investigated in terms of availability in hydrology works. FFBPNN and GRNN methods were examined on the rainfall-runoff modeling for ANN. ANN algorithm was created using Matlab software. Besides, hydrological drought analysis were examined using data mining techniques. Drought analysis was carried out using the SRI method. Seyhan Basin was preferred to carry out these techniques. As compared to many data mining works with hydrological elements, few works are present in the literature, thus using data mining techniques for streamflow data can be a novelty of this study. There is a need for new studies that will enable the use of data mining methods in the field of hydrology in order to fill this gap in the literature. Due to the lacking number of available hydrological and meteorological data, it is necessary to complete missing data in the basin modeling/hydraulic structures design studies and estimate for the future. Examining these data in the same basin could provide great contributions in order to investigate applicability. Consequently, it is thought that the application of these different techniques (ANN and data mining) in the same basin could make a great contribute to the literature. Also, the use of several hybrid data mining methods can be planned in future studies.

2. Materials and Methods

2.1. Artificial Neural Networks (ANN) Methods

2.1.1. Feed Forward Back Propagation (FFBPNN) Method

This method is commonly used in ANN studies. The method consists of input, hidden and output layers. The output of cells in a layer provides input values, by means of weights, to the next layer (Dawidowicz et al. 2018). As the input layer processes the data obtained with the help of a weighted coefficient input vector, this input layer transmits along the cell structures in the hidden layer. Therefore, the output data is produced by changing the hidden and output layers. Using a back propagation algorithm, it tries to provide good convergence (Turhan et al. 2016a).

In this method:
m – the layer number,
${X_i}^m$ – the input data of i unit in m^{th} layer,
${y_i}^m$ – the output data of i unit in m^{th} layer,
${w_{ij}}^m$ – weight coefficient linking i unit in $(m\text{-}1)^{th}$ layer to j unit in m^{th} layer,
w – a random real value in the additional forward values calculated
for each j units in m^{th} layer.

Then, the output data are obtained from Equation 1 (Gumus & Kavsut 2013):

$${y_i}^m = f(\textstyle\sum_i {y_i}^{m-1}\, {w_{ij}}^m) \tag{1}$$

For the output, the error terms shown as δ are calculated by Equation 2:

$${\delta_i}^m = \left({y_i}^M - {y_i}^m\right) f'\left({X_i}^M\right) \tag{2}$$

Also, the error terms are calculated for the backward hidden layer units by Equation 3:

$${\delta_i}^{m-1} = f'\left({X_i}^{m-1}\right) \textstyle\sum_i {\delta_i}^m\, {w_{ij}}^m \tag{3}$$

All these weights are obtained by Equation 4:

$${w_{ij}}^{next} = {w_{ij}}^{previous} + \Delta {w_{ij}}^m \tag{4}$$

η is the learning coefficient and changes in the weight coefficient during learning are shown by Equation 5:

$$\Delta {w_{ij}}^m = \eta {\delta_i}^m {y_i}^{m-1} \tag{5}$$

The process is repeated for each step until the total error reaches a minimum value (Konate et al. 2015).

2.1.2. Generalized Regression Neural Networks (GRNN) Method

Regression of dependent variable *y* by independent variable *x* is shown by Equation 6 (Kisi 2006):

$$E\left[\frac{y}{x}\right] = \frac{\int_{-\infty}^{\infty} y\, f(x,y)dy}{\int_{-\infty}^{\infty} f(x,y)dy} \tag{6}$$

If the probability function is not known, this function can be estimated from X_i and Y_i values by Equation 7:

$$f(X,Y) = \frac{1}{(2\pi)^{(p+1)/2}\, s^{(p+1)}} \frac{1}{n} \sum_{i=1}^{n} \exp\left[-\frac{(X-Xi)^T(X-Xi)}{2s^2}\right] \exp\left[-\frac{(Y-Yi)^2}{2s^2}\right] \tag{7}$$

where:
p – the size of the x vector,
n – the number of observed data,
s – the correction parameter.

D_i^2 is to be regarded as a scalar function in Equation 8:

$$D_i^{\,2} = (X - X_i)^T (X - X_i) \tag{8}$$

Consequently, the dependent variable is obtained by Equation 9:

$$Y(X) = \frac{\sum_{i=1}^{n} Y_i \exp(-\frac{D_i^{\,2}}{2s^2})}{\sum_{i=1}^{n} \exp(-\frac{D_i^{\,2}}{2s^2})} \tag{9}$$

Figure 1 shows the general schematic structure of the FFBPNN and GRNN.

The formula used in the normalization process can is shown below (Equation 10):

$$Q_n = \psi\, \frac{Q_e - Q_{min}}{Q_{max} - Q_{min}} + \rho \tag{10}$$

Q_{max} and Q_{min} are the maximum and minimum flow values for each Flow Observation Station (FOS), respectively. Q_e indicates the normalized flow value, Ψ and ρ are evaluated to be constants the values of *0.6* and *0.2*, respectively. *N* represents total data, normalization has been completed by performing an inverse equalization process (Turhan et al. 2016a).

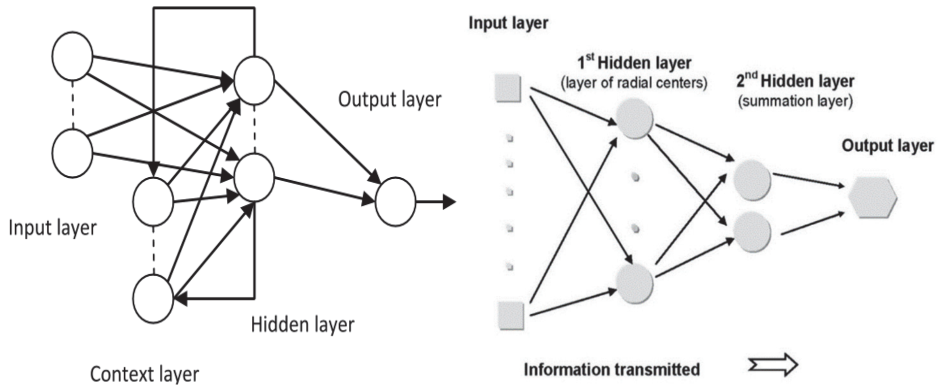

Fig. 1. General schematic structure of FFBPNN (left) and GRNN (right) (Ikiel & Ozyildirim 2013, Cigizoglu 2005)

Mean Square Error (MSE) and R^2 (Coefficient of determination-R^2) formulas are shown Equation 11 and 12:

$$\mathrm{MSE} = \frac{1}{\mathrm{N}} \tag{11}$$

$$\mathrm{R}^2 = \frac{\sum_{i=1}^{N}(Q_{\mathrm{observed}} - Q_{\mathrm{average}})^2 - \sum_{i=1}^{N}(Q_{\mathrm{observed}} - Q_{\mathrm{calculated}})^2}{\sum_{i=1}^{N}(Q_{\mathrm{observed}} - Q_{\mathrm{average}})^2} \tag{12}$$

2.2. Drought analysis methods

2.2.1. Standardized Runoff Index method (SRI)

Different drought indices have been used for hydrological works in the literature. The Standardized Precipitation Index (SPI), Standardized Precipitation Evapotranspiration Index (SPEI), Evapotranspiration Deficit Index (ETDI) and Soil Moisture Deficit Index (SMDI) are based on precipitation, precipitation-temperature, evapotranspiration and soil moisture, respectively. In these indices, while calculating the SPI value, firstly the precipitation value at a certain time is subtracted from the average precipitation value. Then, this value is divided by the standard deviation and the SPI value is then obtained (Shukla & Wood 2008). Besides these, the SRI based on runoff or streamflow data, describes the events of hydrological drought. SRI method is largely similar to the SPI method except for the use of streamflow values instead of precipitation values. Formulas for the SRI are modified by setting the these streamflow data. The SRI value is calculated with the help of formula below (Equation 13):

$$\mathrm{SRI} = \frac{X_i - X_i^{\mathrm{mean}}}{\sigma} \tag{13}$$

where:
X_i – the monthly average streamflow values over a certain time period,
X_i^{mean} – the average of monthly streamflow values within a selected time period,
σ – the standard deviation value.

Furthermore, the standard deviation value is calculated as shown below (Equation 14):

$$\sigma = \sqrt{\frac{n\sum x^2 - (\sum x)^2}{n(n-1)}} \tag{14}$$

where:
n – the number of observations for a given month,
x – the mean streamflow value of that month.

Calculation of the index shows a complex structure due to the fact that the streamflow data doesn't conform to normal distribution during periods of *12* months or less. Accordingly, first of all, the streamflow series are made to conform to this distribution. Drought seasons can be determined for a selected time period by applying normalization procedures to the SRI values.

In the drought analysis using SRI values, the negative time period in which the index takes a continuous negative value is determined as the drought season (Kumar et al. 2009, Kubiak-Wójcicka & Bak 2018). The month when the index falls below zero is regarded as the starting point of the drought, and the month when the index has a positive value is predicted as the end point of the drought. The classification of the SRI value-drought categories, prepared using the SPI method, is shown in Table 1 (Keskin et al. 2007).

Table 1. Classification of the SRI Value – Drought Category (Keskin et al. 2007)

SPI Value	Drought Category	SPI Value	Drought Category
≥ 2	Extreme Rainfall	0.00-(-0.99)	Mild Drought
1.50-1.99	Severe Rainfall	-1.00-(-1.49)	Moderate Drought
1.00-1.49	Moderate Rainfall	-1.50-(-1.99)	Severe Drought
0.99-0.00	Mild Rainfall	≤ -2	Extreme Drought

2.3. Data mining methods

Data Mining is the processing of large amounts of data with automatic or semi-automatic methods to find meaningful patterns. This method is an interdisciplinary study. Statistics and machine learning are the scientific disciplines on which data mining is based most. The underlying meaning of data mining is the knowledge discovery in databases (KDD) process. KDD refers to the broad process of finding knowledge in data. The seven steps of the KDD is shown as in Figure 2 (Kaya Keles 2017). The KDD uses data mining methods to identify knowledge, according to the characterization of measures using preprocessing and transformations of the database.

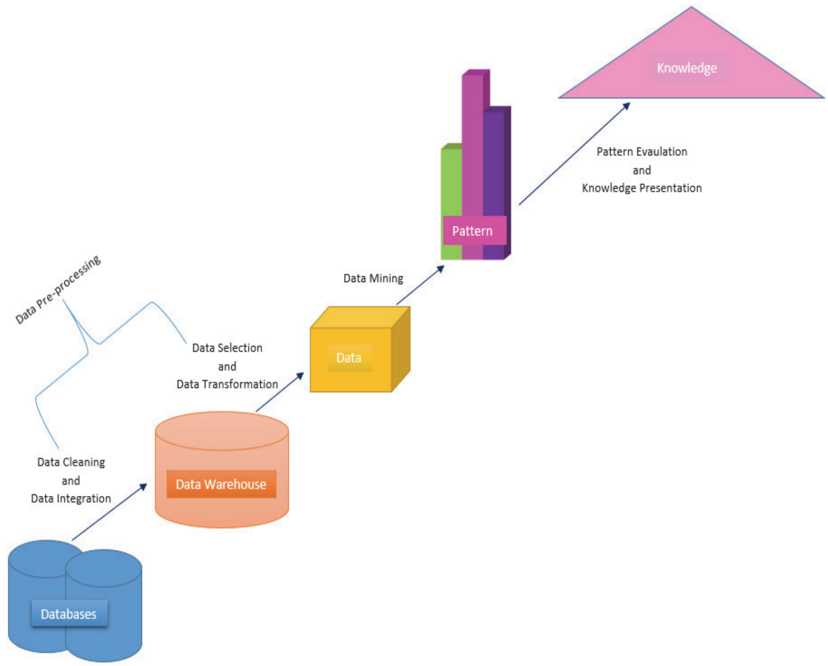

Fig. 2. Knowledge Discovery in data bases (KDD) Process (Kaya Keles 2017)

Waikato Environment for Knowledge Analysis (Weka) software was used for data mining process. The Weka is one of the packages used in data mining and machine learning which are the important subjects of computer science. It is a data analysis tool under the GNU (General Public License) developed by the University of Waikato with java language. It is basically a data mining program where machine learning algorithms and data pre-processing needs are combined together. It uses methods such as clustering, classification and association rule mining to perform data mining process. The file extension format is *'.arff'*. In the field of civil engineering where there are many sub-disciplines, due to the increase in knowledge in parallel with technological developments, information needs to be processable.

2.3.1. Multi-Layer Perceptron (MLP)

MLP called multi-layer feedforward network, was proposed as an enhancement of the perceptron model. This model is the most widely used neural network architecture for classification tasks. The main characteristics of the MLP are:

- The entire network is hierarchically trained. It uses back propagation learning.
- Sigmoidal units are used in hidden layers and in the output layer.
- It can make more modeling using at least 1 hidden layer (Aggarwal, 2014).

Although, in theory, MLPs are considered to be capable of performing any sort of classification task, in practice, in cases of insufficient number of hidden layers or insufficient training, data classification performance may be low. As shown in Figure 3, the units in the network are arranged in layers including an input layer, several hidden layers and an output layer.

The layers are organized in sequential order that follows the data flow from the input layer to the hidden layers and ends at the output layer. In this process known as forward propagation of the network, each unit in a layer receives data from the previous layer's units and the output units ensure the final decision of the classification. Forward propagation refers to the transfer of data from the input layer to the output layer, while the back propagation refers to the spread of error derivatives from the output layers to the hidden layers. The back propagation training algorithm as shown in Figure 4, which is designed to minimize an error criterion of the feed forward network, is an iterative gradient descend algorithm.

The MLP classifier in Weka is a classifier that uses back-propagation to learn a multi-layer perceptron when classifying samples. This classifier is located under the functions tab in Weka under the name MLP. In this study, the default values are preferred when using MLP. For learning rate, the value of *0.3* was used. For momentum rate, the value of *0.2* was used. For threshold, the value of *20* was used. With Weka, the user can find the classification accuracy by measuring the success rate with cross-validation method. In this paper, 10-fold cross validation method was used with MLP classifier.

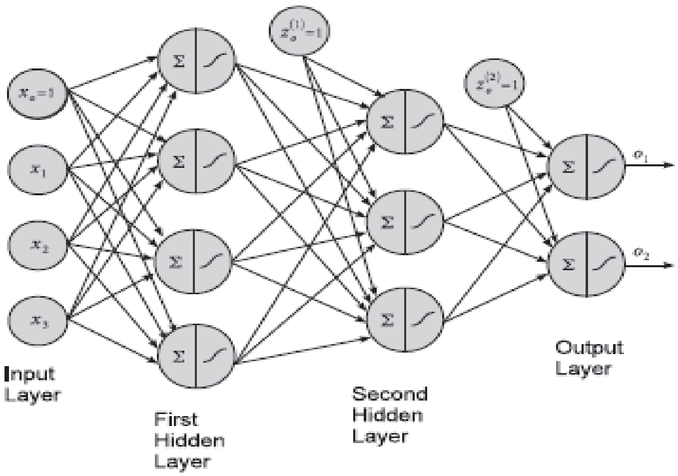

Fig. 3. An MLP network made of one input layer, two hidden layers and one output layer (Aggarwal, 2014)

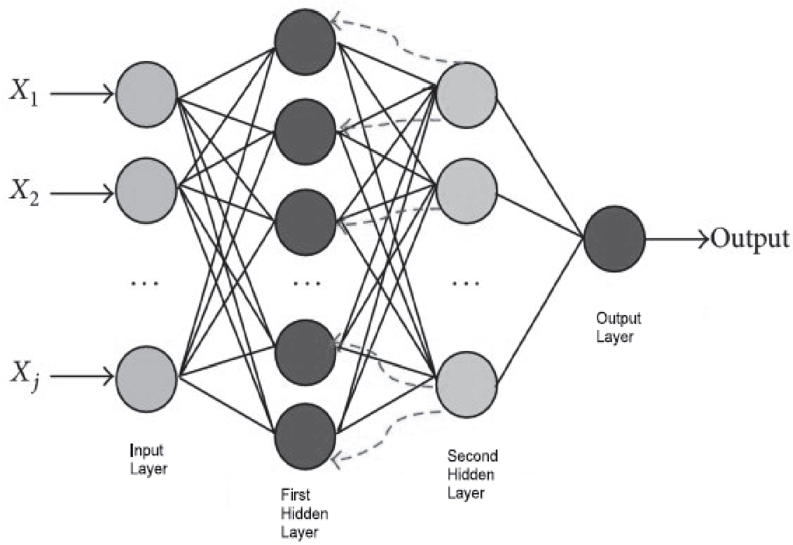

Fig. 4. An MLP network made of one input layer, two hidden layers and one output layer with backpropagation (Aggarwal, 2014)

2.4. Case study

All input data were obtained from the Seyhan Basin observed data for analysis. The Seyhan Basin is one of the most important basins in the south of Turkey in terms of social, economic, agricultural and numerous endemic species. The Seyhan Basin's area is approximately 20450 km^2 and covers of the 2.82% of Turkey with regard to surface area (Topcu & Seckin 2016). Thus, it is thought that the Seyhan Basin is an interesting basin for the hydrological studies (Fujihara et al. 2008, Tuncok 2016, Cavus and Aksoy 2019). The location of the Seyhan Basin can be seen in Figure 5. The average values for each FOS and Precipitation Observation Station analyzed, observed data and the time periods are given in Table 2.

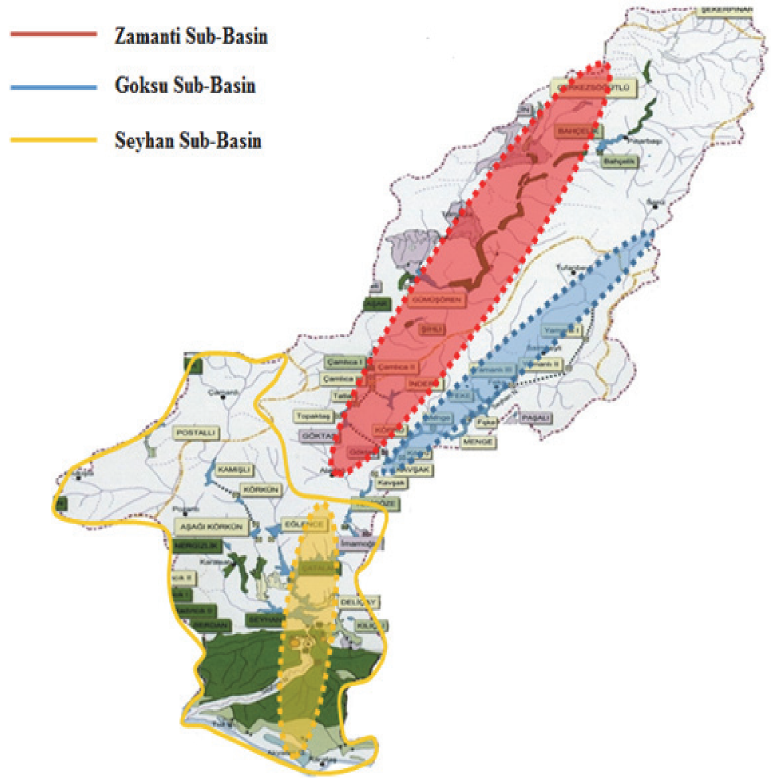

Fig. 5. A map of the Seyhan Basin (The Ministry of Forestry & Water Affairs (MFWA), 2016)

Table 2. Parameters of FOS and POS (Electrical Work Surveying Administration (EWSA), 2008)

FOS-POS	Location	Average Flow Values (m^3/s)	Average Precipitation Values (mm)	Observed Periods
1801 Göksu River FOS	Kozan-Saimbeyli	30	-	1936-2005
1818 Seyhan River FOS	Adana and on Uctepe Bridge	145	-	1966-2005
1821 Eglence Stream FOS	Adana-Karaisali	10.7	-	1971-2000
1822 Zamantı River FOS	Border of Adana-Kayseri	20	-	1970-2005
Catalan POS	Adana-Karaisali	-	819.54	1964-1987
Karaisalı POS	Adana-Karaisali	-	910.57	1957-2000

3. Results and discussion

3.1. Artificial Neural Networks (ANN) results

Monthly average flow and precipitation data in the Seyhan Basin were used as input data for the ANN methods. For both models, five data were provided as input data, and two intermediate layers were used (Figure 6). As a result, one output value was determined. All data were scaled from *0.1* to *0.9*, and a logarithmic sigmoid transfer function was used. The output layer was a linear function. For this reason, the data was normalized without entering the network structure. Even though meteorological data were very high for the ANN, normalization was easily performed. The algorithm required for calculation was created and simulated in Matlab software. Seventy percent (70%) of these data were available for training and the rest (30%) for testing. The MSE value was close to zero (0) and R^2 was close to the value of *1*, indicating a good result was predicted. The value of two neurons or the cell number was used in the hidden layer. The output value was the value of *1*. Many trials were performed and only the five models giving the best results are shown in Table 3.

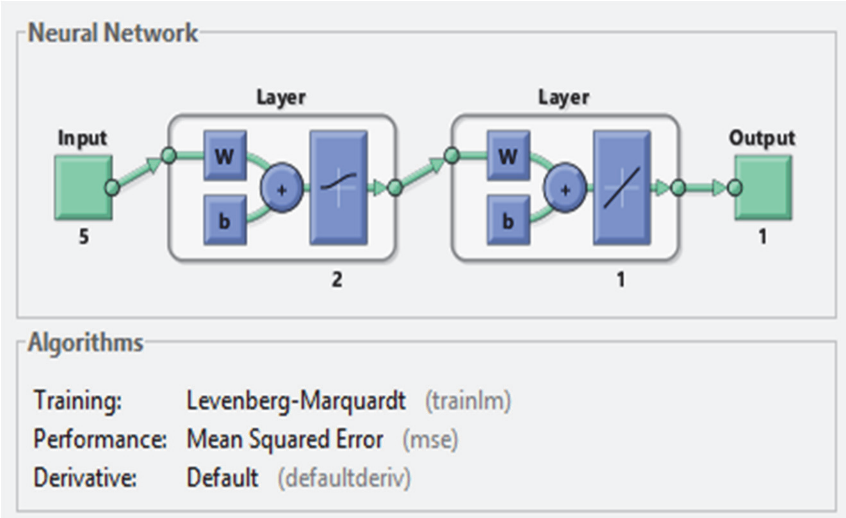

Fig. 6. ANN structure

Table 3. FFBPNN and GRNN Results for Training and Testing

Model No	FFBPNN				GRNN			
	Training		Testing		Training		Testing	
	R^2	MSE	R^2	MSE	R^2	MSE	R^2	MSE
1	0.898	20.222	0.945	5.625	0.967	6.658	0.799	23.602
2	0.977	5.208	0.946	6.817	0.989	2.544	0.894	7.877
3	0.972	5.206	0.945	6.818	0.988	2.550	0.892	7.892
4	0.977	5.209	0.943	6.812	0.989	2.536	0.894	7.880
5	0.977	7.965	0.945	12.515	0.987	4.405	0.912	12.406

According to Table 3, the FFBPNN is the best model, giving the highest R^2 and lowest MSE values. The structure of model numbers can be shown as five input and one output data in the following:

- Model No-1: $Pcatalan_t$, $Pkaraisali_t$, $Q1801_t$, $Q1822_t$, $Q1818_{t+1}$--- $Q1818_t$
- Model No-2: $Pcatalan_t$, $Pkaraisali_t$, $Q1801_t$, $Q1818_t$, $Q1822_{t+1}$--- $Q1822_t$
- Model No-3: $Pcatalan_t$, $Pkaraisali_t$, $Q1818_t$, $Q1822_t$, $Q1801_{t+1}$--- $Q1801_t$
- Model No-4: $Pcatalan_t$, $Pkaraisali_t$, $Q1801_t$, $Q1822_t$, $Q1818_{t-1}$--- $Q1818_t$
- Model No-5: $Pcatalan_t$, $Pkaraisali_t$, $Q1801_t$, $Q1818_t$, $Q1822_{t-1}$--- $Q1822_t$

In Figure 7, for trial number-2 flow (m3/s)-time (month), the graphs were created and compared to the calculated and observed data. In Figure 8 for the same trial (no 2), the calculated flow data–observed data (m^3/s) were drawn.

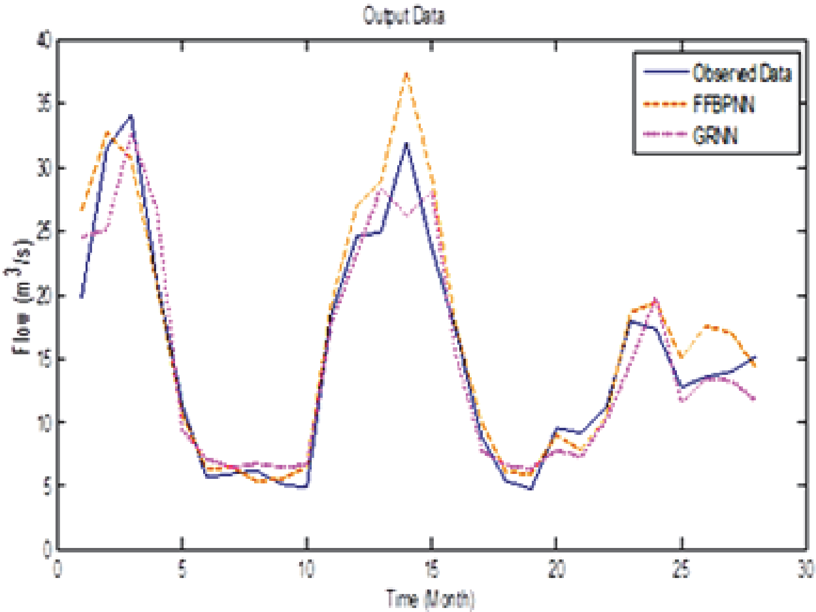

Fig. 7. Comparison between flows (m^3/s)-time (month)

When Figure 7 and 8 are examined in detail, the FFBPNN values were quite good results according to the observed data. Although the GRNN calculated a higher R^2 value than the FFBPNN in the training phase, FFBPNN calculated the highest R^2 and least MSE values in test phase**.** The best result of the FFBPNN model is the input data $Pcatalan_t$, $Pkaraisali_t$, $Q1801_t$, $Q1818_t$, $Q1822_{t+1}$ and the output data is $Q1822_t$ (structure 5-2-1-1). Many studies can be seen higher FFBPNN results than the GRNN (Gumus & Kavsut 2013, Tayyab et al. 2016). However, it can be seen that GRNN and other artificial neural network methods produce high values in network structure changes (Gumus et al. 2013, Turhan et al. 2016a).

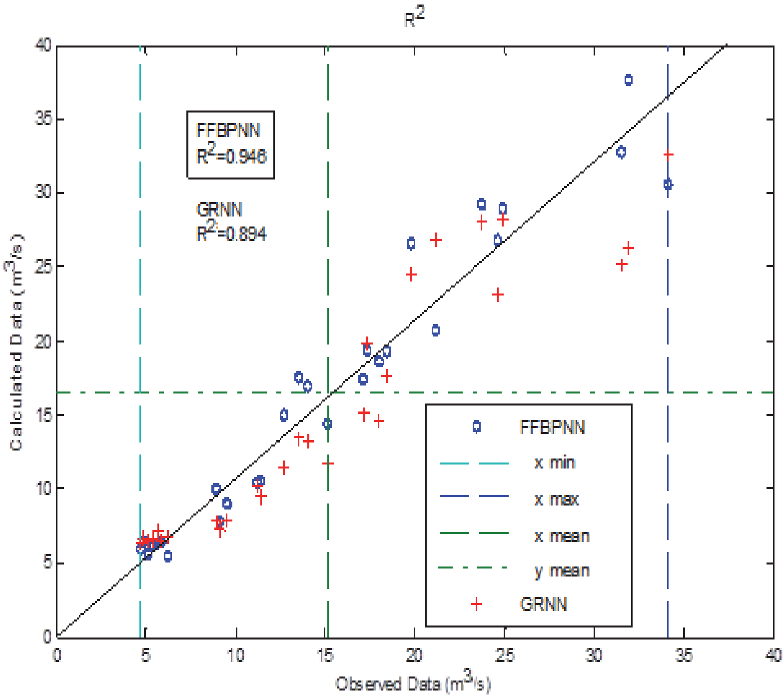

Fig. 8. Comparison between calculated and observed flow data (m^3/s)

3.2. Meteorological and hydrological drought analysis results

SRI drought analysis results for *1801, 1818, 1821* and *1822* can be seen in Figure 9. Drought analysis calculations were performed with the help of MS Excel and missing data were completed by using the ANN methods.

3.3. MLP prediction results

The generated SRI data, 1818_{t-1} data, 1818_{t-2} data, 1818_t monthly flow data for *1818* FOS were used to predict the class of the drought. To analyze drought, Table 4 (McKee et al. 1993, World Meteorological Organization (WMO) 2012), which is the SRI values table was used and data were normalized using this table for SRI analysis. Since data mining classification algorithms aim to increase the success of classification with fewer classes, SPI values in Table 4 consisting of 7 classes were used in this study.

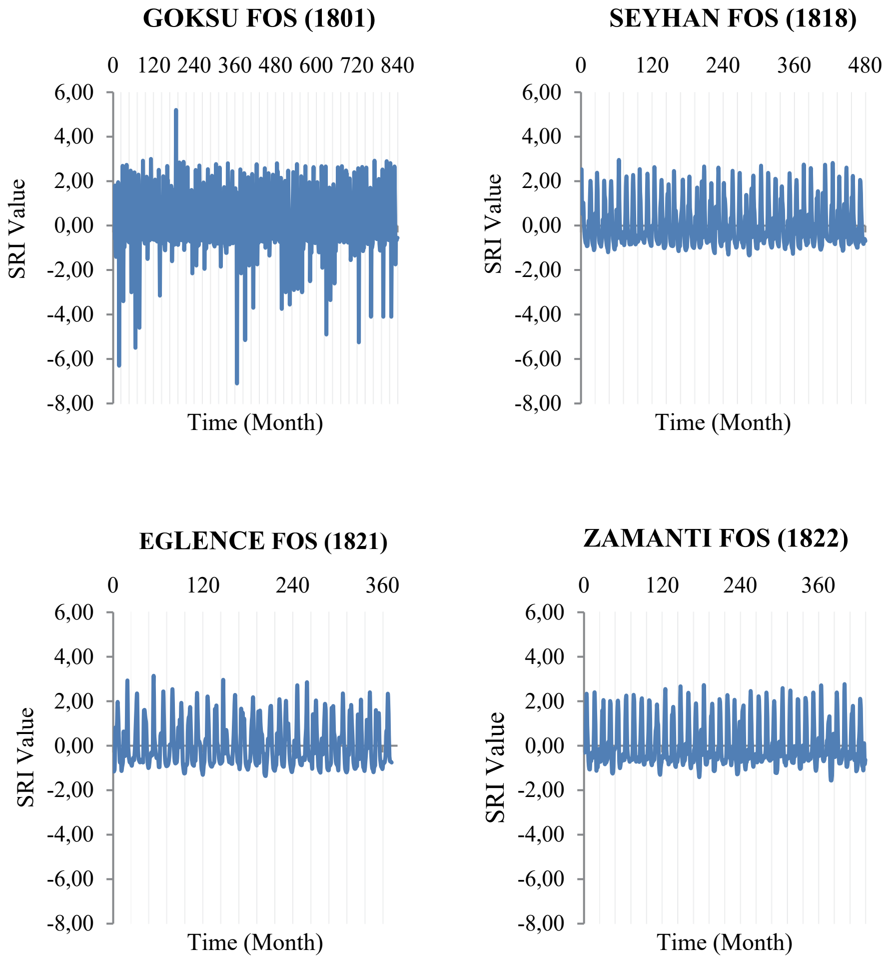

Fig. 9. Hydrological drought analysis results

Table 4. SRI values for Data Mining methods

2.0+	extremely wet
1.5 to 1.99	very wet
1.0 to 1.49	moderately wet
-.99 to .99	near normal
-1.0 to -1.49	moderately dry
-1.5 to -1.99	severely dry
-2 and less	extremely dry

This table was used to test and measure the success of the SRI value using the data mining method. According to Table 4, SRI values were classified as extremely wet, very wet, moderately wet, near normal, moderately dry, severely dry, and extremely dry. To measure the validation of the system which used data mining techniques, classification accuracy, F-Measure, Root Mean Squared Error methods were used. All processes were done for 1801, 1821 and 1822 FOS, too. Classification Accuracy shown in Equation 15 (Powers 2011) is the ratio of number of correct predictions to the total number of input samples.

$$\text{Accuracy} = \frac{\text{Number of Correct Predictions}}{\text{Total Number of Input Samples}} \tag{15}$$

F-Measure shown in Equation 16 (Powers 2011) is also called as F1 Score, F-Score, or F-Value. It is the weighted average or harmonic mean of precision and recall. It ranges from the values of *0* to *1*. Precision means positive predicted value, while recall means sensitivity.

$$\text{F} - \text{Measure} = \frac{2*\text{Precision}*\text{Recall}}{\text{Precision}+\text{Recall}} \tag{16}$$

Root Mean Squared Error (RMSE) shown in Equation 17 (Kamble & Deshmukh 2019) is evaluated as the root squared value of the total of differences between the probability distribution output from the classification algorithm and the vector of probabilities symbolizing the real class of all samples (Mehdiyev et al. 2016). The RMSE is a quadratic scoring rule which sets the medium magnitude of the error (Guo et al. 2015).

In RMSE formula, $\sum$ means summation, x_i means predicted values, $\bar{x}_i$ means observed values, *N* means sample size.

$$\text{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{n}(x_i - \bar{x}_i)^2} \tag{17}$$

After the missing data was completed, the data set was analyzed with MLP algorithm to predict the drought types using Table 4. For each flow observation stations including *1818, 1821, 1801 and 1822*, all SRI values were calculated for 3, 6 and 12 months. The classification accuracy, F-Measure and the RMSE values of MLP algorithm is shown in Table 5 for each station and the SRI values.

Table 5. MLP results for different SRI time series

FOS	SRI values for 3, 6 and 12 months	MLP Results		
		Performance Evaluation Criteria		
		F-Measure	Accuracy	RMSE
1818	SRI-3	0.883	89.25%	0.157
	SRI-6	0.656	73.66%	0.234
	SRI-12	0.721	77.96%	0.218
1821	SRI-3	0.829	84.95%	0.182
	SRI-6	0.672	75.00%	0.229
	SRI-12	0.677	75.54%	0.224
1801	SRI-3	0.789	83.87%	0.229
	SRI-6	0.737	80.91%	0.210
	SRI-12	0.751	80.11%	0.199
1822	SRI-3	0.834	88.71%	0.170
	SRI-6	0.542	64.52%	0.256
	SRI-12	0.686	76.34%	0.222

According to this table, the success of MLP algorithm was greater than 65% for all stations and SRI values. But for 3-months SRI values, the success of MLP was greater than 84%. It shows that using 3-months SRI values, the drought type of the next period can be predicted with a higher success rate. It was observed that the success rate of MLP in all stations was higher when using SRI-3 month data. The estimation success of the 3-month data is followed by 12-month data. The least success was the 6-month SRI data. According to these results, MLP algorithm showed the highest success in drought estimation with 3-month data (SRI-3) as 89.25% accuracy rate and 0.883 F-Measure value for the *1818 FOS*. For *1821 FOS*, the MLP algorithm showed the highest success in drought estimation with 3-month data (SRI-3) as 84,95% accuracy rate and 0.829

F-Measure value. For *1801 FOS*, the MLP algorithm showed the highest success in drought estimation with 3-month data as 83,87% accuracy rate and 0.789 F-Measure value. For *1822 FOS*, the MLP algorithm showed the highest success in drought estimation with 3-month data as 88,71% accuracy rate and 0.834 F-Measure value. This shows that by using data mining methods, it is possible to estimate the drought type of the next period with a success of over 83% using SRI-3 month data.

When compared with other studies in the literature, it was observed that the results obtained within the scope of the study produced similar results with Sattari's study (2011). In both studies, it was observed that the estimation ability of the ANN model was weakened as the estimation time increased. When Terzi's study (2012) was compared with this study, it was observed that similar results were reached. In contrast to this study, although the MLR algorithm, which is a regression based algorithm, is used in Terzi's study, according to the results obtained, just like in this study, data mining methods can be used successfully in monthly estimates in the field of hydrology. Also, as in the results of MLP, which is a function-based algorithm obtained in this study, in Sattari's study (2017), Support Vector Regression, which is a function-based algorithm produced higher accuracy rate than tree-based M5 tree algorithm.

4. Conclusion

In this study, ANN methods such as Feed Forward Back Propagation (FFBPNN) and Generalized Regression Neural Networks (GRNN) were used for rainfall-runoff relationship modeling. An ANN algorithm was created using the software program. It is seen that the FFBPNN method is the best model for the ANN in terms of giving the highest R2 and lowest MSE values. Subsequently, hydrological drought analysis was carried out using the SRI analysis. MLP method, which is one of the data mining methods, was performed to predict the drought type according to limit values. The generated monthly flow data, for 1818, 1801, 1821 and 1822 FOS were used to predict the class of drought using the SRI tables. With these SRI values, data from the data set prepared within the scope of the study were classified and the type of drought was tried to be analyzed using MLP algorithm. MLP algorithm showed the highest success in drought estimation with 3-month data (SRI-3) as 89.25% accuracy rate and 0.883 F-Measure value for the 1818 FOS. The least success was the 6-month SRI data. Consequently, it is foreseen that these techniques may be used easily in terms of modeling of hydrological cycle elements for completion missing data or the other basin planning and management works.

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Abstract

Proper water resources planning and management is based on reliable hydrological data. Missing rainfall and runoff observation data, in particular, can cause serious risks in the planning of hydraulics structures. Hydrological modeling process is quitely complex. Therefore, using alternative estimation techniques to forecast missing data is reasonable. In this study, two data-driven techniques such as Artificial Neural Networks (ANN) and Data Mining were investigated in terms of availability in hydrology works. Feed Forward Back Propagation (FFBPNN) and Generalized Regression Neural Networks (GRNN) methods were performed on rainfall-runoff modeling for ANN. Besides, Hydrological drought analysis were examined using data mining technique. The Seyhan Basin was preferred to carry out these techniques. It is thought that the application of different techniques in the same basin could make a great contribute to the present work. Consequently, it is seen that FFBPNN is the best model for ANN in terms of giving the highest R2 and lowest MSE values. Multilayer Perceptron (MLP) algorithm was used to predict the drought type according to limit values. This system has been applied to show the relationship between hydrological data and measure the prediction accuracy of the drought analysis. According to the obtained data mining results, MLP algorithm gives the best accuracy results as flow observation stations using SRI-3 month data.

Keywords:
artificial neural networks, drought analysis, data mining, Multilayer Perceptron, Seyhan Basin

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Assessment of Emergencies Threatening a Particular Region

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1. Introduction

Civil protection can be defined as a system of tasks and measures aimed at protecting life, health and property, in particular by analysing possible threats and by taking measures to reduce the risk from threats, as well as by identifying procedures and actions to address the consequences of emergencies.

This topic is relevant to the whole world and is therefore addressed by experts to find solutions, measures and procedures to prevent or deal with emergencies that have already arisen.

As the role of civil protection is to protect life, health and property and to create conditions for survival in emergencies, the role of health care facilities in this context (Vichova & Hromada 2018) as well as the quality of emergency supplies (Bai et al. 2018, Šimko 2014) should also be addressed. An interesting paper is "Preparedness against Mobility Disruption by Floods", which addresses the safety of people in an urban emergency (Arrighi et al. 2019), and it is necessary to consider the innovative links between data and information serving to aid assessment of the impacts and risks on the urban environment (Li et al. 2019, Straka et al. 2019).

Natural disasters relating to long-term changes in temperature and changes in sea levels at global level are also the subject of world-wide research (Yuan et al. 2017), and this is confirmed by experts Huang, Hall and Berg, who have been working on research to address the effects of temperatures on flood risks (Huang et al. 208). Among natural disasters, the opposite of floods is a period of drought, which is also a very interesting phenomenon due to the extreme diversity of its severity and duration (Trinh et al. 2017). The issue of floods also affects the area of the province of Concepción (Chile), where this disaster affected the local population (Lara et al. 2017). Analysis of floods on the River Elbe has drawn the attention of the experts Mudersbach, Bender and Netzel 2017, while the consequences of several extraordinary major storm events in New Jersey are described in the conference paper by Primm, Molloy and Carlin 2017.

Fires are also a natural disaster and fire protection itself needs to be addressed to provide a specialized response to such emergencies (Tomescu et al. 2019). An interesting study that examines the future of fire safety is from Olawoyin (Olawoyin 2018), and the Australian experts Johnson and Lobel also address this issue (Johnson & Lobel 2018).

A method for assessing the risk of catastrophic slope failure can be found in the article "A novel risk assessment method for landfill slope failure: Case study application for Bhalswa Dumpsite, India" (Jahanfar et al. 2017).

Another contribution in the field of emergencies focuses on assessing urban seismic vulnerability (Lorenzo 2017).

The study "Assessment of attack likelihood to support security risk assessment studies for chemical facilities" concentrates on the area of industrial accidents, which is an integral part of the assessment of safety risks in urban areas (Landucci et al. 2017), while an article by the National Institute of Occupational Safety and Health provides information on legislative processes related to the issues addressed (Van Wely 2017).

The possibility of terrorist attacks forms part of the environmental safety assessment. In "Small-building defense against terrorism" (Lawless & Gumpertz 2006) we learn about sophisticated methods of protection against terrorism based on risk assessment and various defence mechanisms. The aim of the paper "Reducing the attractiveness of chemical plants to terrorist attacks: Dehorning rhinos" was to highlight terrorist attacks on chemical factories, which are a major threat to the population (Khakzad 2018).

Kovacs and Moshtari, considering the significant costs of natural disasters and man-made disasters, decided to create a methodological perspective (Kovacs & Moshtari 2019).

It is necessary to consider the importance of links and cooperation between local and state institutions in disaster management (Shah et al. 2019) and the related human resources management needs (Tomčíková et al. 2018).

2. Theoretical basis

2.1. Emergencies and their impact on the environment

An emergency is often a very serious, time-consuming and spatially limited event, caused by a natural disaster, technical or technological accident, operational failure, or deliberate action by a person that has caused disruption of system stability or of ongoing events and activities. This event threatens people's lives and health, material and cultural goods or the environment.

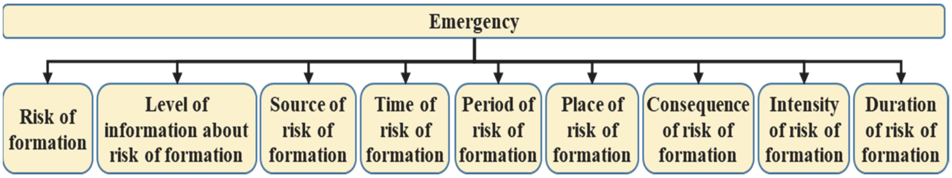

Fig. 1. Emergency Factors (Frištiková 2006)

These factors (Fig. 1) accurately define the cause, time, period, level of awareness. They determine the impact, intensity and duration of each given incident. They provide important information to understand the nature and course of an emergency, to seek precautionary measures, tools and procedures for effective and efficient solutions. General factors in an emergency are phenomena that describe it and are characteristic of it from the perspective of the subject in question.

2.2. Classification of emergencies

A natural emergency is an extraordinary event caused by natural forces, resulting in the release of accumulated energy and matter, or the action of dangerous substances, or other destructive factors with a negative impact on humans, animals, material values and the environment (Nemčok et al. 1974).

The most common natural emergencies include:

- floods (from precipitation and watercourse),
- atmospheric disturbances (storms of various types, extreme cold and heat, drought),
- landslides and slope movements,
- earthquakes and volcanic eruptions,
- destructive fires.

The main processes affecting natural emergencies are:

- rapid movements of mass (earthquakes, landslides, slope movements),
- release of tectonic energy and its transfer to the surface (volcanic eruptions, earthquakes),
- increase in the water levels of rivers, lakes and seas (floods and tsunamis),
- atmospheric equalization of temperature differences (atmospheric disturbances, destructive fires) (Poledňák & Orinčák 2011).

Other random phenomena and processes that would endanger the lives and health of people, disrupt the life of society, or damage material values:

- civil unrest,
- terrorist acts,
- the collapse of large manufacturing organizations,
- stoppage of the supply of strategic raw materials from abroad and the consequent lack of certain products on the market,
- large-scale epidemics (mass illnesses of humans or livestock), etc.,
- spreading of false alarms,
- migration.

3. Case study

3.1. Analysis of the risk of emergencies in Bratislava Region

At the beginning of this analysis of the Bratislava region it is necessary to provide an economic and geographical description of the territory. All sectors of traditional industrial production are represented in the economy of the studied area. The most important industries include the chemical, automotive, engineering, electrical and food industries. Recently, the Bratislava region has developed into a European centre for automotive production. The structural changes in the region's economy include the increasing importance of the tertiary sector, particularly in trade and services, banking and insurance. Agricultural production is mainly focused on winemaking and, to a lesser extent, on crop and livestock production. Another major industry is the construction industry.

From the geographical point of view, it is important that Bratislava region is on both banks of the Danube River, the second largest river in Europe, at the foot of the Small Carpathians and it occupies the margins of the Záhorie and Danube Plains at coordinates of 48° 9' north and 17° 7' east, spreading over an area of 367.6 km^2. The district is situated on the border of two countries. The boundaries of the district are formed to the south by the Danube and in the south-west by the Morava River, which are also the borders between Slovakia and Austria. In the urban area the boroughs of Petržalka, Jarovce, Rusovce and Čunovo form the border with Hungary. In the east, the district shares a boundary with Senec district, in the north-east with Pezinok district and in the north with Malacky district. From the point of view of local government divisions, the city is divided into seventeen boroughs.

The northern part of the district is rugged, formed by the western part of the Small Carpathians, divided from the north to the south by the Lamač Gate. The highest point is at Devínska Kobyla with an altitude of 514 metres above sea level. There are the highlands of Kráľova Hora and the Jesuit forests, as well as

Devínska Kobyla, between the borough of Karlova Ves and the borough of Devín. In the southwest, the Za Blatom mountain range is located in the borough of Devínska Nová Ves, and Dúbravská Hlavica and the Švábsky Vrch hill are located above the borough of Dubravka. The western foothills of the Small Carpathians are located above the boroughs of Lamač and Záhorská Bystrica. The southern slopes of the Small Carpathians are the winegrowing area of the district, with the vineyards planted up to an altitude of approximately 300 m. The Danube lowlands are represented by the Danube Plain, which occupies a wide area along the River Danube. Morphologically, as a result of its steady descent, it is a flat young plain, divided only by oxbow lakes and flowing channels, meanders and canals. As a neogeneous basin on a deep crystalline core, it is filled with ungrained sediments of Neogene (Pleistocene clays, sands and gravels) that are covered by various coarse Quaternary sediments (Pleistocene loess and loess loams and Holocene alluvial and proluvial sediments). There are no major differences in the geomorphological values of the Danube Plain rocks (Ministerstvo vnútra SR 2019). The Bratislava Region is significant for a number of unique natural areas (Table 1).

Table 1. Protected areas in Bratislava region (Protected area – PA, Nature reserve – NR, Natural monument – NM, National natural monument – NNM, National nature reserve – NNR, Protected landscape element – PLE, Protected bird area – PBA, Area of European Importance AWI, Wetlands of International Importance WII (Ministerstvo vnútra SR 2019)

Title	Category	Area [m^2]	Title	Category	Area [m^2]	Title	Category
Pine wood	PA	8 012	Kopáčsky island	NR	826200	Sysľovské polia	PBA
Bôrik	PA	14 284	Topoľové hony	NR	600600	Danube floodplain	PBA
Horský park	PA	229 615	Fialková valley	NR	205879	Záhorské Pomoravie	PBA
Green space by waterworks	PA	2 348	Slovanský island	NR	343772	Devínske lake	AEI
Bajdeľ	PA	86 800	Štokeravská vápenka	NR	127085	River Morava	AEI

Table 1. cd.

Title	Category	Area [m^2]	Title	Category	Area [m^2]	Title	Category
Poľovnícky forest	PA	75 000	Island meadows	NR	549300	Devínske floodplain	AEI
Devínske alúvium Moravy	PA	2 531 600	Starý háj	NR	766520	Devínske alluvium of the Morava	AEI
Lesné diely	PA	5 250	Danube islands	NR	2197100	Vydrica	AEI
Sihoť	PA	2 349 100	Panský diel	NM	156 000	Homolské Karpaty	AEI
Jarovská bažantica	PA	782 579	Rössler quarry	NM	23 828	Devínska Kobyla	AEI
Hrabiny	PA	70 500	Devínska forest steppe	NM	50 966	Bratislava floodplain	AEI
Chorvátske channel	PA	98 463	Devínska castle rock	NNM	17 000	Biskupické floodplain	AEI
Soví forest	PA	418 700	Devínska Kobyla	NNR	1 011 157	Island meadows	AEI
Pečniansky forest	PA	3 953 500	Vápenický stream	PLE	-	Devínske lake	WII
Gajc	NR	627200	Small Carpathians	PBA	-	Alluvium of the Morava	WII

The River Danube, especially after the water level was increased by the Gabčíkovo dam, directly affects all the surrounding areas of standing water. The most important lakes include Zlaté Piesky, Veľký Draždiak, Kuchajda, and Vajnory. Smaller lakes in the district are Štrkovec, Kalné, Malý Draždiak, Trávníky, Rusovské and Čunovské. These were created by gravel mining. Rye Island's groundwater is the largest reservoir of quality drinking water in Europe. Because it is protected, this area is declared a water management area.

Based on the demography of the Bratislava region, we can evaluate the threat of unusual phenomena, related to the weather and climate. Bratislava's relatively complex location is reflected in the specific characteristics of the city's climate and its surroundings. Particularly the Small Carpathians influence circulation and thereby all the other climatic characteristics. Tab. 2 shows extreme values in the monitored area.

Table 2. Historical extremes observed over the entire observation period in the district (Ministerstvo vnútra SR 2019)

<table>
<tr><td colspan="5">Weather and climatic characteristics of Bratislava district
in terms of possible emergencies</td></tr>
<tr><td>Element / characteristics</td><td>Periodicity of 10 years</td><td>Periodicity of 50 years</td><td>Historical data</td><td>Date of occurrence</td></tr>
<tr><td>Wind</td><td colspan="4"></td></tr>
<tr><td>maximum wind speed</td><td>34.5 m/s</td><td>39.2 m/s</td><td>40.0 m/s</td><td>4.8.1979</td></tr>
<tr><td>temperature extremes</td><td colspan="4"></td></tr>
<tr><td>maximum air temperature</td><td>37.5 °C</td><td>39.2°C</td><td>39.4 °C</td><td>8.8.2013</td></tr>
<tr><td>minimum air temperature</td><td>-17.7 °C</td><td>-21.2°C</td><td>-24.7 °C</td><td>9.2.1956</td></tr>
<tr><td>thunderstorm
and torrential rain</td><td colspan="4"></td></tr>
<tr><td>average number of days
with storms in year</td><td colspan="4">21 days</td></tr>
<tr><td>short-term torrential rain – 15 min</td><td>18.8 mm</td><td>23.2 mm</td><td>-</td><td>-</td></tr>
<tr><td>maximum daily
total precipitation</td><td>55.0 mm</td><td>67.8 mm</td><td>86.4 mm</td><td>16.8.1951</td></tr>
<tr><td>snow cover</td><td colspan="4"></td></tr>
<tr><td>maximum height
of snow cover</td><td>46 cm</td><td>62 cm</td><td>71 cm</td><td>24.1.1987</td></tr>
<tr><td>air temperature inversion</td><td colspan="4"></td></tr>
<tr><td rowspan="3">burden of the territory
by inversion</td><td rowspan="3">Borská lowland Small Carpathians, Danube Plain, Danube Highlands</td><td colspan="3">average inversion area</td></tr>
<tr><td colspan="3">low to moderate inversion area</td></tr>
<tr><td colspan="3">moderate inversion area</td></tr>
</table>

3.2. Areas of potential flood risk

Hydrologically, the area is part of the basin of the Danube, the second largest European river. The Danube flows into the district at the Devín Gate and forms a natural border with Austria. On the boundaries of the boroughs of Karlova Ves and Petržalka it flows through the district and forms the boundary with the district of Bratislava V., within the region. South of the village of Hamuliakovo, the main flow of Danube forms the border with Hungary. The length of the river in the region is 29.8 km, the average width is 300 m and Q100 = 11000 m^3/s. In the districts of Bratislava V and Senec, it forms the Hrušov water reservoir as part of the Gabčíkovo dam complex. Close to the Bratislava borough of Čunovo the Čunovo dam is built on the Danube. The Little Danube flows through the region for a length of 27.18 km, the average width of the river is 20 m and Q100 = 90 m^3/s. The Morava River flows through the region for 60 km from the village of Veľké Leváre, to its confluence with the Danube near Devín, forming the border with Austria. The width of the river ranges from 40 to 250 m, Q100 is 1400 m^3/s.

The risk of these rivers overflowing is likely with 100-year waters in the Bratislava boroughs of Devín and Devínska Nová Ves. The existing embankments the Danube provide sufficient protection in Bratislava itself. The existing system of protection is followed by the Gabčíkovo dam. From SNP Bridge (Slovakia) to Wolfsthal (Austria), a new embankment has been built, following on from the flood protection in Austria. The Morava River has no continuous flood protection in Bratislava. The area outside its course is relatively wide with considerable flow capacity (Ministerstvo vnútra SR 2019).

In terms of floods in Bratislava, the most dangerous rivers are the Danube and the Little Danube. There are 21 hydrological structures in Bratislava. The flows of the Bratislava region and the water structures situated on them are listed in Table 3.

Table 3. Hydrological structures in Bratislava region (Ministerstvo vnútra SR 2019)

Title	Water flow	Hydrological structure / Sedimentation	Type of structure
Danube embankment in Bratislava (Petržalka pumping station, closing structure and MVE Pálenisko), pumping station by Chorvátske channel	Danube	hydrological structure	protective embankment – earth, flood walls
GABČÍKOVO DAM	Danube	hydrological structure	system of hydrological structures
SLOVNAFT service station block 127	Danube	hydrological structure	pumping station
Mouth of Vydrica and Čierny stream	Danube	hydrological structure	flood protection line, shut-off structure with mobile pumping station
borough of Devín – Slovanské bank	Danube	hydrological structure	flood protection line
borough of Devín	Morava	hydrological structure	flood protection line

Table 3. cont.

Title	Water flow	Hydrological structure / Sedimentation	Type of structure
borough of Devínska Nová Ves	Morava	hydrological structure	flood protection line, closing structure with mobile pumping station
MCHB WWTP SLOVNAFT	Danube	hydrological structure	concrete tanks
Pálenisko – old (Little Danube – old)	Little Danube	hydrological structure	weir
Small reservoir at 2nd quarry	Vydrica	hydrological structure	Earth dam
Small reservoir at Pod Slivom	Constant flow of Vydrica	hydrological structure	earth dam
SLOVNAFT oil separator WWTP blocks 11 and 17-18	-	hydrological structure	oil separator
Small reservoir at Srnie	Vydrica	hydrological structure	earth dam
Železná studnička – pond no. 1, no.2, no.3, no.4	Vydrica	hydrological structure	earth dam
VN Koziarka	-	hydrological structure	earth dam
Polder on Pieskový stream I	Pieskový stream	hydrological structure	polder
Polder on Banský stream	Banský stream	hydrological structure	polder

3.3. Areas of potential fire and explosion hazard

Forest fires can break out in the Bratislava Forest Park (its area is 3100 ha, including parts of the boroughs of Staré Mesto, Nové Mesto, Karlova Ves, Lamač, Dúbravka, Devín, Devínska Nová Ves, Záhorská Bystrica, Rača and Vajnory), Devínska Kobyla and Lamač, Záhorská Bystrica, the alluvial forests, Pečniansky forest and the forest parks near the Veľký Draždiak and Malý Draždiak lakes, mainly due to human intervention and by exceptionally extreme weather conditions.

The Bratislava region is also exposed to potential risks with regard to fires and explosions in manufacturing plants resulting from the nature of their activities.

In terms of fire situations, the number of flammable substances stored by legal entities and natural persons in the chemical, engineering and food industries also influences the situation in Bratislava. See Table 4 for a list of important manufacturing plants where industrial fires may occur.

Table 4. List of important manufacturing companies (Ministerstvo vnútra SR 2019)

Title	Borough	Activity	Risk arising from the nature of the activity
Volkswagen Slovakia, a.s.	Devínska Nová Ves	Automotive manufacture	classified under Act 128/2015 into category "A"
SLOVNAFT, a.s.	Ružinov	chemical production	classified under Act 128/2015 into category into category "B"
Duslo, a.s., Bratislava	Nové Mesto	chemical production	classified under Act 128/2015 into category into category "B"
Rajo, a.s.	Ružinov	food production	leakage of hazardous substances
Mondeléz SR Production, a.s.	Nové Mesto	food production	leakage of hazardous substances
Prvá Bratislavská pekárenská, a.s.	Petržalka	food production	none
Slovakian Door Company (SDC), s.r.o.	Devínska Nová Ves	development and manufacture of spare parts for cars	none

4. Results, discussion and conclusions

From the point of view of the effects of possible emergencies in the district of Bratislava, the most likely situations are natural disasters (floods, hailstorms, storms, landslides, ice) and accidents (fires, explosions and releases of dangerous substances). The most likely situations can be considered to be natural disasters (Table 5), which arise after cloudbursts and subsequent torrential rains, overflowing watercourses, the rise of groundwater and consequent flooding of nearby houses and adjacent agricultural and forest areas, thereby endangering the life and health of the population, domesticated and wild animals, deterioration of agricultural production, pollution of sources of drinking water, flooding of roads and outages of sources of electrical power that are close to watercourses.

Table 5. Analysis of expected consequences by individual source of risk (Ministerstvo vnútra SR 2019)

Endangered borough	Risk Source / Threat	Crisis Phenomena 1	Crisis Phenomena 2	Crisis Phenomena 3
Ružinov	Transpetrol, a.s.	Leakage of hazardous chemicals	Explosions	Fire
	Bratislava Airport			
Ružinov	Bratislava Airport	Viruses	Bacterial infectious disease	
Devínska Nová Ves	Volkswagen Slovakia, a.s.	Leakage of hazardous chemicals	Explosions	
Vajnory	Linde Gas k.s.			
Nové Mesto	Duslo, a.s.			
Ružinov	Slovnaft, a.s.,			
Ružinov	Rajo, a.s.			
Ružinov	Ružinov sports club V. Dzurilla Arena			
Nové Mesto	STaRZ O. Nepela Arena			
Dúbravka	STaRZ, Harmincova 2 Arena			
Ružinov	Ice-Berg Slovakia, s.r.o.			
Ružinov	Messer Tatragas, s.r.o., o.s.			
Nové Mesto	Mondeléz SR Production, s.r.o.,			
Podunajské Biskupice	Probugas, a.s.			
Podunajské Biskupice	River Danube	Flood	Insect swarms	-
Devín	River Danube			
Karlova Ves	River Danube			
Petržalka	River Danube j			
Staré Mesto	River Danube			

Table 5. cont.

Endangered borough	Risk Source / Threat	Crisis Phenomena 1	Crisis Phenomena 2	Crisis Phenomena 3
Staré Mesto	Pine wood, Bôrik, Horský park, green space by waterworks	Fire	Forest fires	Destruction of soil and plant cover
Podunajské Biskupice	Bajdeľ, Polovnícky forest, Gajc, Kopáčský island, Topoľové hony			
Nové Mesto	Rossler quarry			
Devín	Devín alluvium of the Morava			
Karlova	Sihoť			
Devín	Fialkova valley, Slovanský island			
Petržalka	Hrabiny, Soví forest, Starý háj			
Karlova Ves	Pečniansky les			
Jarovce	Jarovská Bažantica			
Rusovce	Danube islands			
Čunovo	Island meadows			

Assessment of possible threats to Bratislava from the following emergencies:

1) Flooding of the River Danube – endangered boroughs – Podunajské Biskupice, Devín, Karlova Ves, Petržalka, Staré Mesto
2) Flooding of the River Morava – endangered boroughs – Devínska Nová Ves,
3) Threats from forest fires in the Small Carpathians, Bratislava Forest Park, Devínska Kobyla, Lamač and Záhorská Bystrica, floodplain forests, Pečniansky forest and the forest park near the Veľký Draždiak and Malý Draždiak lakes
4) Threat to residents from leakage of dangerous substances in road and rail transport
5) threats to residents from leakage of hazardous substances from static sources: Rajo, a.s., V. Dzurilla Arena, Harmincova Arena, O. Nepela Arena, ICE-BERG, s.r.o., Messer Tatragas, s.r.o., Mondeléz SR Production, s.r.o., Probugas, a. s., Transpetrol, a. s., M.R. Stefanik Airport Bratislava, a.s. (BTS), Volkswagen Slovakia a.s., Linde Gas k.s., Duslo, a. s., Bratislava, SLOVNAFT, a.s.
6) threat of misuse of biological or chemical agents in terrorist attacks. Within the territory of the district there are numerous shopping centres, where a large number of inhabitants circulate throughout the day. Table 6 shows places where a large number of people congregate and thus become a weak point in terms of counter-terrorism security.

Table 6. Overview of buildings and places with a large number of people (Ministerstvo vnútra SR 2019)

Title	Boroughs	Maximum accumulation of persons
Bratislava Main Railway Station	Staré Mesto	10 000
Slovak Lines, a.s.	Ružinov	700
Slovak National Theatre new building	Staré Mesto	2000
Slovak National Theatre historic building	Staré Mesto	500
Nová Scéna Theatre	Staré Mesto	854
ASTORKA Korzo 90 Theatre	Staré Mesto	187
Aréna Theatre	Petržalka	264
LUDUS Theatre	Staré Mesto	175
Slovak Philharmonic	Staré Mesto	1000
Joint property fund of the confederation of trades unions in the Slovak Republic (Istropolis, Trnavské mýto)	Staré Mesto	1690
Cultus Ružinov, a.s.	Ružinov	740
STARZ hl. m. SR Bratislava	Nové Mesto	9942
STARZ hl. m. SR Bratislava	Nové Mesto	426
Ružinov sports club	Ružinov	3215
Inter – SC, spol. s. r. o. (Hant Arena)	Nové Mesto	4609
National Tennis Centre	Nové Mesto	4081
Incheba, a.s.	Petržalka	5455
Bratislava Airport (BTS)	Ružinov	2417
Tesco Stores SR, a.s. OD MY Bratislava	Staré Mesto	889
Tesco Stores SR, a.s. Petržalka	Petržalka	350
Tesco Stores SR, a.s. HM Lamač	Lamač	550
CBRE, s.r.o. (Polus City Center)	Nové Mesto	2530
Aupark, a.s.	Petržalka	7890
Ikea Bratislava, s.r.o.	Ružinov	1750
Ikea Centres Slovenska, s.r.o.	Ružinov	3642
Eurovea, a.s.	Staré Mesto	6934
Centrál shopping centre	Ružinov	-
Bory Mall – shopping centre	Lamač	2810

4.1. Recommendations for developing population protection plans

Prepare a population protection plan under section 3c of Act no. 42/1994 on Civil Protection of the Population, as amended, including anti-radiation, anti-chemical and anti-biological measures. Particular attention should be paid to the following individual measures:

- Monitoring of the area,
- Warning the population and notifying people,
- Evacuation,
- Regulation of the movement of persons and means of transport,
- Pre-medical first aid and emergency medical care,
- Removal of leaks of hazardous substances and prevention of their uncontrolled spread,
- Banning and regulating the consumption of contaminated food, water and feed,
- Measures to ensure rescue work.

4.2. Recommendations to prevent the spreading and consequences of an emergency

The planning of rescue work is based on the worst-case scenario of the emergency, while the most important measure to protect the population is warning the population and possible evacuation. Special attention should be paid to the following measures:

- Checking measures around hydrological structures and watercourses,
- Performing checks on legal persons and natural persons – entrepreneurs who manufacture, store and handle hazardous substances,
- Preparation of directing organizations, forces and means of carrying out rescue work,
- Preparing the population for self-protection and mutual assistance in the event of an emergency,
- Mutual cooperation between emergency units in preparation for emergencies,
- Exchange of experience and knowledge with neighbouring districts.

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Abstract

The paper focuses on emergencies in a particular region of the Slovak Republic. The focus is mainly on describing the emergencies to which the region is most vulnerable and classifying them, as well as specific locations or businesses where there is a high risk of an emergency occurring. From the point of view of the effects of possible emergencies on the district of Bratislava, the most likely situations are natural disasters (floods from precipitation and watercourses, hailstorms, storms, landslides, ice) and accidents (fires, explosions and releases of dangerous substances). When planning rescue work, it is necessary to start from the worst-case scenario of the emergency, while the most important measure to protect the population is issuing warnings and possible evacuation. Special attention should be paid to the following measures: checking the safety measures around hydrological structures and watercourses, carrying out checks on legal entities and natural persons – entrepreneurs who manufacture, store and handle hazardous substances, preparing controlling organizations, forces and resources to carry out rescue work, preparing the population for self-protection and mutual assistance in the event of emergencies, mutual cooperation of rescue teams in preparation for emergencies, exchange of experience and knowledge with neighbouring districts.

Keywords:
floods from precipitation and watercourses, natural disasters, landslides,
slope movements, earthquakes, volcanic eruptions, natural fires

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Sustainable Development Approach in Environmental Engineering Study Programmes

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1. Introduction

Sustainable development is still an actuality in all the fields of living. Among 17 Global sustainable development goals (SDGs) new areas came into effect in January 2016. Such areas as climate change, sustainable consumption, economic inequality, innovation, quality education, peace and justice will have significant consequences for national development planning in both developed and developing countries in the period of 15 years starting from year 2015 (Allen et al. 2016). Allen et al. (2016) discuss scenario analysis and quantitative modelling as important analytical tools to support national sustainable development planning and an available tool to decision makers.

The United Nations declaration of the Decade of Education for Sustainable Development (UN DESD) advocates the need for universities to embed sustainability in all learning areas (Bina et al. 2016). Bina et al. (2016) examines how selected post-graduate top-level programmes in urban studies are adapting their curricula to promote sustainable urban development. There is reviewed extensive literature and identified the principles and practices characterising the UN DESD, topics and themes considered essential for teaching, aimed at the promotion of sustainable urban development. Based on this literature review there has been defined an analytical framework in five parts, related to various aspects of curricular content and teaching and learning approaches: programme orientation, skills, ethics and critical reasoning, interdisciplinary and content related to sustainable urban development issues.

The higher education institutions (HEI) the DESD advocates the need to address the complexity of current real-world contexts by embedding sustainability in all learning areas across university curricula.

UNESCO (Nations 2014) states that a full integration of sustainable values into higher education systems has yet to take place in most countries, the further efforts should be implied that sustainability and sustainable development become an integral part of the academic culture. Education for sustainability is still lacking a consistent interdisciplinary conceptual framework (Jabareen 2012).

Chin & Jacobsson (2016) state that global sustainable development is the challenge that defines our time. SDGs will only succeed when they are owned by every citizen in the world, and when everybody is empowered to become change agents.

As Holm et al. (2015) state sustainability aspects in higher education must be enhanced with more concrete actions. Universities are globally required to have quality assurance to secure and improve teaching and learning, and they use management systems for this aim. Integrating education for sustainable development and management systems are alike in that they are based on continuous improvement and systematic thinking; for both processes all stakeholders need to be involved. Although quality assurance is compulsory for higher education, education for sustainable development has barely been examined or integrated in this context. The research examines how voluntary integration of education for sustainable development into management systems at universities could facilitate a scheme to overcome the challenges to integrating education for sustainable development that were identified in previous research. A process framework for integrating education for sustainable development with management systems was developed in a network of 11 universities in the Nordic countries. The framework included planning, assessment, monitoring, and implementation of education for sustainable development. It was piloted and applied to identify relevant sustainability aspects in different disciplines, examples of which are provided in the article. The framework can be applied to visualize the implementation of education for sustainable development.

As companies and other organizations increasingly recognize society’s demand for greater social and environmental sustainability, university and college business schools have responded with new pedagogic approaches. Business schools have begun to offer courses in business models and business model innovation that focus not only on profit-normative goals but also on social and environmental goals. This paper describes an Experiential Workshop where the students take the role of problem-owners and problem-solvers as they co-create new business models ideas for the cooperative. The paper presents the students’ achievement of three Learning Objectives as they engage in meaningful, “real-world” simulations with a high degree of autonomy that allows them to combine their theoretical knowledge with practice. Implications for educators who wish to test the Experiential Workshop in their classrooms are proposed. The paper concludes with the suggestion that Education for Flourishing is a useful expansion of the ESD (Hoveskog et al. 2017).

Kankovskaya (2016) analyses the spread of the concept of sustainable development in Russian higher education as a subsystem of the national innovation system. There have been analysed state educational standards and educational programmes of universities and identified problems in the implementation of the concept of sustainable development in Russian higher education, and formulated principles for the national innovation system based on the concept of sustainability (Kankovskaya 2016). The aim of this paper was to formulate the principles of development of national system of innovation (NSI), and higher education as the main subsystem in NSI, based on the concept of sustainable development, taking into account the current state of higher education in Russia. Priorities are formulated for the development of a sustainable approach to Russian higher education, including incorporation of principles of sustainable development in the main part of educational programmes as general cultural or general professional competences, an inter-disciplinary approach and inter-faculty integration in the realization of educational programmes. Identified problems suggest that it is advisable to devote time in further studies to examining the constraining factors in the development of higher education for sustainable development.

One of the sustainable development goals is sustainable consumption and production policy (Liobikiene & Dagiliute, 2016), which is a key objective in the renewed European Union (EU) Sustainable Development Strategy (SDS). SDS targets are concerned more with production than consumption side. Three main aspects: smarter consumption, better products, as well as global markets for sustainable products are highlighted in SDS.

The change of energy policy and the overall energy consumption model presumes a holistic approach which should consider and manage a series of parameters such as technology, the economy, politics, society and education (Ocetkiewicz et al. 2017). The paper presents the results of research related to the evaluation of Polish teachers' experiences working in lower secondary schools (3rd stage in the Polish educational system) in terms of education for sustainable development. Unfortunately, the research has shown that Polish school teachers are not well prepared for the inclusion of key issues of sustainable development in school curricula. They are neither aware of the need for those issues to be considered, nor take responsibility for them knowing that sustainable development is the predominant economic, social, and environmental doctrine in Europe and in the world. The teachers know neither the educational principles behind sustainable development, nor their priorities and the objective of promoting a better and multifaceted understanding of the issues which our civilization faces. Teacher training is necessary, as well as raising the teachers' awareness of the principles of sustainable development and changing their attitudes towards it, not only at the school level, but also in everyday life.

Marta et al. (2018) state that High Education Institutions (HEI) play an important role in the promotion of sustainability and an increasing number of stakeholders expect them to be sustainable organizations. Marta et al. (2018) have investigated how the main stakeholders (leaders, faculty, staff, students, and external stakeholders) of Public HEI perceive: the concepts of sustainability and sustainable HEI, the role of higher education for sustainable development, and the barriers, challenges and obstacles to implementing sustainable initiatives in Public HEI. The qualitative approach, using semi-structured interviews and content analysis procedures are applied to explore the perspectives of stakeholders from Public HEI. The results suggest that, although aware of the concept of sustainability, the different stakeholders are not familiar with the concept of sustainable HEI. The lack of financial resources due to the decline in funding for higher education and falling numbers of Portuguese university students is perceived as the main barrier to sustainable development in higher education (i.e. practices are still associated with spending financial resources). This research highlights the importance of a conceptual and organizational change in HEI, notably through identifying new sources of financing, more flexible organizational forms, more comprehensive mission statements, more tailored educational offers, life-long learning and commitment to internationalization, and more strategic human resource management. The present article reviews how HEI could promote sustainability, the main concepts underlying this subject, and the way higher education for sustainable development is understood and could be improved in Portuguese HEI. Finally, raising more funding, attracting more students, transferring knowledge, promoting quality and excellence, and increasing the internationalization of HEIs seem to be the most prominent issues for the future of HEIs. It is suggested further to make the research on identification of sustainability practices already being implemented in HEIs, taking into account: the four pillars of sustainability (economic, environmental, social, and institutional) and the core activities of HEIs (education, research, operations and community engagement).

2. Methods

All the students from Environmental Engineering Faculty of Vilnius Gediminas Technical University (Lithuania) (attending Energy and Water related courses on the second and third years of study in autumn and spring semesters) were instructed about the survey of the quality of studying. Totally 148 students were divided into working teams approximately up to 20 people in each group and all the students answered their questionnaires used for study quality improvements and new curricula development, new knowledge obtaining, lecturing, knowledge used in related practice and other related activities. All the answers were estimated annually, daily and each semester following the results obtained by the students. All the students attended an online survey situated near the university study programmes. The students' answers were related with all theories, some exercises, laboratory works and industrial facilities. All the students were involved in water and energy related projects design, quantities measurements on used energy and water flows. Working teams in the second and third academic years were involved in answering their questionnaires separately with possibilities to evaluate improvement needs following age indicator. Some working team members were absolute "leaders" in answering all the questions and their explanations were related with high load of some exercises or laboratory equipment treatment.

Open presentations on survey progress were carried out annually and according to each semester mostly related to knowledge exchange and corrections of obtained mistakes. All responsible lecturers were advised to estimate statistically approved maximum, minimum and average numbers of the answers and related quantities. Some comparison techniques were in use when evaluating different demand for survey following related activities (study time - schedule, exercises, laboratory equipment treatment etc.). Finally, after last discussions by the end of the academic year we obtained the finished reports on study improvement and possible changes in different courses balanced on annually, practically used and possible academic loads quantities.

Some similarities in different answers for lecturing and practical exercising were obtained in surveys and nearly all the studying groups agreed on possible use of the questions or this survey of study programme improvements. All possible study improvements were carefully estimated and best practice examples taken from each survey to quantitative analyse using software equipment related to analysing of the students' answers, reliability and obtained feedback. The answers obtained by every student, were valid for one semester, two and 3 semesters, imitating possible changes in related improvements and all the changes in study quality were recorded and compared.

Students follow a structured timetable prepared at the Faculty level taking into account the lecturers' timetable and suitability to students' needs. The study process attempts to address a balance between academic subjects, research and skills development and encourages systematic independent work by the students. The study process is regulated by Studies Regulations and the annual plan of study.

3. Results

Investigated Study programme started at University first cycle Bachelor' s studies at Faculty of Environmental Engineering. Official length and form of programme (length in years): 240 ECTS credits, continual studies for four-year studies.

Study programme aims were - to educate professionals who, after they have acquired knowledge while studying the general subjects, basic subjects and specific subjects of university studies, would be able to analyse, model and simulate the energy conversion processes, to identify, formulate and solve the engineering problems related with heat production and conversion, water supply, gas supply and consumption, as well as with indoor air quality, while planning, designing, using new and available energy, thermal equipment and systems, which exhibit high efficiency, cost effectiveness, quality and reliability of energy conversion, consumption and management in a coherent and sustainable demand for resources and environmental impact. Prospective study programme results are described in Table 1.

Professional outcomes: Graduates are employed in heat or water supply, heating, ventilation and air conditioning design, maintenance and production companies; or continue education for Master's degree.

Study programme was updated while implementing 2010-2012 means of Human Resources Development Programme priority 2 “Lifelong Learning” VP1-2.2-ŠMM-07-K, “Improvement of study quality, increase in internationalisation” project “Updating of Study Programmes in Sustainable Living Environment Area of Studies, Strengthening of Interdisciplinary Interaction Applying Innovative Learning Methods and Introducing the Concept of Sustainable Development”. The main aim of the project was to update five first cycle study programmes at the Faculty of Environmental Engineering. Innovative teaching methods, problem-driven teaching, systematic thinking were sought to apply in majority of courses, at the same time granting students’ knowledge of environmental sustainability, its implementation principles, application of advanced technologies. The first objective of updating the study programme was to undergo transition to ECTS credits system, edit the learning outcomes, relate them to courses and create new module cards for course units. The description of 21 modules was created in the Moodle medium while updating the study programme. Study material consisting of 6 modules was prepared to the principles of sustainable living environment. There were created problem-driven teaching materials consisting of two modules.

Table 1. Prospective study programme results

Knowledge	Research skills	Special skills	Social skills
Knowledge of fundamental sciences, nature and its phenomena.	Understanding of laws of fundamental sciences and natural sciences and possibilities of their applicability in professional activity.	Ability to apply knowledge and understanding of the boundaries of production, conversion and use of non-renewable and renewable energy sources, their structure, properties, function, components and processes of interaction, the overall integrity of these systems, their interaction with environment, independently identifying, formulating and addressing the specific environmental engineering problems.	Knowledge and understanding of phenomena in a field of environmental engineering, ability to apply the information of fundamental, social, humanitarian sciences and other technological sciences.
Knowledge of humanities and social sciences to develop the erudition and philosophic outlook.	Understanding of principles of humanities and social sciences and their application in engineering.	Ability to collect, interpret and process the data using computer technologies required to tackle the tasks and challenges in the area of energy engineering, having the skills operating the measuring equipment and laboratory skills working with related equipment.	Knowledge and understanding, ability to formulate and reasonably justify the own decisions, demonstration of a motivated and responsible attitude to their profession.
Knowledge of general basics of technological sciences	Understanding of new and significant problems of researches and development in a field of technological sciences.	Ability to transfer information, ideas, problems and solutions, to reason them, to defend against audience of professionals.	Ability to properly collect, use and interpret data, provide explicit and consistent responds to particularly defined problems and challenges in the field of environmental engineering.

Table 1. cont.

Knowledge	Research skills	Special skills	Social skills
Knowledge of basics of trend of environmental engineering studies.	Understanding the basics of trend of environmental engineering studies.	Skills of self-development, self-learning necessary to continue studies in the next cycle, ability to make rational decisions in the field of environmental engineering, to apply the acquired theoretical knowledge in practice considering the aspects of energy efficiency, energy safety, economics and environmental impact.	Ability to communicate at least in one of the main foreign languages, use modern information and communication technologies, skills to operate in a multi-disciplinary team.
Special knowledge of trend of environmental engineering studies.	Understanding of traditional and innovative technologies of environmental systems and their application methods. Understanding of principles of sustainable development, having a holistic approach to engineering solutions, combining the costs, benefits, safety, quality, reliability and impact on environment.		Ability of learning and self-development, ability to plan and organize professional life, a holistic approach to processes going in the field, contiguous areas and in general society, understanding and ability to explain the principles of sustainable development, ability to assess and forecast the phenomena, their causes and consequences.

Reviewing of study results is overseen by each study programme committee and faculty committee for studies. Social stakeholders and students are also involved in the reviewing process as members of both committees. To receive the feedback the cooperation with graduates, employers and associations is performed, Alumni club is created, student surveys are continuously carried out. Based on such cooperation the needs of the interested parties are determined and considered when learning outcomes of the programme are reviewed. To have a particular course responsible lecturers make an annual review of the contents and improve them if it is necessary. Before starting to deliver a course, lecturers present students with updated detailed course descriptions.

Involvement of students in research and practical activities is facilitated through team work with projects in some of the study subjects, conducting research practice and through their final thesis.

Having acquired practical qualification, students can seek employment as qualified specialists or work in a managerial position in companies, which produce heat or supply water, deal with building, engineering companies that design, install engineering systems or industrial and public buildings with maintenance of these systems.

In order to be qualified for the abovementioned positions, students must meet the following requirements: – abilities to determine and solve problems related to heat production, transformation, supply of heat and water, exploitation of the economy of this sector, as well as engineering problems related to indoor air quality by using modern engineering measures in heat production, transformation, supplying and exploitation of heat and water and indoor air quality engineering systems, designing projects for heat production, transformation, supply and exploitation of heat and water and indoor air quality engineering systems, carrying out research into their impact on economics and environment, using informational technologies to solve problems of general and special engineering activities.

Main results of the survey of Industrial Practice are presented in Table 2.

The results of the survey of Ventilation course with project and laboratory works are presented in Figure 1.

Assessment criteria of students' achievements by Assessment levels is applied to all students.

The threshold assessment (5-6). Has basic knowledge of ventilation methods, equipment and systems, and their design and operation principles, and has a fragmentary understanding of their interconnections with related fields of knowledge, but lacks the ability to apply them. With the assistance of a teacher is able to perform and defend ventilation laboratory works in accordance with the given descriptions, has initial skills using measuring equipment, but they are demonstrated with the teacher's encouragement. Is able to carry out standard calculations of ventilation system design, select equipment using the method, tool and software offered by the lecturer, but the lecturer must encourage to demonstrate these abilities.

Table 2. The results of the survey of Industrial Practice

Career Practice	Year		2013	2014	2015	2016	2017	2018
Company size	1-249 employees	percentage	65.71	51.61	78.05	73.33	77.14	80.00
	250 employees		34.29	48.39	21.95	26.67	22.86	20.00
Workloads	qualified		50.00	25.81	63.41	60	71.43	70.00
	assistance		50.00	74.19	36.59	40	28.57	30.00
Workloads related to Study Program	Very good		30.00	35.46	26.83	46.67	45.71	70.00
	good		50.00	35.50	46.34	46.67	42.86	15.00
	satisfactory		17.00	25.81	26.83	6.66	8.57	15.00
	Not applied		2.00	3.23	0.00	0.00	0.00	0.00
	Can't answer		1.00	0.00	0.00	0.00	2.86	0.00
Useful practical knowledge	Very useful		44.29	45.16	56.10	53.33	68.57	70.00
	useful		44.29	40.32	31.70	46.67	31.43	25.00
	satisfactory		8.57	11.29	12.2	0.00	0.00	5.00
	Non-useful		2.85	3.23	0.00	0.00	0.00	0.00
	Can't answer		0.00	0.00	0.00	0.00	0.00	0.00

The typical assessment (7-8). Has a good knowledge of ventilation techniques, systems and elements, knows the design and operation principles, limited to study materials, is able to connect this knowledge with the knowledge of related fields and apply it in practice in new business situations. Is able by itself to carry out and defend the ventilation laboratory work, in accordance with the descriptions, is able to explain it based on study literature, possesses initial skills in using measuring equipment and demonstrates them during the classes. Is able by itself to choose the appropriate method, tool, software used for ventilation design calculations and equipment selection, explain them on the basis of study literature, demonstrates the abilities during the classes.

The excellent assessment (9-10). Has very good knowledge of environmental techniques, systems and elements, knows the principles of designing and operating them, not limited to the study material, is able to systematically associate this knowledge with the knowledge of related fields and apply it creatively in practical situations. Analysing the solutions of ventilation systems, they are critically evaluated in the context of changing technologies. Is able by itself to quickly perform and defend the ventilation laboratory works, reasonably explain their theoretical and practical significance based on the literature not limited to the study material, has skills in measurements and usage of measuring equipment, demonstrates skills in cooperation with other students during the classes. Is able by itself quickly and accurately select the appropriate method, tool, software used for ventilation design calculations and equipment selection, as well as reasonably explain their theoretical and practical significance based not only on study materials, demonstrates the abilities in cooperation with classmates during classes.

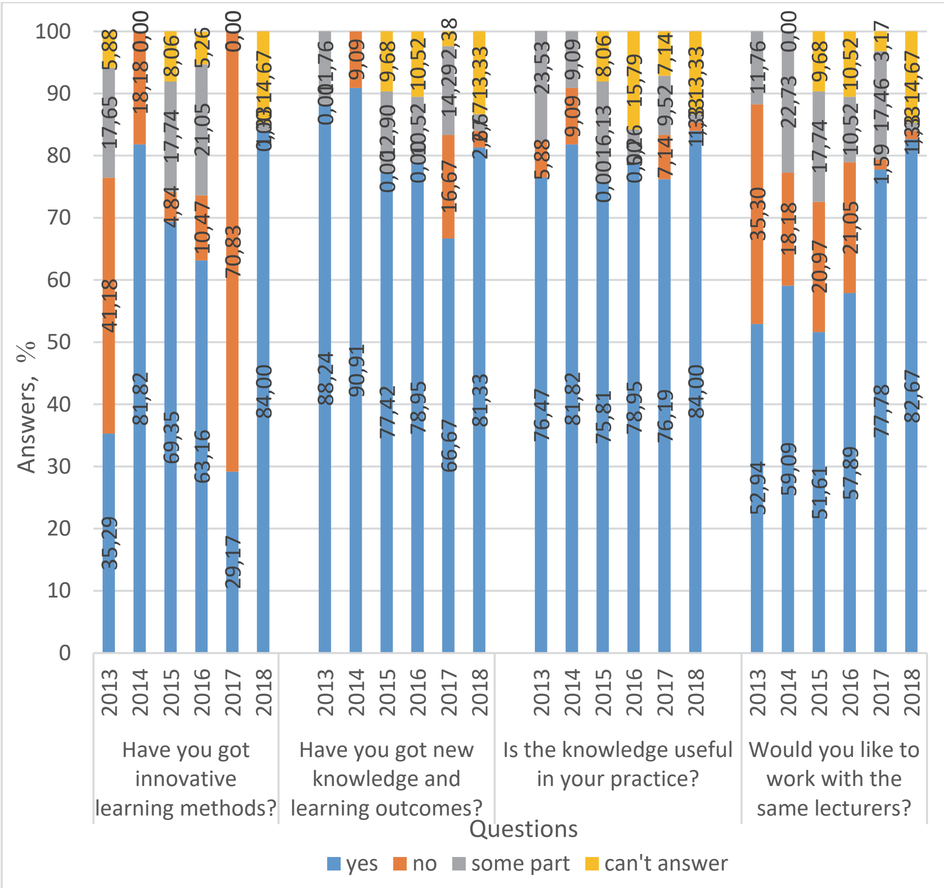

Fig. 1. The results of the survey of Ventilation course with project and laboratory works

The results of the survey of Building Services Systems course are presented in Figure 2.

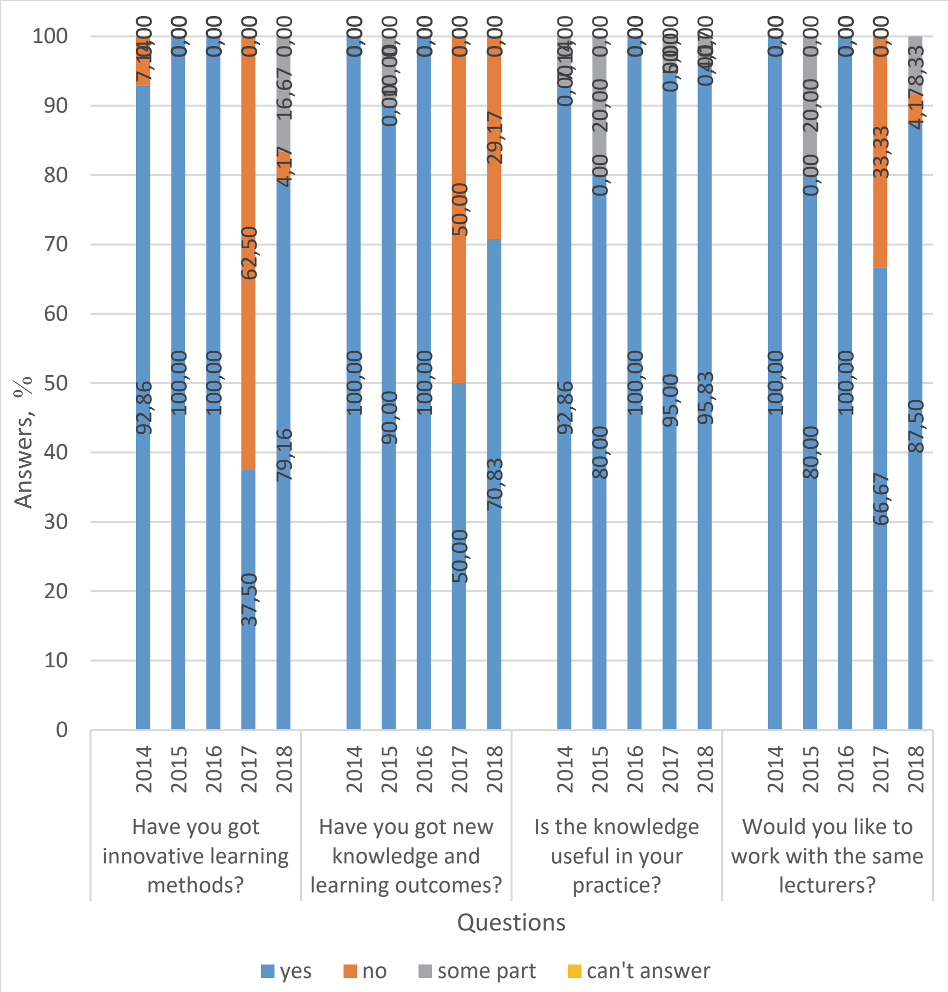

Fig. 2. The results of the survey of Building Services Systems course

Evaluation criteria for knowledge assessment were according to the threshold levels.

The threshold assessment (5-6).

Basic knowledge about water related systems design, fragmented understanding of connection between different subjects without ability to apply. Able to self-selection of useful design methods and under lecturer's control can evaluate design stages and analyse results.

The typical assessment (7-8).

Good knowledge about water systems related elements with limited study knowledge, able to connect similar knowledge and apply to a practical new situation. Able to use background study literature to plan, select a useful design method, to analyse and critically evaluate obtained results.

The excellent assessment (9-10).

Excellent understanding about water related systems without limits to study materials, able to connect with similar knowledge of systems design and creative thinking to practical activities. Able to apply newest scientific literature to the calculations and to evaluate water related systems design, trends, analysis, interpretation and connection with presented elements.

The results of the survey of Fluids Machinery course with laboratory works are presented in Figure 3.

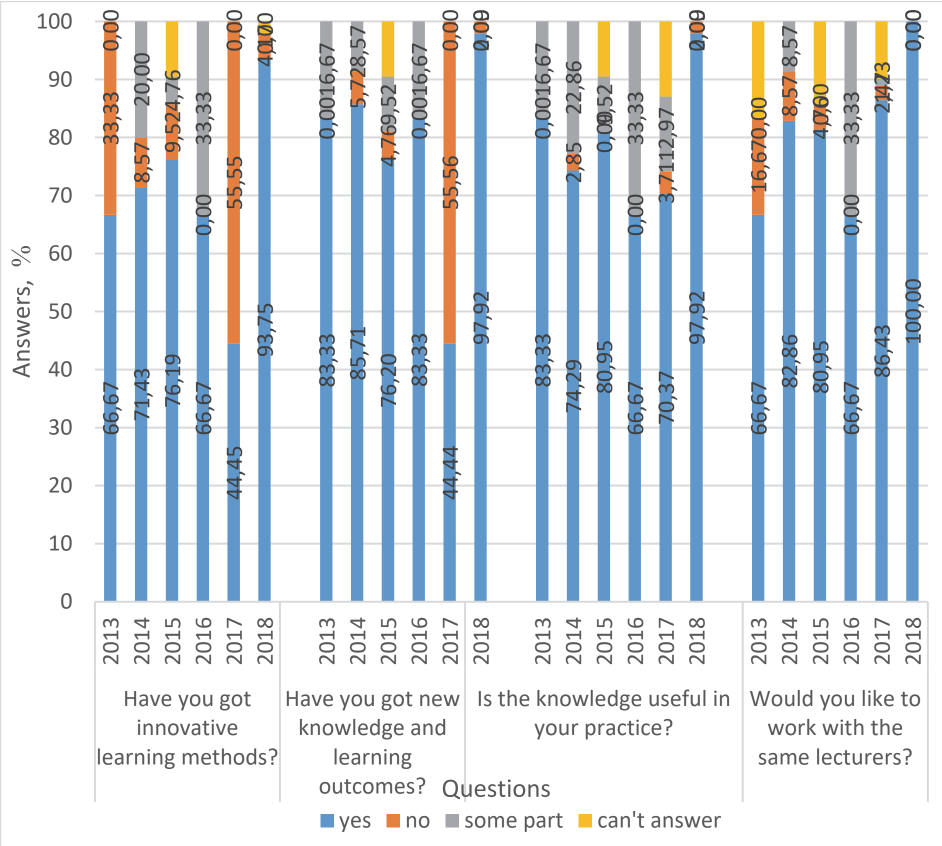

Fig. 3. The results of the survey of Fluids Machinery course with laboratory works

The threshold, typical and excellent assessment marks were made according to obtained knowledge and professional skills.

The threshold assessment (5-6)

Has basic knowledge of fluid supply systems and background of their hydraulic calculation. Is able to do simple hydraulic calculations of water and water heating supply systems, choose fluid movers that are needed in a way, that teacher suggests, has initial skills for using measuring devices, but only demonstrates them after being encouraged by teacher. Is able to choose the appropriate method and solve problems of hydraulic systems while supervised by teacher, understands how they are related with practical examples presented.

The typical assessment (7-8)

Has a good knowledge of the properties of fluid (gas) supply systems and their structure, knows methods of their hydraulic calculation. Is able to do hydraulic calculations of water and water heating supply systems and apply fluid movers by choosing the right way himself, has basic skills for using measuring and control devices and demonstrates them during classes. Using scientific / study literature, is able to plan, choose the right method, investigate and solve problems and tasks of hydraulic systems, analyse obtained results, relate them to practical examples presented.

The excellent assessment (9-10)

Perfectly understands principles of hydraulic calculations of energy and water supply systems and bases of application. Without being restricted to the study material, is able to systematically associate this knowledge with the knowledge of related areas and apply it in practical situations in a creative way. Is able to solve the problem by precisely selecting the appropriate method for performing hydraulic calculations of water and water and heat supply systems, analyse the results and explain their theoretical and practical significance in a reasoned way, based not only on literature used during studies, has skills to use measuring and control devices and demonstrates them in collaboration with other students during classes. In accordance with the latest scientific literature is able to perform accurate calculations of environmental systems tasks, to critically evaluate the results, interpret and associate them with the practical examples presented, to present their conclusions written and verbally during classes.

4. Conclusions

1. In the light of the above results of the surveys, the Programme is constantly developed while maintaining its high quality and competitiveness among other study programmes, all the more so the present study has been launched by double-diploma education system from this year onwards.

2. The programme should have more specific intended learning outcomes consistent with the specific focus on the programme relating the general aspects to those provided by the study subjects. Some of the study subjects intended learning outcomes should be revised to reflect the level of studies.
3. Practical work for students in companies throughout all years of study including visits to different companies after the first year and inviting experts from industry to present lectures to students provides a good link with industry and improves student's awareness of practical issues and opens opportunities for employment.
4. Students' feedback reflected a high level of satisfaction with their experience, good engagement and understanding of the opportunities offered them by the degree.
5. The programme intended learning outcomes should be re-cast to be more specific to the programme rather than the general form presented. It is also concluded that the programme should continue to develop to meet the modern needs of sustainable development reflecting also the need of the country to comply with the European Union and international obligations.

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Abstract

Completed integration of sustainable values into higher education systems has yet to take place in European Union countries, the further efforts should be implied that sustainable development become an integral part of the academic culture. Education for sustainability is still lacking a consistent interdisciplinary conceptual framework all around European countries. Investigated Study programme of Environmental Engineering for the Sustainable Living Environment was carried out at Vilnius Gediminas Technical University (Lithuania) first cycle Bachelor's studies at Faculty of Environmental Engineering. Involvement of students in research and practical activities was encouraged through team work with projects in all related study subjects, providing research practice and through their final thesis. Students feedback reflected high level of satisfaction of their experience in sustainable development topics, reliable engagement and understanding of the opportunities offered to them by Study Programme related to Sustainable Living Environment topics.

Keywords:
sustainable development, study programmes, education,

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Evaluation of Vegetation as a Habitat Factor in Hunting Ground Based on Satellite Images

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1. Introduction

Habitat evaluation is one of the key elements for successful wildlife management. The quickest way for evaluation and quantification of habitats is using of remote sensing and GIS technologies. New technologies provide possibilities such as real-time and more accurate assessment of the environment, leading to a more realistic habitat evaluation (Kushwaha & Roy 2002).

Examining foreign and domestic research papers on this subject (Radeloff et al. 1999, Gerrard et al. 2001, Clevenger et al. 2002, Chan-Ryul & Woo-Shin 2003, Suchant et al. 2003, Weiers et al. 2004, Maringer & Slotta-Bachmayr 2006, Kunovac & Omanović 2012) it can be seen that GIS has become an important tool for habitat suitability assessment using various different methodologies. Certain papers cite usage advantages of NDVI to define temporal aspects of vegetation development (Pettorelli et al. 2007, Hamel et al. 2009, Jaskula et al. 2018). Previous research has shown that GIS and NDVI can be useful in all types of habitat and vast species of animals (Pettorelli et al. 2005a, Boone et al. 2006, Young et al. 2009).

According to Tomašević et al. (1997) habitat evaluation or suitability of hunting grounds represents the sum of all natural conditions as the basic factors on which the survival depends and further reproduction of the game in the hunting ground. Evaluating the habitat quality of the hunting ground is a process that provides a complex assessment of the degree of suitability of the environment conditions for the life of a particular species of game in the hunting ground, on the basis of which a possible number of game per area is determined. It is the assessment of the basic factors such as: food and water, vegetation, soil, tranquility in the hunting ground, terrain configuration and other factors that have an impact on the survival and proper growth of the game. What's more, each organism reflects also to the shape and boundaries of the habitat (Marković et al. 2014).

Habitat evaluation for hunting grounds is a complex area with special type of methodology being used in Serbia and most parts of the former Yugoslavia. Many types of research that covered this issue agree that habitat evaluation for hunting grounds is a complex indicator of vital conditions for certain species of game (Car 1961). According to Đorđevićet al. (2010) it is very important to reconcile the number of animals with the nutritional possibilities of the habitat and the condition of vegetation. This requires a realistic assessment of habitat conditions in the hunting ground, knowledge of the ecology of the game (especially when there are more species), and professional planning during hunting.Habitat evaluation is done in order to calculate the capacity of the hunting ground through the rating classes. All this indicates that habitat evaluation and determination of hunting capacity is an important and responsible job on which hunting management is based.

The habitat evaluation method using GIS represents the unification of a geographic information system and the usual habitat evaluation method used in Serbia and region. The goal of processing satellite images in GIS is to obtain the percentage representation of certain vegetation component which makes the basic habitat factor in the hunting ground. This research started with the assumption that there are ways to improve this method by applying GIS in the process of vegetation factor in the habitat evaluation process. By combination of knowledge about species biology and their habitat needs a chart was created that enables the rating of this factor.

The main hypothesis is that the method used for determining the vegetation factor within habitat evaluation is dated and doesn't provide accurate assessment of vegetation factor.No official methodology is used except descriptive explanation of suitable habitat. The scores are often transcribed and annual changes cannot be tracked so the evaluation often doesn't display realistic state. Vegetation evaluation using GIS can provide annual tracking of vegetation that can be more precise than the former method which is based on field observations. Aim of the paper is to propose a new way of determining vegetation factor using NDVI that would eventually replace existing method used as a part of habitat evaluation process.

The hunting ground "Kapetanski rit" – Kanjiža was chosen as a suitable location for this research being a sensitive area endangered by flooding (Nađ et al. 2018). This means that wildlife in the hunting ground needs to be closely monitored and all aspects and changes of habitat need to be tracked.

2. Material and methods

In the analysis of vegetation factor assessment by using GIS method, the component of vegetation as a shelter provider was emphasized. Calculation of the percentage of vegetation is done on the basis of analysis of satellite images from Copernicus Open Access Hub–SENTINEL-2, S2A_platform, 10 m resolution, for the dates 15.05.2017. and 05.01.2017. NDVI (Normalized Difference Vegetation Index) is used for these purposes. Fieldwork measurements (to determinate if vegetationtype represents appropriate hiding cover) were used as a control method (Figure 1. and Figure 2.). Twenty control points have been taken for both periods (May and Dec/Jan) for small and big game (40 points in total). On each sample plot a vegetation observation was conducted. The cover was assessed for plants 30 cm above ground for small game, and 80 cm for big game. In case of big game, accuracy was 85%. Only in 3 cases (two cases in May, and one in December/January), the vegetation was shorter than 80cm, and in 17 sample plots vegetation was higher even than 150 cm). In case of small game accuracy was 95% and only in one sample plot (December/January) vegetation was less than 30 cm high. In other 19 sample plots the vegetation was high 45 cm on average. The normalized vegetation index difference is a powerful graphical indicator that can be used to analyze images obtained by remote sensing (Pettorelli et al. 2011). For the measurement and mapping of density and dispersion of vegetation, special satellite sensors are used to obtain multilayer images that allow for various analyzes. On the basis of raw satellite data in NDVI values, it is possible to create images that give a state of the terrain according to the type of vegetation. Also a scale has been made to determine the extent to which vegetation is present in a given area (earthobservatory.nasa.gov). Values on this scale are in the range from 1.0 to -1.0 and generalized vegetation indices are presented in Table 1.

Table 1. NDVI and vegetation types; Source: (Jovanović & Milanović, 2015)

NDVI values	Vegetation indices
-0.3-0.1	water and arable land (without vegetation)
0.1-0.4	grassland, shrubs, pastures
0.4-0.85	forests, higher crops, dense vegetation

For the purpose of this paper, the share of vegetation under the NVDI index in the case of a small game is the range from 0.3 to 1.0 and from 0.4 to 1.0 for the big game (as big game don't use short vegetation for shelter) (Table 2). This range includes vegetation such as bushes, higher crop plants or forests.

According to Vospernik & Reimoser (2008), ideal habitats for roe deer (*Capreolus capreolus* L.) represent areas with smaller forests with plenty of open space. Therefore, larger forest complexes or clear fields are not what corresponds to roe deer. The ideal habitat is represented by agricultural plains with small forest areas (Jepsen et al., 2004). The European hare (*Lepus europaeus* Pall.) has adapted very well to the conditions in areas with arable land that belong to the plant index starting from 0.3. The number of brown hare populations is conditioned by the diversity of available nourishment (cereals, grass, twigs and sprouts). When habitats offer diverse nutrition throughout the year, it reflects on hare reproduction and survival, which consequently affects the population increase (Edwards et al., 2000). Therefore, the significance of vegetation for large and small game can be seen, because besides being used as a shelter it also means more available adequate food supply for game. It should be noted that, for the purpose of assessing this factor, a special table is formed, which is also valid for the large and small game on the basis of which the habitat evaluation is carried out. Collecting, presenting, analyzing and interpreting data was conducted using ArcMap 10.3.

Table 2. NDVI and game shelters

NDVI values	Shelter by species
From -1.0 to 0.3	no shelter for the game
from 0.3	shelter for brown hare
from 0.4	shelter for roe deer and wild boar

Study area is hunting ground "Kapetanski rit", which encompasses 37,691 ha and extends on the areas of arable land (80.28%), meadows and pastures (11.75%), water bodies and wetlands (3.40%) forests (2.44%), other (2.13%) and urban areas (settlements, road network) which represents non-hunting areas and cover 13.60%. The hunting ground is a located in the eastern Bačka hunting area (Vojvodina, Serbia), and it was established as a hunting ground of an open type. The hunting ground is located between the Tisa River and the E-75 highway. In the territorial aspect, the hunting ground "Kapetanski rit" belongs to the North Bačka district, it is located on the part of the territory of the Kanjiža municipality.The hunting ground is managed by the Hunting Association "Kapetanski rit" with headquarters in Kanjiža. According to the management plan, the hunting ground "Kapetanski rit" manages the following species of game: roe deer (*Capreolus capreolus* L.), wild boar (*Sus scrofa* L.) and brown hare (*Lepus europaeus* Pall). The population of roe deer on 2017 spring count was 1496 individuals, while average for 2013-2017 period was 1478 individuals.

According to the habitat suitability evaluation it was determined that habitat for roe deer encompasses 24,500 ha of suitable habitat. The density of roe deer population in this hunting ground is 6.11 individuals/100 ha.The wild boar population is smaller due to habitat conditions. Its population is 36 individuals with 40 being the 2013-2017 average. It was determined that suitable habitat for wild boar encompasses just 1500 ha of hunting ground, with density of 2.4 individuals/100 ha. Brown hare is the most numerous small game. Its population was 3540 individuals determined during the 2017 spring, and on average 5158 individuals during the 2013-2017 period. Due to smaller habitat demands it was determined that suitable habitat is 29,500 ha and the density in this hunting ground is 12 individuals/100 ha.

3. Results

On the basis of the obtained values from the table on vegetation prevalence (Table 3) maps were made showing the areas under vegetation in May 2017 and December2016/January 2017 for big and small game in the study area.

Table 3. Vegetation prevalence and rating

May	Points	Dec. – Jan.
75-100%	10	35-100%
50-75%	8	15-35%
25-50%	6	5-15%
0-25%	4	0-5%

As can be seen from the table, the ranges are given in percentages on the basis of which the number of points is assigned. In order to have a maximum 20 points the hunting ground, according to previous similar research (Andersen et al. 2004, Pettorelli et al. 2005b) this methodology suggest it is necessary to have over 75% of the vegetation in May and over 35% of the vegetation in December and January based on the results of the NVDI value in the study area. On the basis of the results obtained in GIS, the values for May and December/January are summated and the final number of points for this factor is acquired. This kind of data processing and assessment tables are used for both big and small game.

Figure 1. shows a map of vegetation prevalence for big and small game given for the month of May. It is noticeable that these maps provide a clear insight into the possible area of grouping of game during that period. These are very useful information for the management of the hunting ground because they allow the display of possible plots where a big and small game could bring up their

offspring. Often, females of both big and small game hide in the bushes and other vegetation in order to give birth. Hence, knowing this, disturbance can be minimized and thus it is possible to actively affect the population.

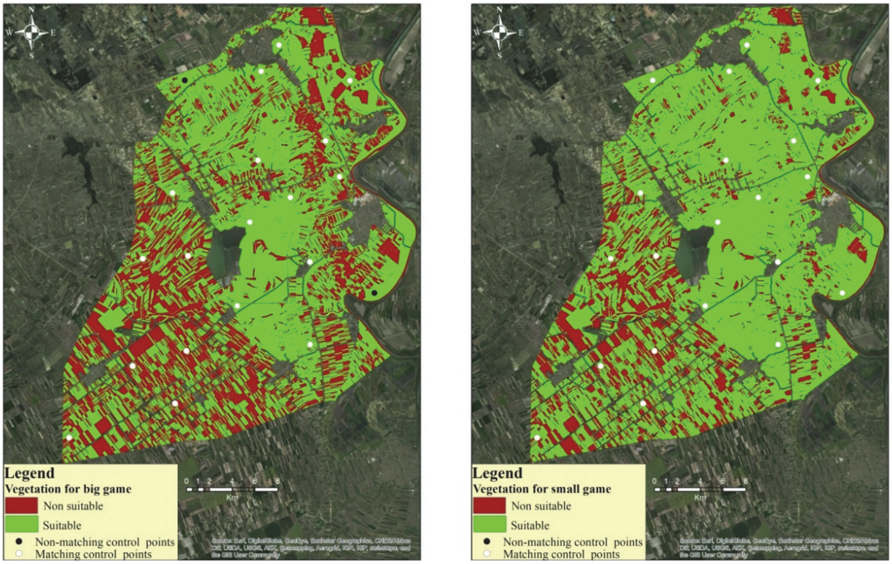

Fig. 1. Distribution of vegetation for big (left) and small (right) game in May with marked control points

Based on the calculation for big game, it was found that the suitable vegetation covers 60.2% in May, giving 8 points. Calculations for small game found that the suitable vegetation in the hunting ground covers 74.5% in May, which also gives 8 points.

Figure 2 represents a map of vegetation for big and small game for the months of December/January. It provides a clear insight into where game can be expected to stay during winter. These are extremely useful information for the management of the hunting ground, as they allow planning the dispersion of facilities during winter, that is, it points out the places where food delivery should increase in this period and the number of predators should be regulated.

As shown in Figure 2. the vegetation for big game in the hunting ground covers 6.2% in December and January, which according to the table gives this factor 6 points. For small game, vegetation covers 21.7% which gives 8 points.

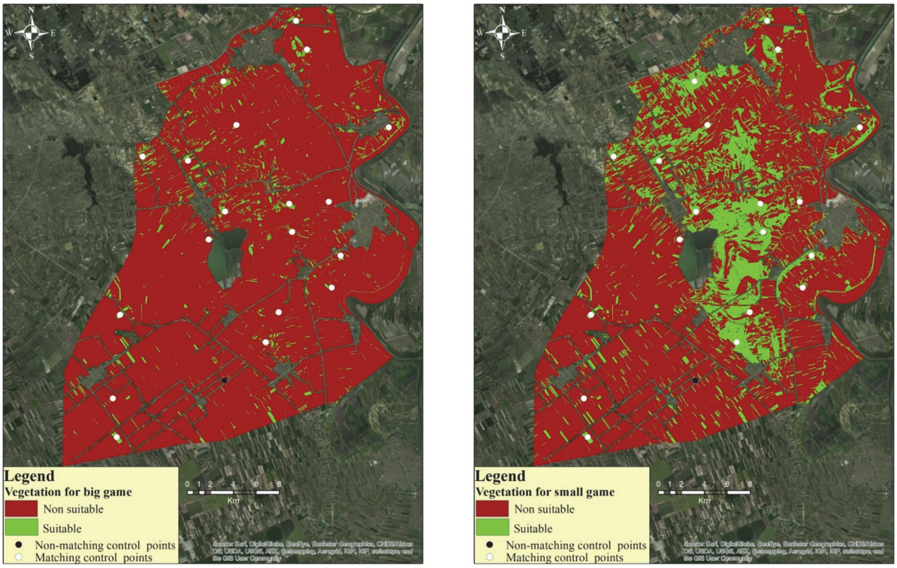

Fig. 2. Distribution of vegetation for big (left) and small (right) game in Dec/Jan with marked control points

It is known that the game is usually most commonly grouped around the forests and other areas of hunting ground with abundant vegetation during the whole year. This way, not only the management of the hunting ground can have a clearer overview of the vegetation cover, but it also helps in the planning process and analysis of the territorial distribution of the game. The overall rating of this factor on the example of the hunting ground "Kapetanski rit" Kanjiža is 14 (from max 20) points for big game, and 16 (from max 20) points for small game in this hunting ground.

According to the current game management plan, in the case of a big game, the vegetation factor was given 18 points. According to GIS methodology, the vegetation factor gets 14 points, i.e. 4 points less. This indicates to the fact that natural conditions in the hunting ground do not correspond to the subjective estimates stated in the game management plans, and that the existing vegetation is not sufficient for the proposed capacity of big game. So, it is necessary to reduce the nurtured number of roe deer from 6.11 to 5.91 individuals/100 ha or to increase the suitable vegetation area for at least 1% in May and at least 8.8% in December/January period. In the case of the small game, according to the current game management plans, this factor was given 16 points, the same is obtained according to the GIS methodology, which indicates that the assessment made in the hunting ground management plans is adequate.

4. Discussion

Vegetation provides food and shelter for game and is one of the most important factors in the hunting ground. This habitat factor includes all existing vegetation in the hunting ground, regardless of whether it is on agricultural, forest or non-arable lands. Vospernik et al. (2007) have noted the importance of vegetation presence in habitats for roe deer. The main importance of vegetation is noted for forage, cover from predators, shelter from adverse weather and daytime loafing area for this species. Similar can be applied for other types of game.

In Serbia methodology used for habitat evaluation in hunting grounds dates to period of former Yugoslavia. The methodology itself differs from the methodologies throughout Europe.Two types of habitat evaluation methods can be mentioned (Srdić 1955; Car 1961) in which the habitat evaluation and determination of hunting capacity is calculated for the main species of small and big game. The basis, from which these habitat evaluation methods were elaborated, was mainly based on the Uckermann method (Drenić 1997) where habitat evaluation was rated based on five to seven factors. The total number of points ranges from 40-100, with the habitat quality of hunting grounds being divided into four, and not to three grades as in Uckermann method. Based on this rating, the capacity of hunting grounds is determined according to the scale given for each species of game. It can be seen that this methodology is quite dated and wasn't improved for decades.

The current methodology used for evaluating the vegetation factor is based on subjective assessment made by the evaluator according to the written instructions. The question arises as to what extent the assessment of the factors involves the subjectivity of the evaluators themselves, since the scoring is based only on description of each factor? Which method could include a more accurate assessment of the factors? For breeding the game, it is crucial that hunting management documentation objectively appreciate all facts from the field (Ristić et al. 2014).

Although remote sensing technology has recently emerged to support data collecting and analysis in forest management (Paivinen et al. 2009, Kuvan et al. 2011, Kalamucka et al. 2016), it is still not sufficiently used, especially in fields of hunting ground management (Franklin 2001). Osborne et al. (2001) have applied NDVI on habitat modeling of great bustards. Even though a different methodology was used it was seen that NDVI is a reliable source for vegetation estimate. Due to importance and complexity of the vegetation evaluation process, we have indicated that NDVI can establish clear mechanism for provision of essential information about vegetation conditions in hunting ground. Through our analysis of NDVIs, controlled by fieldwork measurements, it has become evident that we have obtained reliable results.

According to the methodology of habitat evaluation for big and small game used in the Republic of Serbia, the minimum number of points can be given for the abundance of vegetation is 8, while given a maximum of 20 points it is considered that the hunting ground has exceptional conditions for survival and keeping of game when it comes to vegetation. In this paper, the assessment of vegetation factor was done by processing satellite images for two periods of the year – May and December/January. In May, most wildlife in hunting grounds in Serbia brings up their offspring, so it is extremely important to have the information about the presence of vegetation. Vegetation at that time serves to hide youngling from predators and disasters, but also to ensure protection from disturbance. For the second period, December and January are taken as part of the year when vegetation coverage is minimal due to winter, and therefore game is depleted of natural sources of food. During this period it is necessary that management of hunting ground organizes the providing of food and salt on a regular basis. It is important to emphasize is that feeders for game are positioned precisely in forests and areas of hunting grounds that have a lot of vegetation. This way, the game is ensured to have calmness while taking food and salt, which in the winter months can be a key factor in the survival of wildlife in the hunting ground.

5. Conclusion

The former method of evaluation of crucial factors in the hunting ground proved as very subjective and often imprecise. On the basis of such estimates, it was not possible to get the right state of the hunting grounds, which is proved by the incompatibility of the planned number of game with the number of game calculated during spring counts. With this in mind, it can be concluded that then there is a wrong assessment in the preparation of planning documents and that consequently influences the game management process. The abundance of vegetation is one of the most important factors of the presence, quantity, and quality of game in one habitat or hunting ground. Having numerous, healthy and game with strong trophies is one of the main objectives of hunting management, the need for precise estimates related to the habitat is clear.

This paper proposes a new method by using GIS technology. Using satellite imagery detailed vegetation coverage assessment is enabled in different periods of the year. After the analysis, maps of the hunting ground were made showing the detail dispersion of the vegetation in the hunting ground. In addition, the percentage range is obtained for each of these months. The fieldwork control measurements show the high percentage of reliability of this method for vegetation assessment.

This methodology can be used in both big and small game. Also, one of the advantages over the previous method of assessing vegetation factor is that there is the possibility of making maps of the hunting ground which show the vegetation distribution in the hunting ground, which was not the case with the classical method of evaluation. Besides that, the assessment is much more accurate, since it is done on the basis of the digitization of the hunting ground, therefore it is determined much more precisely. Access to each of the factors in this way will allow evaluation with a lot of data on the actual situation in the hunting ground. Given the widespread degradation of the habitat, new ways for better management of hunting grounds and conservation of game must be sought, and that is the use of GIS for this purpose. NDVI can be of great help in acquiring new and improving data about the state of vegetation. Taking into consideration that NDVI is relatively cheap and quick, it is easy to be implemented. In order to properly manage with hunting grounds, a more comprehensive analysis of natural conditions as vegetation through the applications of NDVI offers to hunting stakeholders more sophisticated possibilities for hunting ground management.

The paper has proven that there are differences in results between the old and proposed new methods of vegetation evaluation. It can be noted that the difference in the results is not very prominent, but even that can make a difference in the field during the hunting management process. Further research is necessary and other types of hunting grounds need to be included to confirm this methodology.

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Abstract

Recent researches have determined that vegetation is one of the essential factors for game habitat quality. Vegetation is important in the form of the following components: as a food supplier, as a shelter provider, as the creator and regulator of the micro-climate of the habitat, etc. Past practice has shown that the classical methods for evaluating habitat factors involve a lot of subjectivity and often lead to an unrealistic estimate of hunting ground capacity that can affect sustainable game management. Instead of the classical analyses, paper proposes assessment of this factor using Geographic Information System (GIS). NDVI – normalized difference vegetation index is a graphical indicator that can be used to analyze images obtained by remote sensing and is used for these purposes. The researched area was hunting ground “Kapetanski rit” – Kanjiža, Serbia. In order to assess the vegetation factor, the analysis of satellite images is done for two periods of the year (May and December/January). In May the game prepares shelters for bringing an offspring and the period December/January is taken as part of the year when vegetation coverage is minimal due to winter and game is in need of additional food and shelter. Based on the results and maps, the user of the hunting ground can have a clearer view of the vegetation types and distribution, hence assistance in planning and analyzing the territorial distribution of the game. Comparing classical methods for evaluating vegetation and the use of GIS for this purpose shows the advantages of new improved GIS methodology.

Keywords:
habitat evaluation, vegetation, GIS, NDVI, hunting ground

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Protecting and Securing an Environment Affected by Industrial Activity for Future Utilization

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1. Introduction

Extraction of minerals is one of the main activities of the world economy involved in creating social goods. However, this activity causes environmental damage, and these negative impacts, along with some socio-economic impacts of extraction, threaten our sustainable development goals. Experts around the world are addressing this issue and are looking for appropriate solutions and methods for environmental safety in extraction industries (Perminova & Lobanova 2018, Sánchez-Sierra et al. 2018, Straka et al. 2016, Trubetskoy et al. 2017, Vartanov et al. 2017, Vilamova et al. 2016).

From the case study "Challenges to access and safeguard mineral resources for society: A case study of kaolin in Portugal" we learn about the importance of mineral raw materials for society (Lopes et al. 2018).

Ensuring the safety of extraction activities in Russia is mentioned in the scientific paper "Risk-oriented provision of extraction operations safety at the enterprises of mineral resources sector in Russia" (Vartanov et al. 2018).

Researchers Vartanov, Petrov and Fedash also deal with the development of "safety in mining" (Vartanov et al. 2017).

The study "A hybrid semi-quantitative approach for impact assessment of extraction activities on sustainable development indexes" was prepared to present a general assessment of the impact of extraction on sustainable development indicators (Amirshenava & Osanloo 2019).

The long-term planning of extraction using the energy triangle is addressed by Marx and Wolff in their publication (Marx & Wolff 2018).

The case study by Hummel, Ruiz and Kelafant addresses the renewal of coal mining in India with environmental and economic perspectives (Hummel et al. 2018).

In northern Spain, experts compiled a study dealing with the effects of extraction on the contaminated Nalón River (Garcia-Ordiales et al. 2019).

The impacts of surface extraction and the subsequent reclamation in Red Hill Mine are discussed in "Post-reclamation Age Effects on Soil Physical Properties and Microbial Activity Under Forest and Pasture Ecosystems" (Adeli et al. 2019).

The case study of the Yanzhou coal area deals with the consequences of underground mining on the surrounding ecosystem (Xiao et al. 2018).

You can read about the environmental safety of the mining industry in "Environmental Impact of Abandoned Mine Wastes on an Urban Area in NW Caucasus" (Drebenstedt & Alekseenko 2018).

The topic of the development of mining and quarrying with regard to the environment is addressed by the conference document "Land-and-Ecological Problems of Kuzbass Mineral Resources Development" (Solovitskiy et al. 2018).

Conditions of extraction of existing mineral deposits are more problematic and complicated. For this reason, the issue of using existing deposits is particularly topical and this is justified by Gridina and Andreev in their article (Gridina & Andreev 2018).

Sustainable development of extractive industries is not possible without the use of modern solutions. A publication on this issue was prepared by Rylnikova et al. 2018.

The several authors commented on the closure of mining enterprises and pointed out that, in addition to improving the ecological situation, closure also leads to activation and emergence of new dangerous geological processes and phenomena (Posephov et al. 2018, Loučanová & Olšiaková 2019).

The specialist article "Natural and formal-legal aspect of the environmental impact assessment of the planned reclamation of mining damage in the Szotkowka valley (Southern Poland)" is also of interest. The article deals with the problem of liquidation of mining damages, using post-extraction waste (Soltysiak et al. 2018).

Other important publications in which the authors deal with the environmental impacts of mineral extraction are "Radon bearing water protection in underground uranium mining - A case study" (Yun et al. 2017), "Thermo-hydraulic modeling of artificial ground freezing: Application to an underground mine in fractured sandstone" (Vitel et al. 2016), and "Regional Impact of Uranium Mining on Piezometric Surfaces in a Multi-layered Water-bearing System, Bohemian Cretaceous Basin, Czech Republic" (Lipansky 2017).

The safe and efficient development of underground resources is addressed in the paper "Ensuring the Environmental and Industrial Safety in Solid Mineral Deposit Surface Mining" (Trubetskoy et al. 2017).

The implementation of a long-term strategy for sustainable technological development in the mining industry is discussed by Berger, Director, Fedoseev, Geologist and Saraskin (Berger et al. 2017).

2. Theoretical base

2.1. Capacity of the deposit and its importance for future use

The reserved deposit of andesite at Ruskov and the extraction area of Ruskov I are located about 1 km east of the village of Ruskov, about 10 km as the crow flies east of Kosice. At present, the Ruskov I extraction area has two parts, the new Strahuľka deposit, which has been quarried since 2008 and the currently unused part, the Ruskov – Old Quarry deposit (Fig. 1).

The main reason for writing off the deposits at Ruskov – Old Quarry was in particular the special and complex extraction and technical conditions as well as the economics of extraction (Dobrovic et al. 2018).

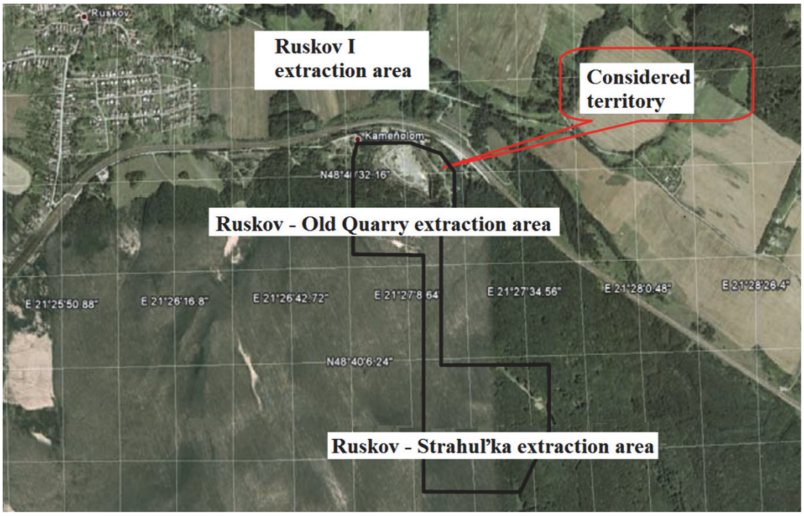

Fig. 1. Organization of extraction in the Ruskov I extraction area

In effect, this ended activities in the quarry and it is now only being maintained in terms of security and stability. The high walls of the quarry have gradually weathered and become overgrown with trees. Occasionally, under the influence of weathering, blocks of stone or stone debris have fallen. Access to the quarry was blocked, the original equipment gradually lost its functionality, it was technologically abandoned and written off.

In 2010, the demand for processed commodities from the Strahuľka quarry increased to such an extent that it would not be sufficient to cover construction demand. Therefore, the overall level of deposits at Ruskov, including the existing unused extraction area of Ruskov – Old Quarry, was reviewed. For this purpose, four exploratory boreholes were drilled and the results from past exploratory drilling work were re-examined.

At the same time, the parameters of the overburden for the expected quarrying were also examined. Based on the above-mentioned geological survey and calculation of deposits, it can be stated that this survey confirmed that the body of the andesite deposit is continuous, in particular in the direction of the depth from the floor of the quarry, to a depth of at least 30 m. The second analysis verified the anticipated deposits in the south-south-west direction from the walls of the current quarry so that the safety inclination ratios of the side walls are preserved and the limit of the existing extraction area, or more precisely, to retain the current safety distance around the extraction area to the edge of the highest cut. The total area of both blocks of represents a total area of 8.7 ha. Of this, 5.2 hectares are in the current quarry area and 3.5 hectares are the new extraction area in the southern direction.

Based on the data in the quarry and the allocation of raw material blocks, the stock of raw materials was calculated as 6 279 000 m^3 (Fig. 2).

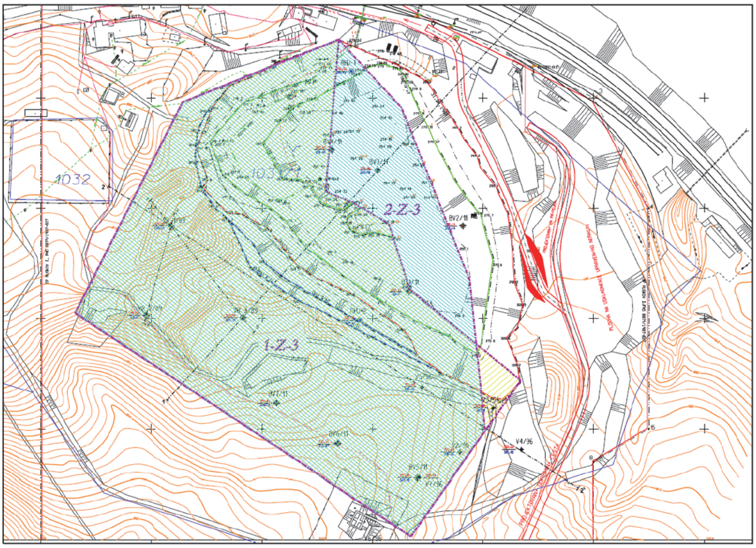

Fig. 2. Geological map of deposit blocks

Verification of the deposits of building stone in the Ruskov I extraction area “based on the results of the final report and the calculation of reserves at the Ruskov reserved deposit, was prepared for the years 2012-2032, which continues the activity previously performed.

Overburden applies only to the area of exploitation outside the existing quarry to the south and southwest. The overburden ratio of 1:8 is currently very unfavourable (despite its partial removal in the past with the assumption of continued extraction) and its volume was calculated to be about 770 000 m^3. Overburden mainly consists of a small volume of soil (partly removed in the past or eroded) but mainly a relatively large volume of weathered material, debris and fillings of fissures, grooves and erosion or tectonic depressions often at a considerable size of up to 18 m.

The expected maximum annual volume of extraction in the old quarry extraction area is 800 000 tons, but fluctuations in extraction are expected, influenced by the implementation of larger investment projects in the region, especially in connection with the construction and modernization of transport infrastructure.

2.2. Regulations and standards defining safety of the extraction site

When carrying out extraction activities, the prepared safety plan must be adhered to, based on the decision of the District Mining Authority of Košice for the permit for extraction activity, Act no. 44/1988 as amended, Act no. 51/1988 as amended, and other implementing regulations issued on their basis, Act no. 311/2011 the Labour Code as amended, operational documentation, basic documentation, the emergency plan, Act no. 124/2006 as amended.

Particular attention should be paid to the Decree of the Slovak Mining Office no. 29/1989 on health and safety protection at work and safety of operations in mining and surface extraction operations.

The operating documentation consists of technical procedures, operating procedures, operating and maintenance instructions, traffic rules. Pursuant to Government Decree no. 117/2002 on minimum requirements for the protection of the health and safety of employees in mining activities and in the extraction of non-reserved mineral deposits, the organization ensures the updating of operational documentation with proposals of safety measures to protect the health and safety of employees in ordinary and emergency situations. Everyone affected who must be in the workplace will be demonstrably instructed in it.

Compliance with safety regulations and safety is the responsibility of the organization and all personnel within the scope of their powers and responsibilities as specified in the Code of Conduct, applicable operating documentation, and safety regulations. This part of this chapter also includes the assessment of the risk of extraction activity on the surface, and evaluation of the unavoidable danger and unavoidable threats inherent to extraction activities and the proposal of protective measures, which are prepared in accordance with Act no. 124/2006 on Occupational Health and Safety Protection at Work, as amended.

There are no old mining works, mines or quarries in the area of the Ruskov quarry or in its vicinity, with respect to the occurrence of explosive gases and dust, spontaneous combustion, fractures of rocks, coal and gases, water and mud flows and other dangerous phenomena.

3. Case study

3.1. Securing the technical properties of the quarry

The reason for securing the quarry in the Ruskov – Old Quarry extraction area is the interruption of extraction and termination of the drainage of the deposit and the removal of extraction waters formed by rainwater and groundwater inflows from the rock massif, for economic and technical reasons, resulting in the flooding of the lower quarry. The reason for the technical modifications - is to ensure safety and protection from falls into the unsecured space, the open depth. Currently, the quarrying company does not intend to continue extraction in view of the market situation, which however may change in the future due to market conditions.

The whole area of the quarry and other structures located outside the quarry which were not used for quarrying (waste management, sanitary building, etc.) are located in the area, which is guarded by a guard service outside working hours and during working hours there is a shipping employee on the access road, i.e. entry to the premises is only possible on the basis of an entry permit. The quarry itself is partly fenced on the top of the highest cut (crown) and partly protected with embankments. On the access roads there are signs with a ban on unauthorized entry.

The quarry will be secured in such a way that access to the quarry itself is prevented by a boom barrier and there will be a sign stating that there is to be no unauthorized entry. Access to crowns above the highest cuts with the danger of people falling into the quarry will be prevented by appropriate technical measures, embankments or similar (adding wires with warning tape) and “Danger Quarry” and "No Entry” signs with appropriate pictograms will be placed at regular distances. Technical adjustments to the quarry floor will not occur due to permanent flooding.

No significant adverse effects on the surface are anticipated at the time of securing the quarry. The risk of water erosion and landslides is minimal due to the area of the quarry. Sufficient measures against landslides were taken during the extraction activity. This was mainly about adhering to the set parameters of final slopes.

Ruskov I – Old Quarry, is currently spread over three levels of varying heights from 15 to 20 m. Adjusting the quarry slopes is not considered during the process of securing and technical refinement, the bottom of the quarry is flooded. Tippings are not found in the Ruskov I quarry.

When performing adjustment works, checks will be performed once per shift. Checking the status of safety features (fences, barriers, warning boards) will be carried out by a shift technician at intervals of once per week, or at more frequent intervals as needed. In the case of damage to the safety equipment, repairs will be arranged with possible supplementation. The inspection results will be monitored and recorded (Laboš 2017).

3.2. Securing the environmental properties of the quarry

Securing the territory of the Ruskov quarry is also includes management of extraction water. Drainage of the deposit and removal of quarry water consisting of rainwater and groundwater inflows from the rock massif was designed by catching it and pumping it from the sump in the lowest parts of the excavated area. At higher levels, the inclination and utilization of the terrain morphology, will ensure the drainage of rainwater outside the quarry area.

In 2014, extraction activity ceased and pumping water from the quarry stopped. During extraction, water from the quarry was pumped out of the built-in sumps, according to the amount of water flowing in. Pumping was not continuous.

According to information from the customer, there were no problems with leakage of extraction waters outside the extraction area when draining the quarry. Since 2014, when pumping water from the quarry ceased, until now, no springs or waterlogging of slopes in the surrounding area have emerged, which would indicate leakage of quarry water outside the extraction area of the deposit.

According to the measurements, the water levels in the quarry were normal. The area of the flooded part of the quarry is 19 400 m^2. With an average level of approx. 3.4 m, it is possible to expect approx. 67 000 m^3 of water in the quarry.

On the basis of this data and knowledge and hydrogeological conditions, it is possible to estimate the amounts of rainfall and groundwater flowing into the quarry.

Bystrý stream represents the local drainage base for the area of the Ruskov quarry. Infiltrated water, which has not flowed into local subsystems, descends to larger depths and integrates into the intermediate flow subsystem (Olšava Valley). The measured runoff of groundwater, calculated from hydrogeological flows, balance and runoff from springs, in the assessed area mostly ranges from 0.8 to 1.1 l/s per square km.

According to the physical and chemical analysis of the water sample, the water in the quarry is of a basic highly magnesium-bicarbonate type. Total mineralization is 375 mg/l, ph – 8.4, contents Na – 13.4 mg/l, Ca – 41.1 mg/l, Mg –
26.2 mg/l, Fe – 0.04 mg/l, Mn – 0.012 mg/l and in hydrogeological investigation the mineralization of precipitation water ranged from 25.8 to 48.0 mg/l, pH 6.0-6.6.

By comparing the values for the tributaries in to the pit of the old Ruskov quarry and the values of groundwater runoff in the volcanic massif, we can state that only a part (approx. 50%) of the groundwater from the volcanic massif is involved in inflow into the quarry. The greater part of the underground runoff is into the local flow sub-system in the local erosion base, which is represented by the valley of the Bystré stream, or incorporated into the intermediate flow stream (Olšava valley, erosion base).

In the previous extraction activity in the Ruskov Old Quarry, as well as after was flooded in August 2014, no adverse effects on the flow and groundwater regime were observed in the evaluated area.

Based on the re-evaluation of the hydrogeological conditions of the area, we can state that after the interruption of extraction at the Ruskov – Old Quarry deposit and the end of pumping of quarry waters, there is no expected adverse influencing on the flow and groundwater regime in the evaluated area (Fabian 2017).

3.3. Ensuring the safety features of the quarry

There are no old mining works, mines or quarries in the area of the Ruskov quarry or in its vicinity, with respect to the occurrence of explosive gases and dusts, spontaneous ignition, rock falls, coal and gases, water and mud slides and other dangerous phenomena.

The danger and hazard assessment of the safety of the Ruskov quarry according to established site criteria is analysed in Table 1.

A danger is understood to be a condition or property of a factor of the working process or the working environment that can harm health. Another state is a hazard, meaning a situation in which it cannot be excluded that the health of an employee will remain unaffected. Other conditions are unavoidable dangers and unavoidable hazards, dangers and hazards that cannot be ruled out or limited with current scientific and technical knowledge.

Table 1. Assessment of Danger and Hazards in Securing the Ruskov Quarry

No.	Working process and environmental factor	Unavoidable danger	Unavoidable hazard	Place of occurrence	Proposal of protective measures
1	Human factor	Lack of discipline, forgetfulness, physical fitness, indisposition and so on	Injuries of varying nature	The whole area of the quarry	Regular inspection of the quarry by the supervisory authority and other technicians
2	Walking in the quarry area	Fall while walking	Various injuries	Quarry site	Keep walking paths in a safe condition
3	Working with fire – welding in mechanisms during maintenance	Occurrence of fire	Burns	Locations with increased fire hazard	Prohibition of open flames, no smoking
4	Intrusion of persons into unauthorized areas	Damage to equipment damage	Various injuries	The whole area of the quarry	Exclude the presence of persons in dangerous working and driving areas

Table 1. cont.

No.	Working process and environmental factor	Unavoidable danger	Unavoidable hazard	Place of occurrence	Proposal of protective measures
5	Weather conditions	Freezing, fog, rain, storm activity	Various injuries	Quarry site	Maintenance of traffic routes, control of water drainage system from working areas
6	Possibility of landslides	Threats to people and mechanisms	Various injuries	Quarry area	Perform loading and unloading in accordance with the operating documentation. Machine operators and drivers must constantly observe the quarry walls, and in the event of danger, stop work at and move away from the danger area

4. Results, discussion and conclusion

The proposed activity is caused by the exceptionally increased interest in building aggregates in connection with the intensification of construction development in eastern Slovakia and abroad. Therefore, the investor has decided to review its levels of deposits within the existing extraction area of Ruskov I and restore extraction activity in it without opening a new quarry and a new intervention in the landscape. After the geological survey, it was confirmed that there is a sufficient amount of extractable reserves of raw materials in the deposit, using existing equipment and technology used in extraction in another part of the Ruskov I extraction area, in the Strahuľka quarry. This concerns in particular the raw material processing equipment. There will be no new intervention in the landscape outside the existing quarry, and this will be rationally exploited until the deposits are fully exploited. At the end of extraction, the final disposal of the quarry and its landscaping and biological reclamation will be carried out so that the final landscape of the quarry is harmonized with the wider surroundings.

According to the physical and chemical analysis of the water sample, the water in the quarry is of a basic high magnesium-bicarbonate type. The total mineralization 375 mg/l, ph – 8.4, content of Na – 13.4 mg/l, Ca – 41.1 mg/l, Mg – 26.2 mg/l, Fe – 0.04 mg/l, Mn – 0.012 mg/l and in the hydrogeological investigation the mineralization of precipitation water ranged from 25.8 to 48.0 mg/l, pH 6.0-6 6.

In terms of future investments, it is necessary to take into account activities and structures that may have a negative impact on conservation objectives in the area under discussion and which create additional research opportunities.

Important activities affecting further development:

- landfill,
- introduction of telecommunication masts and transformer stations,
- introduction of long-distance and local electricity distribution,
- construction of buildings,
- performing activities changing the state of wetlands or watercourses,
- geological work,
- extraction of building stone,
- discharge of waste water,
- the spread of non-native plant species,
- the spread of all non-native animal species.

Important structures affecting further development:

- landfill,
- telecommunication masts and transformer stations,
- long-distance and local electricity distribution,
- building,
- extraction works,
- roads of classes I to III.

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Abstract

At the present time, there are many abandoned areas and places that are affected by extraction activity, but which continue to be of importance due to valuable mineral resources. This article deals with environmental protection for their future use in terms of potential mineral resources. The area of Ruskov in Eastern Slovakia is typical with its rich deposits of andesite. Currently, there is no extraction activity at the site. The problem is related to effectively securing and protecting the environment for future use. The aim of the article is to indicate the possibilities for securing and protecting the area. The procedure can be applied universally to similar types of areas.

According to the physical and chemical analysis of the water sample, the water in the quarry is of a basic high magnesium-bicarbonate type. The total mineralization 375 mg/l, pH – 8.4, content of Na – 13.4 mg/l, Ca – 41.1 mg/l, Mg – 26.2 mg/l, Fe – 0.04 mg/l, Mn – 0.012 mg/l and in the hydrogeological investigation the mineralization of precipitation water ranged from 25.8 to 48.0 mg/l, pH 6.0-6 6.

From the comparison of values for inflows to the pit of the old Ruskov quarry and the values of groundwater runoff in the volcanic massif, we can state that only a part (approx. 50%) of groundwater from the volcanic massif is involved in the inflow to the quarry. The greater part of the underground runoff flows in the local sub-system to the local erosion base, which is represented by the valley of the Bystré stream, or it joins the flow of the intermediate stream (Olšava valley, erosion base).

In the previous extraction activity in the Old Quarry of Ruskov, as well as after it was flooded in August 2014, no adverse effects on the flow and groundwater regime were observed in the evaluated area.

Based on the previous evaluation of the hydrogeological conditions of the area, we can state that after the interruption of extraction at the Ruskov – old quarry deposit and the termination of pumping of quarry water, there is no expected adverse influence on the flow and groundwater regime in the evaluated area.

Keywords:
safety, environment, protection, risks, principles

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Graphene – the Nanomaterial for Preparation of Next Generation Semipermeable Membranes

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1. Introduction

Water is essential for any form of life on Earth. The continuous population growth (from current 7 to predicted 10 billion of people in 2050, urbanization and intensive industrialization as well as climate change and limited fresh water resources are key factors resulting in a number of stresses in global water demand. 98% of all water resources appears in the form of saline water, whereas only 2% corresponds to freshwater, among which almost 70% is cumulated in snow and ice, while 30% appears in the form of ground waters (Yang et al. 2018). More than 1.2 billion of people suffers due to the limited access to clean and sanitary safe freshwater, and the water scarcity will continue to increase in next decades (Montgomery & Elimelech 2007).

Nowadays, reverse osmosis (RO) is the main process used to water, especially seawater, desalination, as it is well recognized and corresponds to market demands. As of June 30, 2016 the total number of desalination plants worldwide was 18,983 and these plants have cumulative fresh water production capacity of 95.6 million m^3/day (Voulkov 2018). Nevertheless, despite a number of features of this desalination process, its economy, environmental impacts, feed water preparation issues and utilization of used membranes. Most of commercial RO membranes are based on thin film composite (TFC) polyamide and polyamide derivatives membranes. Their main disadvantage is related to relatively low water permeability (from 2 to 8 $L/m^2{\cdot}h{\cdot}bar$ for brackish- and 1 to 2.2 $L/m^2{\cdot}h{\cdot}bar$ for seawater desalination), insufficient selectivity and high fouling affinity as well as poor chemical and mechanical stability (Werber et al. 2016). The energy demand, which has been significantly improved since 1990s, when it was 5 kWh/m^3

to current 1.8-2.0 kWh/m^3), is still much lower than for other desalination methods, especially thermal ones (Elimelech & Phillip, 2011). Nevertheless, conventional polymeric membranes used in RO systems suffer due to severe fouling, highly undesired phenomenon responsible for membranes' capacity decrease (Matin et al. 2011). The similar problems are connected with membranes from other membrane techniques (Basile et al. 2015).

Next generation of membranes should overcome limits related to water and wastewater treatment by improvement of structural and physico-chemical features and introduction of antibacterial, photocatalytic or adsorption properties. Recent analyses have indicated that the use of RO membranes of three times higher water permeability results in 15% energy demand decrease and 44% decrease in number of pressurized tanks required for seawater desalination process, as well as 45% energy demand decrease and 63% pressurized tank number decrease in wastewater treatment (Cohen-Tanugi et al., 2014).

In recent years, the growing interest in the use of nanomaterials for development of next generation of membranes of advanced antifouling properties to be used in water desalination and wastewater treatment, has been observed (Werber et al. 2016a). The development of nanomaterials and nanotechnologies enables the improvement of a structure and transport properties of membranes. Among available nanostructures, the most of attention is given to fullerene, carbon nanotubes (CNTs) and graphene based materials (Manawi et al. 2016, Goh et al. 2016).

A number of recent research in the field of water desalination and wastewater treatment is dedicated to the use of graphene-based materials (Goh et al. 2016; Cohen-Tanugi et al. 2012), what is confirmed by latest articles discussing the positive role of graphene oxide (GO) in membranes' manufacturing. In this paper methods of synthesis of membranes containing graphene and its derivatives, their properties and application areas are discussed.

2. Graphene and graphene oxide

Graphene is a thin layer sheet of densely packed carbon atoms, which are bonded with each other in the form of uniform hexagonal structures, similar to honeycomb lattice (Fig. 1). As the thickness of a single graphene sheet corresponds to the thickness of single carbon atom (i.e. 0.3 nm), its special structure is simplified to 2D (Suk & Aluru 2010) (Fig. 1a). Carbon atoms within graphene structure are bonded by means of strong sigma bonds of sp^2 hybridization and very short length (0.142 nm) (Cohen-Tanugi et al. 2014). Graphene characterizes with a large specific surface area, very low weight (1 m^2 sheet of graphene weights ca. 0.77 mg), outstanding heat transfer (from $4.84 \cdot 10^3$ to $5.3 \cdot 10^3$ W/m·K at room temperature), exceptional flexibility, relatively high conductivity (from 10^2 S/m) and mechanical strength (from 100 to 300 times higher than steel, tensile strength – 130 GPa, Young module – 1 TPa), is also excellent, mobile charge carrier (Marinho et al. 2012, Lee et al. 2008).

Despite negligible thickness of a graphene monolayer accompanied with unique durability, defect-free graphene sheets are not permeable to all gaseous and liquids (Wang & Karnik 2012). It is caused by repulsing forces generated by dense and delocalized electron clouds of π orbitals, which fill gaps in aromatic graphene rings and are able to block the permeation of the smallest particles, such as hydrogen of helium, even at high pressure (Koenig et al. 2012). In order to enable graphene use if membrane separation, nanoporous graphene (NPG) permeable to water and other fluids needs to be obtained. For this purpose, in the monolayer of unsaturated carbon atoms, nanopores of different diameters, geometry, edge quality and density, which are simultaneously neutral to surface structure, need to be formed (Wang et al. 2013, Becton et al. 2014). These pores have to be properly large to allow for water particles permeation, while on the other hand they should enable rejection of ions and other undesired chemical compounds. In last years a number of techniques, which are usually based on high-energy bombarding of graphene structure targeted at dislocation of thousands of neighborhooding carbon atoms, have been investigated. The formation of nanopores of various sizes in monolayer graphene can be obtained using electrons/ions beams, ultraviolet digestive oxidation and ionic helium beam (Lee et al. 2011, Hung et al. 2014, Fischbein et al. 2008). The size of nanopores and their chemical character as well as on the method used for their functionalization significantly influences on separation effectiveness (Han et al. 2013). Nanopores of NPG are most often functionalized with hydrogen, hydroxyl groups and sometimes with nitrogen, and this action is carried out for the improvement of separation effectiveness (Cohen-Tanugi & Grossman 2012).

Despite huge applicability potential of NPG in production of membranes for water desalination (Cohen-Tanugi & Grossman 2012) and other environmental techniques (Wang et al. 2012b), the transfer of the technology to industrial scale is an open issue, that needs to be solved (Aghigh et al. 2015). On the other hand, membranes formed from graphene oxide (GO) overcome this barrier and make the material more suitable candidate for manufacturing of membranes dedicated to separation of ions and particles. Even though GO nanopores characterize with high hydrophobicity, GO nanosheets are hydrophilic (Hu & Mi 2013; Han et al. 2013). GO is modified form of graphene and oxygen and hydrogen atoms, which are all connected via carbon atoms (Fig. 1b). GO reveals properties similar to graphene, except for asymmetry of its sheets, which results from the presence of oxygen base functional groups localized at the edges and in the basal plane (Fig. 1b) (Perreault et al. 2014, Cho & Lee 2011, Compton & Nguyen 2010,).

The presence of functional groups containing oxygen and hydrogen favors dispersion in aquatic environment, but also in other solvents and thus, the use of surface active agents or other stabilizing compounds is not required and formation of thin GO film from the solution is enabled (Perreault et al. 2014). This functional groups also allow for performance of a various surface modifications, which may be used in preparation of functionalized GO-based membranes utilized to separation processes.

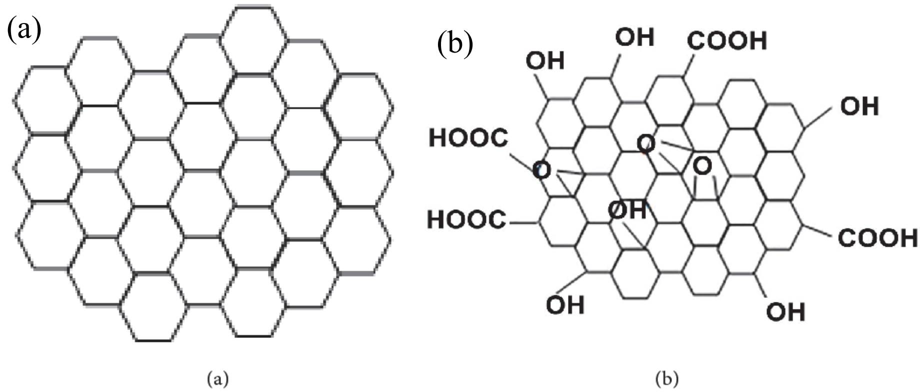

Fig. 1. An exemplary structure of graphene (a) and graphene oxide (b)

GO is usually obtained by oxidation of graphene with strong acids and oxidants (Hu and Mi 2013) as well as by chemical exfoliation and oxidation of graphite. During oxidation, functional groups, i.e. hydroxyl, carboxyl and epoxide one may be introduced to the compound structure (Cohen-Tanugi & Grossman, 2012, Han et al. 2013). Oxidation of cheap graphite results in formation of GO nanosheets of 2D dimension composed only from C, O and H, which possess a lot of hydrophilic functional groups.

The presence of oxygen-based functional groups in GO structure modifies its character and favors its reactivity, allowing the reactions to be performer on the surface of the material (Huang et al. 2014). Additionally, nanopores may also be introduced to GO structure. Such functionalized and porous GO sheets used as a membrane reveal the ability of selective separation of ions and particles, improve capacity and antifouling character (Hu & Mi 2013). Another important aspect is the possibility of production of GO nanosheets piles. The pile like structure of GO characterizes with the thickness ranging from 1 to 30 μm and possesses a number of functional groups reach in oxygen localized at edges and on the surface (Dikin et. al. 2007). Amorphous character of epoxide, hydroxyl and carboxyl groups cause the tendency of the material to curving, thus basal place of GO nanosheets can be defected, however it results in enhanced water permeation through GO nanosheets piles. Even hydrophobic character of GO sheet piles may form frictionless surface allowing for efficient permeation of water through the formed membrane. Contiguous GO nanosheets form nanochannels and nanocapillaries, which also favor water/solvent transport, while dissolved substances are retained (Fig. 2) (Yang et al. 2018). The presence of functional groups also favors the formation of nanochannels (Dai et al. 2016). The distance between GO nanosheets is also important and it may change in dependence of external/operational environment (Mi, 2014). It is assumed, that hydrated ions and particles of other dissolved substances of radius greater than 0.45 nm are rejected by hydrophobic nanochannels, whereas ions of radius below 0.45 nm permeate through (Mi, 2014). Due to amphiphilic GO nature, water particles are adsorbed by hydrophilic spots, and thus their diffusion though hydrophobic carbon place is enabled. Simulation studies by means of molecular dynamics of GO membranes (Nicolai et al., 2014) suggest that water permeability may be regulated in the range from 208 to 16,640 L/bar·h·m^2 by modifying distances between GO sheets and the thickness of sheets as well. However, the distances equal to 1.5 nm (which were determined for highest water fluxes, i.e. 16,640 L/bar·h·m^2) allow for poor NaCl retention equal to 50%. It has also been found that transport of particles through GO sheet (in multilayer GO) takes place between edges of contiguous sheets and through pores localized within a sheet plane (Wei et al., 2014; Huang et al., 2013).

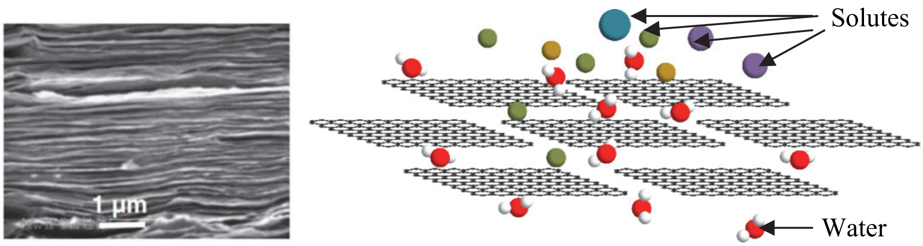

Fig. 2. The image of GO nanosheets pile and mechanism of water transport

It also has to be noted that GO based materials reveal excellent antibacterial properties. Liu et al. (2011) have compared four carbon derivatives, i.e. GO, reduced GO (rGO), graphite (Gt) and graphite oxide (GtO) in regard to their antibacterial properties using *Escherichia coli*. They have observed, that at the same concentration, incubation time and process conditions, GO reveals the best antibacterial features and if followed by rGO, Gt and GtO, what allows for the use of membranes based on GO to biofouling control. Moreover, hydrophilic GO character enables antifouling modifications of membranes' properties, as GO possesses the ability to stop bacteria cells growth during the direct contact (Liu et al. 2011, Akhavan & Ghaderi 2010, Hu et al. 2010). These antibacterial features are durable and GO remains unwashed at the surface and inside membrane pores during a long time operation).

3. Preparation of membranes from graphene and graphene oxide

Novel, composite membranes for desalination and water and wastewater treatment, which contain NPG and GO can be divided into two groups (Manawi et al. 2016):

1. Membranes made of only GO or NPG named as freestanding,
2. Polymeric/ceramic membranes modified by GO or NPG.

The former group uses directly GO/NPG as a membrane, while the latter applies nanomaterials as membrane surface modifiers or introduces GO/NPG to a polymeric/ceramic matrix (Hegab & Zou 2015). The most commonly used methods to production of membranes based on GO/NPG are filtration, self-assembly layer by layer (LBL), dip or spin coating, GO/NPG sheets casting, interface polymerization or phase inversion techniques (Songa et al. 2018, Kim et al. 2013, Hu & Mi, 2013, Sun et al. 2012, Wang et al. 2012b, Hu & Mi, 2014).

3.1. Freestanding GO/NPG membranes

Freestanding membrane may be defined as a set of GO/NPG nanosheets, which create a series of layers packed and placed one on one with properly kept distances between particular layers (Hegab & Zou 2015). GO monolayer characterizes with a thickness of 0.5 nm, while the lateral thickness may vary from hundreds of nanometers up to dozens of micrometers (Hu & Mi 2013). Nair et al. (2012) have minimized distances of GO/NPG sheets to 1 nm using dip or spin coating with stabile solutions of dispersed GO. Additionally, for preparation of GO/NPG membranes of proper distances between particular nanosheets a range of vacuum filtration techniques can be used (Xu et al. 2013). Freestanding GO/NPG membranes are flexible and mechanically stable (Eda & Chhowalla 2010) and even though they are completely impermeable for gases, vapors and liquids, including helium, they allow water to permeate unlimitedly. Additionally, the rate of water permeation for such membranes is ca. 10^6 time higher than of helium (Nair et al. 2012), due to almost frictionless flow of water monolayer through 2-D capillaries formed between shortly-distanced graphene sheets (Goh et al. 2016). It has also been shown, that hydroxyl and epoxide functional groups present in GO/NPG nanosheets are responsible for keeping proper distances between sheets (Wang et al. 2012b).

Freestanding GO/NPG membranes can be prepared by filtration methods, which relies on introduction of GO/NPG on a porous membrane (usually micro- or ultrafiltration one) (Wang et al. 2015) at vacuum conditions (Chen et al. 2015), and next it involves filtration and drying applied for porous layer formation. This method can be used to preparation of GO/NPG containing membranes, of the thickness of their layer from several nanometers up to several microns, however, bindings between particular layers are relevantly weak, thus the stability of a membrane is rather poor. The self-assembly layer by layer method of films preparation relies on staggered laying of a charged substance on a surface charged of opposite charge (Xu et al. 2017). Sequential adsorption of charges polymers and/or nanoparticles is a valuable technique of multilayer preparation.

Nicolai's et al. (2014) have found that freestanding GO membranes allow for complete retention of salts at doubled permeation of water, in refer to commercial RO membranes permeation, due the very low membrane thickness. Sun et al. (2012) have prepared freestanding GO nanofiltration membranes using drop casting with distances between particular layer equal to ca. 0.82 nm. The membranes have next be used to efficient separation of sodium salt from organic impurities and copper. Cohen and Grossman (2012) have stated that graphene layer with nanopores of diameter below 0.55 nm may be applied to water desalination, and the retention of salt is higher than in case of commercial RO membranes, while water permeability is several orders higher. Han et al. (2013) have obtained GO nanofiltration membranes of capacity 21.8 $L/m^2 \cdot h$ and 40% retention of salts. This poor retention has been explained by the presence of cracks formed during membrane preparation. Hu and Mi (2013) have also observed poor salt retention ranging from 6-46% while performing desalination tests with graphene oxide membrane, even though the water flux has been equal to 80 and 276 $L/m^2 \cdot h \cdot MPa$ in dependence of a number of GO nanosheets. At presence of NaCl or Na_2SO_4 the distance between GO sheets decreases with solution ionic strength (~1-2 nm at 100 mM), due to hydration and impact of charge, which compresses double electrical layer and favors transportation of K^+ and Na^+ ions, what disables water desalination (Joshi et al., 2014).

The possible method of the prevention of enlargement of distances between GO nanosheets is the partial decrease of a film thickness. In case of water desalination, distances between GO layers should be below 0.7 nm in order to retain hydrated Na^+ ions (Hu and Mi 2013). Mi (2014) and Yuan et al. (2017) have stated that these distances may also be decreased by GO reduction or by covalent binding of small particles with GO sheets, what may overcome hydration forces. For example, membrane after GO carboxylation (GO-COOH) with glycine has revealed higher salt retention and permeability, as negatively charged

GO-COOH surface favors electrostatic repulsion, improves surface hydrophilicity and multiplies number of channels for water transport (Yuan et al., 2017). Nano-sheet distances may be also increased by immersion of a membrane in a polar solution of e.g. sodium hydroxide. Xu et al. (2017) have stated that water permeability and GO membrane selectivity depend on a membrane interlayer nanostructure. This interlayer structure, in turn, depends on a rate of layers' embedding during membrane preparation, so, it may be adjusted by controlling the amount of sprayed GO. The retention of salts and water flux observed for membranes prepared by slow laying of GO (interlayer distances of 0.82 nm) is approximately 4 times higher than in case of GO membranes prepared with fast laying (0.84 nm).

Xu et al. (2013) have used a vacuum filtration technique to prepare GO/TiO_2 membrane by introducing TiO_2 nanoparticles between GO nanosheets. Freestanding membranes have been made by preparation of stable GO-TiO_2 dispersion followed by vacuum filtration. The average pores' diameter of the prepared membrane have been equal to 3.5 nm. It has been stated, that TiO_2 nanoparticles react with GO nanosheets, what finally results in the increase of distances between nanosheets and enlarges channels for water transport through the membrane. Nanofiltration GO-TiO_2 membranes have revealed complete retention of orange methylene and rhodamine B, what confirms their usability to the removal of dyes from wastewater.

In Table 1, selected data of freestanding GO/NPG membranes is presented.

Table 1. Exemplary characteristics and efficiencies of freestanding GO/NPG membranes

Preparation method	Membrane type	Process/ conditions	Permeability/Flux	Retention	Reference
LBL	GO/PAA/PAN	NF/5 bar	0.84 L/m^2hbar	43.2% Na^+, 92.6% Mg^{2+}	Wang et al. 2012b
LBL	GO/PSF	NF/3.4 bar	27.6 L/m^2hbar	46% Na_2SO_4 93-95% rhodamine	Hu & Mi 2013
LBL	GO/PAH/PAN	NF/FO NF – 3.45 bar	6 L/m^2hbar	FO: 99% sucrose	Hu & Mi 2014
Vacuum filtration	GO/TiO_2/PC	NF/100 kPa	7 L/m^2hbar	100% methyl orange	Cohen-Tanugi & Grossman 2015
Vacuum filtration	GO- PAN nanofibres	NF/1-3 bar	2 L/m^2hbar	56.7% Na_2SO_4 100% Kongo red	Wang et al. 2016a
Vacuum filtration	GO/PDA/Al_2O_3	PV/90°C	48.4 L/m^2h	99.7%- 3.5% NaCl	Xu et al.,2016a; b
Vacuum filtration	Epoxy	FO	0.5 L/m^2h	97% NaCl	Abraham et al. 2017

Table 1. cont.

Preparation method	Membrane type	Process/ conditions	Permeability/Flux	Retention	Reference
Casting	fGO-280 nm	FO/0.25M NaCl and KCl- water	0.36 L/m^2h	-	Chen et al. 2017b
Self-assembly	GO-COOH	NF/1.5 MPa	-	48.2% NaCl 91.3% Na_2SO_4	Yuan et al. 2017
Vacuum filtration	Graphene Various supports	NF/5 bar	21.8 L/m^2hbar	>99% dyes ~20-60% salts	Sun et al. 2012
Vacuum filtration	GO/ Cationic Porphyrin	NF	9.3 L/m^2h	87.7% Na_2SO_4	Xia & Ni 2015
Oxygen plasma etching	NPG single layer	RO/17 kPa	106 g/m^2s	~100% monovalent ions	Ali et al. 2016

GO – graphene oxide; PAA – polyallylamine; PAN – polyacrylonitrile; PSF – polisulphone; PEI – poliethylenimine; PVP – polyvinylpyrrolidone; PVDF – polyvinylidene fluoride; PDA – polydiacetylene; PC – polycarbonate; fGO – functionalized grapheme oxide; PC – polycarbonate; PAH – polyaromatic hydrocarbons; NPG – nanoporous graphene; RO – reverse osmosis; NF – nanofiltration; FO – forward osmosis; PV – pervaporation; LBL – layer by layer

3.2. Modification of polymeric/ceramic membranes with GO/NPG

A modification of polymeric membranes may be made by introduction of a nanomaterial either to a membrane's surface or to casting solution followed by membrane formation from the mixture of a polymer and a nanomaterial (Yang et al. 2018, Hegab & Zou 2015, Songa et al. 2018, Manawi et al. 2016, Anand et al. 2018).

3.2.1. Modification of a polymeric membranes' surface

Modification of membranes' surface may be done by direct nanomaterial coating with „layer by layer" method, vacuum filtration (Wang et al., 2016a; Hu and Mi, 2014) or interfacial polymerization with TFC membrane finalized with TFN membrane formation (Yang et al. 2018). The introduction of a nanomaterial on a membrane's surface may also be made by covalent (Perreault et al. 2014), electrostatic (Choi et al. 2013) or coordination (Gao et al. 2014) bonding. Modification with graphene and its derivatives may improve a number of properties, including antifouling and antibacterial character and resistance to chlorine (Liu et al. 2011; Tu et al. 2013). Modification of membrane surface additionally requires relatively low nanomaterial amount, what is the economic benefit and, moreover, the production of nanomaterial is environmentally acceptable.

Wang et al. (2016a) have prepared GO containing membranes using polyacrylonitrile fibers by means of vacuum GO suspension filtration. The obtained membranes have revealed high retention of dyes (ca. 100% for Congo red) and moderate retention of bivalent ions (ca. 56.7% observed for Na_2SO_4), while water permeability has been established at ca. 2 L/m^2·h·bar. Similarly, Xu et al. (2016b) have made membranes using vacuum filtration of GO suspension at aluminum oxide surface coated with polydopamine, which next have been introduced to semi-product burning. After thermal processing, GO nanosheets have been strongly bonded with the support surface, thus stability of the obtained membrane has been sufficient. In desalination of seawater, of NaCl concentration equal to 3.5%, membranes have revealed high water flux reaching 48.4 L/m^2·h at NaCl retention 99.7% at 90°C. Hu and Mi (2013) have used cross-linking of GO nanosheets on polysulphone (PSF) support coated with polydopamine using 1,3,5-benzenetricarbonyl chloride (TMC), what has resulted in covalent bonds formation. The obtained GO membrane have revealed water permeability from 8 to 27.6 L/m^2·h·bar at relatively low retention of mono- and bivalent ions (6-46%) and high retention of dyes (93-95%).

Except for vacuum filtration, modified membranes with GO enriched with carboxylic, hydroxyl, epoxide or amine groups may be obtained using LBL method. Kim et al. (2013) have modified RO membranes with polyether-sulphone (PES) support by coating membrane surface with negatively charged GO nanoparticles, on the layer of which they have next laid positively charged with amine groups GO layer. The modified membrane has revealed high water flux equal to 28 L/m^2·h and 98% salt retention. Choi et al. (2013) have also used LBL technique to modify polyamide (PA) membrane surface using GO nanosheets and GO nanosheets containing amine groups (NH_3^+) (Fig. 3). The modified membrane has revealed sufficient resistance to chlorine degradation due to the presence of GO protective layer on PA surface As a result, the fouling resistance of the modified membrane has been significantly improved and the water flux has increased by 10%, while NaCl retention (measured using water NaCl solution of salt concentration 2,000 mg/L) has decreased only by 0.7%.

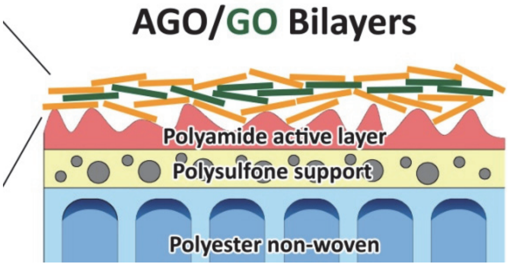

Fig. 3. The scheme of layer by layer coating of TFC polyamide membrane using electrostatic interaction with GO and positively charged amine GO (AGO)

Hung et al. (2014) have prepared flexible, GO containing PAN membranes using LBL technique. The composite membrane have revealed high capacity during pervaporative separation of a mixture composed of 70% wt. isopropanol (IPA) and water. At 30°C, 99.5% of water has passed to permeate, whereas the permeability has reached 2.047 g/m^2·h, while at temperature 70°C the concentration of water in permeate has been kept, while the permeability has increased to 4.137 g/m^2·h. The high selectivity results from dense GO film composed of a highly ordered and packed layers, what allows for water transport and rejection of IPA particles. GO possesses amphiphilic character, i.e. water particles are firstly adsorbed at hydrophilic ends of a layer (containing OH^- groups) and next they quickly diffuse through hydrophobic cores of GO layers (mainly composed of carbon), forming channels used in further water transport, what improves the capacity.

GO may be used to covalent modification of surface of membranes used to desalination. Covalent bond may be obtained using amide binding of carboxyl groups present in nanosheets with other carboxyl groups present in polyamide skin layer of TFC membranes (Perreault et al. 2014) (Fig. 4). The functionization of PA surface in TFC membranes allows GO nanosheets to be uniformly placed on a membrane surface, what has strong and positive influence on antibacterial features and hydrophilic character of modified membranes. It has been found, however, that hydrophilicity increase does not improve water flux in such membranes, as it is mostly regulated by solution-diffusion mechanism in PA skin layer of TFC membrane, regardless of surface modification (Elimelech & Phillip 2011). Despite covalent binding, GO can be attached to membrane surface by electrostatic interactions using LBL method, as it is shown in Fig. 5.

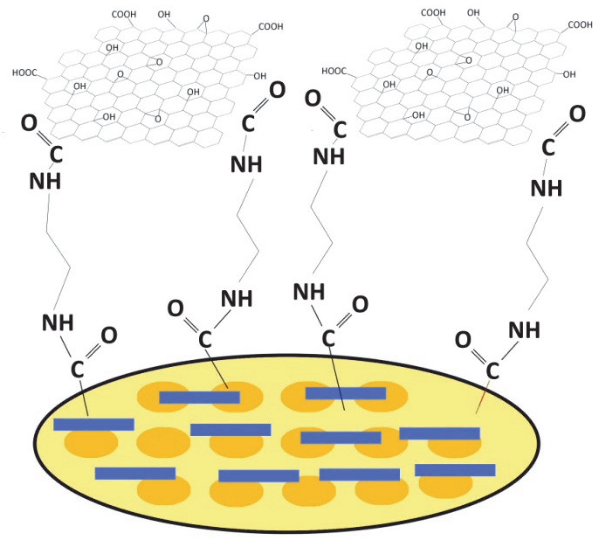

Fig. 4. The scheme of modification of membrane surface by covalent bonging

The main issue of membranes exploitation in water treatment is their affinity to fouling. The intensity of fouling depends on many factors, among which membrane material, chemical character of surface and porosity are of the highest importance (Kochkodan et al. 2014). Membranes containing NPG or GO show improved antifouling character, as they inactivate bacteria during direct contact with their cells (Lee et al. 2008), while their surface is more hydrophilic and smoother after modification. Perreault et al. (2014) have investigated the influence of modification of PA TFC membranes with GO on antibacterial properties. GO nanosheets have been binded to membrane surface by amide and carboxylic bonds. It has been shown that 65% of *E.Coli* cells become inactivated during direct contact with modified membrane within 1 hour. It has turned out, that GO inactivates bacteria due to initiation of physical damage of cells' membrane followed by eventual extraction of lipids from cells' interior (Tu et al. 2013). SEM images show, that cells, which are in contact with GO membrane are flattened and squeezed in comparison with cells, which contact reference, non-modified membrane. Additionally, antibacterial effect of GO modified membranes does not affect their transport properties. Sun et al. (2015) have presented studies on preparation of composite membranes of antibiofouling properties made of cellulose acetate (CA) modified with graphene and containing silver nanoparticles (GO-AgNP). Composite GO-AgNP membrane effectively prevent bacteria growth, thus also the formation of biofilm on the membrane surface, causing *E.Coli* inactivation by 86% after 2 hour of their contact with the membranes. Ma et al. (2017) have introduced in-situ copper nanoparticle (CuNP) to polyamide RO membrane in order to decrease its biofouling. The use of cystamine (Cys) and GO has increased the amount of binded CuNP, decreased their size, caused more uniform distribution of CuNP on membrane surface and improved membrane antibacterial properties, due to formation of covalent bond between CuNP and membrane surface. Zhang et al. (2013) have connected GO with oxidized carbon nanotubes (CNT) in order to modify PVFD membrane surface. Modified GO-CNT membrane has shown significant hydrophilicity increase and antifouling improvement in refer to membranes modified separately with CNT or GO.

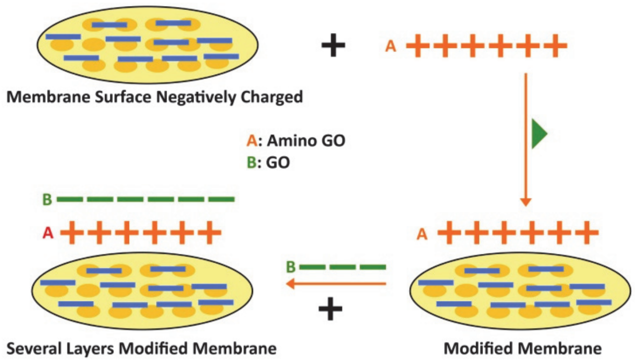

Fig. 5. The scheme of modification of membrane surface by electrostatic interactions using LBL method

In Table 2, the list of selected surface modified membranes with GO/NPG is given together with their characteristics.

Table 2. Selected results of studies on surface modification of polymeric membranes using GO/NPG

Preparation method	Base polymer	Membrane process/ Pressure	Permeability/ Flux	Retention	Ref.
IP	GO-PA	RO -15.5 bar	Ab. 1.06 L/m^2hbar	99% NaCl	Chae et al. 2015
IP	GO-PA	RO - 20.5 bar	Ab. 2.9 L/m^2hbar	94-96 % NaCl	Yin et al. 2016
IP	GO/PA	RO - 15 bar	29.6 L/m^2h	>97% NaCl	Ali et al. 2016
LBL	GO-PA	RO - 15.5 bar	Ab.0.9 L/m^2hbar	96.4% NaCl	Choi et al. 2016
Coordinate bond	fGO-PA	RO - 27.6 bar	Ab.1.45 L/m^2hbar	97.8% NaCl	Perreault et al. 2014
Coating LBL	aGO/GO/aPES	RO - 5500kPa	28 L/m^2h	98%NaCl	Perreault et al.2014
IP	rGO/TiO_2 (0,2%wt.)/PA	RO -15 bar	3.42 l/m^2hbar	99.45% NaCl	Sefarpour et al. 2015
IP	GO/PAN	NF	22 L/m^2h	>88% NaCl >97%$MgSO_4$	Bano et al. 2015
IP	GO/PA	NF - 8 bar	353.5 L/m^2hbar	59.5% NaCl 95.2% Na_2SO_4 91.1% $MgSO_4$ 62.1% $MgCl_2$	Lai et al. 2016
IP	GO/polypiperazine amide	NF - 0.6 MPa	87.6 L/m^2 h	56.8% NaCl 98.2% Na_2SO_4 96.5% $MgSO_4$ 50.5% $MgCl_2$	Wang et al. 2016b

Table 2. cont.

Preparation method	Base polymer	Membrane process/ Pressure	Permeability/ Flux	Retention	Ref.
Coating	PSF-GO (0,3%wt.)	NF - 0.6 MPa	2.45 L/m^2hbar	59.5 NaCl 95.2 Na_2SO_4	Lai et al. 2016
IP	rGO/TiO_2/PSF	NF - 10 bar	60.6 L/m^2h	36.6 NaCl 93.6 Na_2SO_4	Sefarpour et al. 2015
Vacuum fil-tration	GO/PAN	NF - 1.0 bar	8.2 L/m^2hbar	9.8% NaCl 56.7% Na_2SO_4	Wang et al. 2016a
Vacuum fil-tration	rGO-CNT-AAO	NF	31.5 L/m^2hbar	42% NaCl 84% Na_2SO_4	Chen et al.2016
Self-as-sembly LBL	GO-chito-san/PSF	NF	1.78 L/m^2hbar	62% NaCl 92.7% Na_2SO_4	Wang et al. 2015
Coating	GO-PSF	NF -10 bar	5.47 L/m^2hbar	33% NaCl 89.8% Na_2SO_4	Sefarpour et al. 2015
Pressure coating drop by drop	GO/PAN	PV - 5 kg/cm^2	4137g/m^2h	IPA/water 70%-99.5%	Hung et al. 2014
Self-assem-bling LBL	GE/GO/PAN	PV - vacuum 0.3 kPa	2,275 g/m^2h	Ethanol/water 98.7% wt.	Zhao et al. 2015

Table 2. cont.

Preparation method	Base polymer	Membrane process/ Pressure	Permeability/ Flux	Retention	Ref.
UV–LBL	GO-TiO_2/PSF	Photo-catalyse 69 kPa	45 L/m^2h	90% methylene blue	Gao et al. 2014
Covalent bonding	GO/PAN	UF - 1 bar	987 L/m^2hbar	85% BSA	Prince et al. 2016
Self-assem-bling LBL	GO/Ag-PAA GO/TiO_2-PAA	UF -1 bar	396 L/m^2hbar 453 L/m^2hbar	83-91% BSA 26-38% MO	Jiang et al. 2015

IP – interfacial polymerization; LBL- „layer by layer"; CNT – carbon nanotube; PA – polyamide; fGO – functionalized GO; PES – polyethersulphone; aPES – aminated polyethersulphone PSF – polysulphone; PAA – polyallylamine; PVDF – polyvinylidene fluoride; PAN – polyacrylonitrile; PEI – poliethylenimine; AAO – anodized aluminum oxide; GE – gelatine;
BSA – bovine serum albumin; MO –methyl orange

3.2.2. Modification by introducing nanoparticles to polymeric matrix

Polymeric membranes, made of aromatic and aliphatic polyamide, cellulose acetate, polyvinylidene fluoride, polysulphone, polyethersulphone and other polymers, as well as non-polymeric materials (ceramics, metals) and their composites, are widely used to membrane preparation for filtration of various solutions (Basile et al. 2015). Currently, carbon material are added to polymeric matrices in order to obtain membrane of nanomaterial/polymer for RO, NF, UF and other membrane processes. The introduction of carbon nanomaterials to a polymeric membrane matrix influences on its structure and antibacterial properties, hydrophilicity, capacity, retention and mechanical stability (Zhao et al. 2013a, Aba et al. 2015, Chung et al. 2017, Lee et al. 2013, Zhao et al. 2014b, Xu et al. 2014, Zhao et al. 2013b, Wang et al. 2012c, Zhang et al. 2013). In comparison with conventional membranes, the surface of modified membranes reaches beneficial density and pores' structure, which result from precipitation of nanomaterial in phase inversion process. The significant increase of a membrane's hydrophilicity leads to the increase of permeability of a modified membrane (Teli et al. 2012). The introduction of carbon nanomaterials also enables their exploitation in dry state with no permeability affection, what is important in regard to a membrane resistance to bacteria and transport enhancement. The introduction of small amounts of functionalized GO to a membrane material results in porosity and membrane pores' size increase, but only to a certain boundary dose (Xu et al. 2014, Zhao et al. 2013b), but if GO amount exceeds 0.05%, membranes porosity significantly decreases (Zhao et al. 2014a, b). This trend also influence on membranes permeability, which increases with nanomaterial dose increase up to the critical point, after exceedance of which it decreases. This decrease is assigned to pores' blocking and narrowing caused by overamount of GO nanosheets in a membrane matrix. Lee et al. (2013) have explained GO role in a membrane casting process by means of phase inversion. At the absence of GO, polymer solidifies quickly at boundary phase between polymer and non-solvent during phase separation, what is caused by concentration gradient and fast interaction between all mixture components. In instable places on a surface of solid polymer phase, some breakages appear due to the pressure caused by continuous desolvatation shrinking. The introduction of hydrophilic substances (GO) to a membrane casting solution improves the overall hydrophilicity of the solution and influences on a mass exchange rate between solvent and non-solvent during phase separation, what leads to the formation of more porous membrane structure. As a results, the appearance of fractures and micro-breaks is minimized.

Xia & Ni (2015) have prepared PVDF membranes of different GO content using phase inversion method, what has significantly improved water transport rate and antifouling properties. The permeate obtained during NOM-containing solution filtration has been analyzed toward dissolved organic carbon content (DOC), specific UV absorbance (SUVA) and molecular mass distribution. It has been found, that GO, due to the presence of acidic groups, may enable the appearance of a negative charge of a membrane surface within the whole pH range (Dimiev et al. 2013), what favors separation of positive ions due to electrostatic repulsion of negative ions by negatively charged membrane surface. The research carried out by Lai et al. (2016) has shown that higher water flux and salt retention can be obtained by introduction of non-functionalized GO to PSF support coated with polyamide layer. Membranes produced from solution containing 0.3wt.% GO have retained Na_2SO_4, $MgSO_4$, $MgCl_2$ and NaCl in 95.2%, 91.1%, 62.1% and 59.5%, respectively. Zinadini et al. (2014) have prepared NF GO/PES membranes of various GO content and produced modified UF membranes of GO/PVDF type. These membranes have also revealed improved antifouling features caused by higher hydrophilicity and proper surface morphology. Fryczkowska (2018) obtained UF composite membranes of GO-PAN type containing 0.8wt.%, 4.0wt.% and 7.7wt.% of GO in PAN matrix, for the dyes removal from industrial wastewater. Cationic (Indigo – IS; methylene blue – MB) and anionic (thymolic blue – TB; Congo red – CR) dyes have been selected for the research.

GO introduced to membrane casting solutions based on different polymers can be modified with the use of various substances, among which the most often used are: hyperbranched polyethylenimine (HPEI) (Wang et al. 2012c), triethoxy-3-aminopropylsilane (APTS) (Xu et al. 2014) and isocyanate (Zhao et al. 2013b). For example, GO functionalized by HPEI has been mixed with PES (Yu et al. 2013) and PVDF (Xu et al. 2014) solutions, and membranes produced by phase inversion method have revealed polyvinyl alcohol (PVA – 30-70 kDa) and polyethylene glycol (PEG – 20 kDa) retention equal to 90% and 85%, respectively. Also, modified membranes, type isocyanate-GO/PS (Zhao et al. 2013b) and APTS-GO/PVDF (Xu et al. 2014) retain BSA in 95% and 57%, respectively. TEM images of *E.Coli* cells have shown the loose of integrity and cytoplasm efflux during contact with modified HPEI-GO membrane (Yu et al. 2013).

Several authors have modified membranes with GO and Ag in order to improve antibiofouling character of membranes by introducing GO-Ag composite to membrane casting solution and prepared membranes using phase inversion method. For example, Wu et al. (2017) modified PVDF membrane and Mahmoudi et al. (2015) PSF membrane. Chung et al. (2017) have functionalized PSF membranes using graphene oxide nanosheets doped with ZnO. Zinc oxide nanoparticles are known as very good antifouling and antibacterial material, thus they can be used in exploitation of membrane based desalination processes.

In table 3, the comparison of selected GO/NPG containing membranes obtained with the use of wet phase inversion method, including their characteristics, is shown.

Table 3. The selected research on composite membranes obtained with the use of phase inversion method from a mixture of a polymer and GO/NPG

Polymer	Process/ Conditions	Permeability/Flux	Retention	Reference
GO/ /PSF	NF/400kPa	50 L/m^{2}h	72% Na_2SO_4	Ganesh et al. 2013
GO/ /PES	NF/400kPa	53 kg/m^2 h	90.5% Protein	Yuan et al. 2017
GO/PVDF	UF/1 bar	26.5 L/m^{2}hbar	79% BSA	Wang et al. 2012c
GO/Isocya-nine/PSF	UF/1 bar	135 L/m^{2}hbar	95%BSA	Zhao et al. 2013b
GO/HPEI/PSF	UF/1 bar	153.5 L/m^{2}hbar	85% PEG(20,000) 90% PVA	Yu et al. 2013
CNT/PVDF	UF/1 bar	410 L/m^{2}hbar	98.3% BSA	Zhang et al. 2013
GO/PES	UF/4 bar	6 L/m^{2}hbar	96% dye (Di-rect Red 16)	Zinadini et al. 2014
GO/APTS/PV DF	UF/1 bar	401 L/m^{2}hbar	57% BSA	Xu et al. 2014
rGO/Ag-PES (0,2%wt.)	UF/	107.5 L/m^{2}hbar		Vatanpour et al. 2015
Co_3O_4-GO/PES (1,5%wt.)	UF/	347.9 L/m^{2}hbar	89.8% *Escherichia coli*	Ouyang et al. 2015
GO-Ly/PES	UF/0.2 MPa	318 L/m^{2}hbar		Duan et al. 2015

Table 3. cont.

rGO-Ly/PES	UF/0.2 MPa	372 L/m^{2}hbar		Duan et al. 2015
GO/PVDF	MF/0.25 bar	1298 L/m^{2}hbar	80% mushrooms	Zhao et al. 2013ab
GO/C_3N_4/ PES/PA*)	FO/2M NaCl-Demi	41.4 g/m^{2}h	-	Wang et al. 2012b
GO/PSF/PA*)	FO/0.5M NaCl-Demi	19.8 g/m^{2}h	-	Park et al. 2015

*) – phase inversion method and interphase polymerization; GO – graphene oxide; rGO – reduced graphene oxide; PSF – polysulphone; PVDF – polyvinylidene fluoride; HPEI: hyper-branched polyethylenimine; CNT – carbon nanotube; PES – polyethersulphone; PVA – polyvinyl acid; Ly – lysozyme; APTS – 3-aminopropyltriethoxysilane; NF – nanofiltration; FO – forward osmosis; UF – ultrafiltration; MF – microfiltration; BSA – bovine serum albumin

4. Summary and development prospective

Graphene is a novel material, which possesses many advantageous features, that allow for preparation of next generation membranes of high efficiency to desalination and water and wastewater treatment. It excellent mechanical properties, single-atom layer structure, large specific surface area and wide modification possibilities make it highly useable for membranes formation.

Novel composite membrane containing NPG and GO can be divided into freestanding membranes, and polymeric/ceramic membrane modified with the use of graphene-based nanomaterials. Modification of polymeric membranes can be achieved either by introduction of a nanomaterial onto a membrane surface or to a membrane casting solution followed by membrane formation from a polymer and a nanomaterial mixture.

GO/NPG membranes as well as polymeric or ceramic ones containing graphene, when used in pressure driven membrane processes, often characterize with high water/permeate flux and reveal unique antifouling and antibacterial features as well as high mechanical and thermal stability. The capacity of membranes containing NPG/GO is higher than in case of conventional RO or NF membranes, whereas retention of low molecular weight compounds is comparable. The efficiency of membranes is beneficial for dyes removal, separation of mono- from bivalent ions and dewatering of water-solvent mixtures. Additionally, graphene-based separation membranes have been successfully used in pervaporation, forward osmosis, capacitive deionization, electrodialysis, or in formation of photocatalytic membranes, due to their stability and high effectiveness.

The future development of NPG/GO containing membranes should focus on the improvement of their separation features by using various formation techniques. A lot of effort has to be given to understand and properly explain both, role and interaction mechanisms of graphene-based nanomaterial with a membrane, especially in case of freestanding GO membranes. Additionally, the scaling up required for commercial production of ultra-thin membranes of high permeability, based on graphene-oxide, is one of the greatest challenge for scientists and engineers. Moreover, the release of nanomaterial from such membranes and their potential toxicity has to be investigated in detail for their further practical use in desalination processes.

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Abstract

In recent decades, novel and promising materials (e.g. carbon nanotubes, nanoporous graphene and graphene oxide) suitable to be used in preparation of high-capacity membranes for water desalination and water and wastewater treatment have been developed. Membranes made of NPG and GO materials enable to obtain significantly higher water/permeate fluxes than currently used thin film composite membranes for RO and other separation processes as pervaporation, forward osmosis, capacitive deionization, electrodialysis, or in formation of photocatalytic membranes. Novel composite membrane containing NPG and GO can be divided into freestanding membranes (prepared only from NPF/GO), and polymeric/ceramic membranes modified with the use of graphene-based nanomaterials. Modification of polymeric membranes can be achieved either by introduction of a nanomaterial onto a membrane surface or to a membrane casting solution followed by membrane formation from a polymer and a nanomaterial mixture.

The future development of NPG/GO containing membranes should focus on the improvement of their separation features. A lot of effort has to be given to understand and properly explain both, role and interaction mechanisms of graphene-based nanomaterial with a membrane, especially in case of freestanding graphene oxide membranes. GO nanosheets are very promising material for manufacturing of desalination membranes, however more attention has to be dedicated to potential disadvantages such as mechanical instability, nanosheets formation, non-uniform distribution of layers and surface damage.

Additionally, the scaling up required for commercial production of ultra-thin membranes of high permeability, based on graphene-oxide, is one of the greatest challenge for scientists and engineers. The success reached in this area will lead to the decrease in energy consumption in RO installation and in other membrane processes. Moreover, the release of nanomaterial from such membranes and their potential toxicity has to be investigated in detail for their further practical use in desalination processes.

Keywords:
graphene, graphene oxide, separation membranes preparation, desalination,
water treatment, wastewater treatment

Grafen – nanomateriał do wytwarzania nowej generacji membran półprzepuszczalnych

Streszczenie

W ostatnich dziesięcioleciach opracowano nowe i obiecujące materiały (np. nanorurki węglowe, nanoporowaty grafen i tlenek grafenu) odpowiednie do wytwarzania membran o wysokiej efektywności odsalania i uzdatniania wody i oczyszczania ścieków. Membrany wykonane z NPG i GO pozwalają na osiągnięcie znacznie wyższej wydajności wody/permeatu, niż obecnie stosowane membrany kompozytowe cienkowarstwowe do RO i innych procesów separacji, jak np. perwaporacji, osmozy prostej, dejonizacji pojemnościowej, elektrodializy, lub membran fotokatalitycznych. Nowe membrany kompozytowe zawierające NPG i GO można podzielić na membrany „wolnostojące" (wykonane tylko NPF/GO) i membrany polimerowe/ceramiczne modyfikowane za pomocą nanomateriałów z grafenu. Modyfikację membran polimerowych można osiągnąć albo przez wprowadzenie nanomateriałów na powierzchnię membrany lub do roztworu błonotwórczego, z którego wytwarza się membrany metodą inwersji fazowej.

Rozwój membran zawierających NPG/GO powinien koncentrować się na poprawieniu ich własności separacyjnych. Należy uwagę skierować na zrozumienie i prawidłowe wyjaśnienie zarówno roli i mechanizmów interakcji nanomateriału na bazie grafenu z membraną, zwłaszcza w przypadku membran „wolnostojących". Nano-arkusze GO są bardzo obiecującym materiałem do wytwarzania membran do odsalania wody, należy jednak więcej uwagi zwrócić na potencjalne wady takie jak niestabilność mechaniczna, tworzenie nano-arkuszy, nierównomierny rozkład warstw i uszkodzenia powierzchni. Ponadto, należy rozwiązać powiększanie skali wytwarzania membran, co jest wymagane dla komercjalizacji produkcji membran opartych na grafenie i tlenku grafenu oraz stanowi jedno z największych wyzwań dla naukowców i inżynierów. Sukces osiągnięty w tej dziedzinie doprowadzi do zmniejszenia zużycia energii w instalacji RO i innych procesach membranowych. Należy również szczegółowo zbadać proces uwolnienia nanomateriału z membran i jego potencjalną toksyczność, z uwagi na bezpieczeństwo stosowania membran zawierających nanomateriały.

Słowa kluczowe:
grafen, tlenek grafenu, wytwarzanie membran separacyjnych, odsalanie,
uzdatnianie wody, oczyszczanie ścieków

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Numerical Simulation of Groundwater Level Changes: a Case Study of the Strużyna Reservoir

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1. Introduction

Enhancing the dispositional resources of surface waters is one of the more important goals of building water reservoirs (Kałuża et al. 2014). However, reservoirs can fulfil many other specific functions within the river's catchment (Hämmerling et al. 2018, Wiatkowski et. al. 2015, Wicher-Dysarz & Kanclerz 2012). Particular objects often find multilateral applications. According to their purposes, three main categories of reservoirs can be distinguished: farming, recreational, and ecological (Ignatius & Rasmussen 2016, Wiatkowski 2011). Large numbers of reservoirs (15 small retention reservoirs in Great Poland Region) and check dams have been built in central Poland to meet the local residential water demand for flood protection, agriculture irrigation and for soil conservation (Waldon 2012, Zubala, 2009). However, the construction of reservoirs and check dams can lead to changes in local and regional groundwater levels that can cause changes in soil moisture, local flooding and even destruction of buildings (water level in the foundation zone) (Saito et al. 2006, Zhang et al. 2012).

A wide range of solutions can be considered to address problems in groundwater management, which involve both quantity and quality-related issues (Chmist & Hämmerling 2016, Šimůnek & Genuchten 1996). However, the effectiveness of all the solutions and their combinations cannot be verified with field experiments (Šimůnek et al. 2003, Smith et al. 2004, Singh et al. 2006). Moreover, many problems and prospects associated with particular water management options are often not recognized until they are well advanced (Mandare et al. 2008). Simulation models by way of their predictive capability are often the only feasible means of providing input to management decisions (Querner et al. 2012, Poeter 2007). These models can help to forecast the likely impacts of increasing of groundwater level and in a broader context a particular water management strategy. Therefore, the results of simulation studies of existing and proposed dams and water retaining structures for water management may form the basis for the identification of suitable water management plans for the future (Hassan 2004, Gedeon et al. 2007).

Research on the development and application of groundwater flow and transport models has increased significantly over the last decades. One interesting proposal is the Hydrus software (Šimůnek et al. 2003, Šimůnek et al. 2018). These groundwater flow models solve for the spatio-temporal values of filtration hydraulics. The HYDRUS 1D, HYDRUS 2D and HYDRUS 3D programs numerically solve the Richards equation for saturated-unsaturated water flow and the convection-conduction equation for heat transport in one, two and three dimensions, respectively. The program may be used to analyse water in unsaturated, partially saturated, or fully saturated porous media. Examples in which soil thermal parameters have been estimated using HYDRUS include studies by Hopmans et al. (2002), Mortensen et al. (2006) and Saito et al. (2007). The article presents the results of a simulation of groundwater flow in the near vicinity of a small storage reservoir, Strużyna. The aim of this study was to verify the conclusion presented by Kałuża et al. (2017) using the numerical software HYDRUS 2D/3D. The extent of the reservoir's influence on the groundwater in steady flow conditions was determined. The obtained numerical results were compared with field monitoring data.

2. Materials and methods

The Strużyna reservoir is located in Lubuskie state and south of Czerwieńsk City and was built on Strużyna Channel (middle catchment of Odra river). The basic functions of the Strużyna reservoir is water storage, including for agricultural purposes, flattening of the flood wave, creation of the possibility of firefighting water supply of the surrounding forests, recreation and tourism. The reservoir was built in the pre-war period, and after nearly one hundred years of operation the hydraulic structures of the reservoir were in very poor technical condition. After modernization of the spillway and bottom outlet the Strużyna reservoir was filled up again.

According to design project of the modernization, a new hydraulic structure was constructed in the form of a shaft spillway, bottom outlet, fish pass, and earth dam embankment, with an upstream low permeability zone (biomat) on previous foundations (sands). Exact characteristic of geological can found in Chalfen & Czamara (2007). After the reservoir was rebuilt, the normal level of water (NWL) was assumed at the same level as before modernization.

2.1. Impact of reservoir on groundwater level

Kałuża et al. (2017) estimated that modernization of the Strużyna reservoir should not cause significant changes in the level of the groundwater table. Unfortunately, soon after filling the reservoir (March 15. 2012), a building on the left bank of the Strużyna channel was flooded. The cellar of the warehouse building was flooded, with an area of about 80 m^2 being flooded with 5 cm of water. After the intervention of the owner of the building, the level of normal damming was lowered by several centimeters. However, due to the dampness of the walls and floor as well as the storage properties of the goods, the building has not been used.

Kałuża et al. (2017) carried out analyses based on the technical documentation of the reservoir and piezometric measurements (groundwater table).

The calculations of water flow in porous media were conducted using HYDRUS 2D/3D software. The authors also pointed out that some planned solutions have never been applied, such as a piezometer network. That is why a piezometer network around the flooded building was installed, as presented schematically in Figure 1. The measurements have been collected once a week since October 2014, during near half an year. At the same time, measurement of the water level upstream and downstream of the Strużyna reservoir was performed.

Fig. 1. Scheme of analyzed area with installed piezometer network

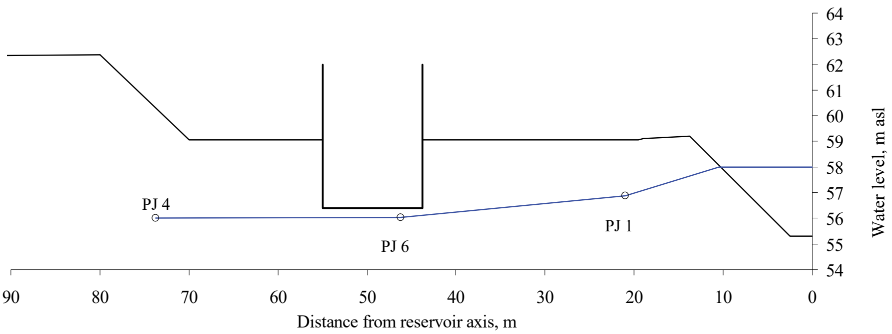

Fig. 2. Cross section (A-A) of groundwater table perpendicular to the left bank of the reservoir

In Figure 1 the line shows a cross-sectional A-A perpendicular to the left bank for which the groundwater table is presented in Figure 2. The building bottom level is 56.10 m asl and and foundation is lower about 0.5 m.

The research conducted during six months (Fig. 3) excluded the influence of rainfall on groundwater level.

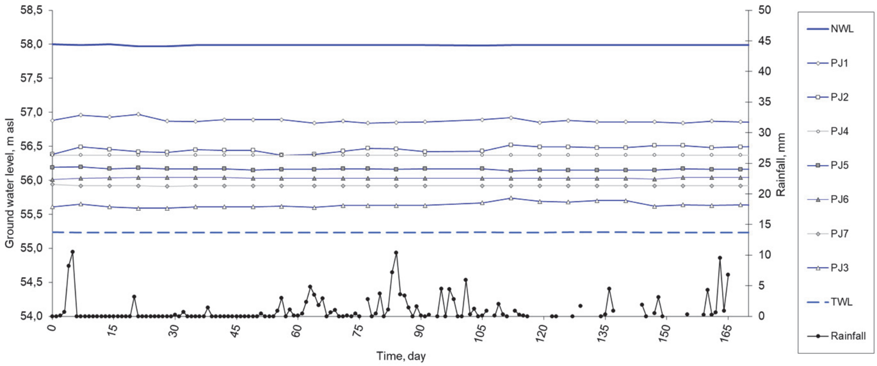

Fig. 3. Variations of water level in piezometers and normal (NWL) and tail (TWL) water level in the Strużyna reservoir in comparison with the precipitation level (Zielona Góra meteorological station)

The results of analyzed groundwater table expressed as piezometric pressure in time can be presented as a spatial direction of groundwater flows. Groundwater flows and levels taking into account the old abutment wall are presented in Figure 4.

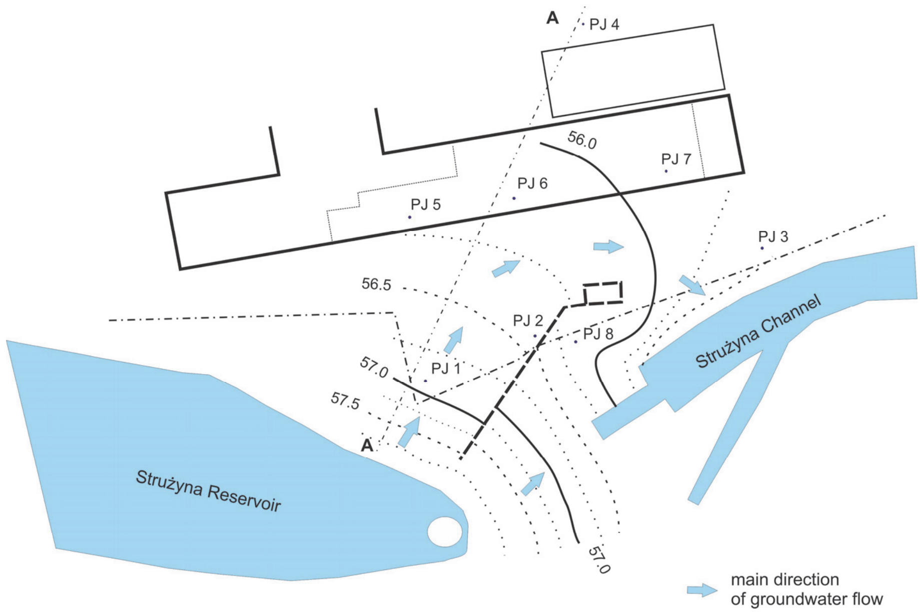

Fig. 4. Directions of groundwater flow taking into account the influence of the abutment wall and buildings

2.2. Numerical model

The Hydrus 3D software is commonly used to simulate water flow, mass and heat in three dimensions in variably saturated media (Błażejewski et al. 2018) and also used to simulate seepage within and under an embankment dam (Šimůnek et al. 2011, Nieć et al. 2017, Nieć et al. 2016a). Flow under unsaturated conditions in soil with laminar flow was calculated in the presented model using the Richards equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x_i}\left[K\left(K_{ij}^{A}\frac{\partial h}{\partial x_j} + K_{iz}^{A}\right)\right] - S \tag{1}$$

where:

θ – volumetric water content [-],

h – pressure head [m],

K – unsaturated hydraulic conductivity [m/d],

K_{ij}^{A} – components of a dimensionless anisotropy tensor KA
(which reduces to the unit matrix when the medium is isotropic),

S – general sink term [1/d],

t – time [d],
x_i, x_j – spatial coordinate [m].

The unsaturated soil hydraulic properties, $\theta(h)$ and $K(h)$, in (1) are in general highly nonlinear functions of the pressure head (Šimůnek et al. 2011). The HYDRUS software also implements the soil-hydraulic functions of van Genuchten (Šimůnek, 1999) and the statistical pore-size distribution model of Mualem (1976) to obtain a predictive equation for the unsaturated hydraulic conductivity function in terms of soil water retention parameters:

$$\theta(h)=\begin{cases}\theta_r+\dfrac{\theta_s-\theta_r}{\left[1+|\alpha h|^n\right]^m} & h<0\\ \theta_s & h\geq 0\end{cases} \tag{2}$$

$$K(h)=K_S S_e^l\left[1-\left(1-S_e^{1/m}\right)^m\right]^2 \tag{3}$$

where:

$$m - 1 - 1/n,\ n > 1 \tag{4}$$

θ_s – saturated water content [-;],
θ_r – residual water content of sand [-],
α, m, n, l – empirical parameters [1/m,- ,-,-],
h – pressure head [m],
S_e – effective water content [-],
K_S – saturated hydraulic conductivity [m/d],
$K(h)$ – unsaturated hydraulic conductivity [m/d].

Initially the two-dimensional numerical model was created in HYDRUS 3D software according to cross section A-A (Fig. 1) due to identify the properties of the ground and biomat. Based on above assumptions and field measurements the soil parameters were appointed and the three-dimensional model was constructed. To obtain numerical solutions it is necessary to set appropriate initial and boundary conditions. The boundary condition II of the second kind $q_n = 0$ (no flow marked by 1) was assumed on the bottom and surface of the cross section. Two kinds of the boundary condition of type I (marked by red nos. 2 and 4) were defined as the constant water level in the reservoir equal to 2.7 m at the bottom of the reservoir and on the left and right side filtration area as the equilibrium from the lowest located nodal point (Fig. 5). The initial condition, defined for the entire seepage area, was established similarly as the second boundary condition with the pressure head as the equilibrium from the lowest located nodal point (groundwater level mapping). The part of the numerical model mesh and the boundary conditions are presented in Figure 5. On the bottom and reservoir banks were implemented 0.2 m thickness layer as a blanket.

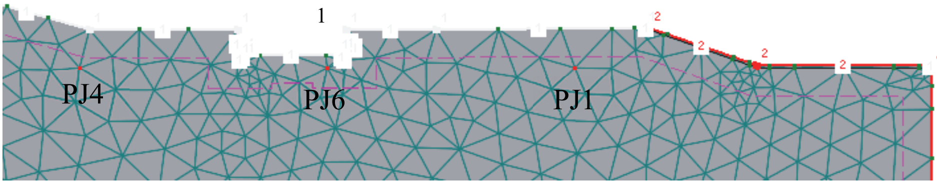

Fig. 5. Part of the numerical mesh with boundary conditions and observation points (PJ1, PJ6 and PJ4)

Soil parameters are presented in Table 1. Subsoil parameters were estimated during field measurements. In practice, it is important to estimate the hydraulic conductivity (HC) and using field test methods appropriate for different soils, as reported by Nieć & Spychała (2014). Using inappropriate methods for estimation of HC can give a different value, even by about one order of magnitude. The parameters of others materials called blanket were estimated in subsequent calculations. Additionally, parameters of the clogging layer – biomat (Finch et al. 2008) – which probably was created on the bottom of the reservoir during one hundred years of operations, were used.

Table 1. Physical parameters of analyzed soils

Soil		θ_r -	θ_s -	α 1/m	n -	K_s m/d	l -
Sand	Subsoil	0.045	0.43	14.5	2.68	7.1280	0.5
Sand (without blanket)	Blanket	0.045	0.43	14.5	2.68	7.1280	0.5
Sandy Loam		0.065	0.41	7.5	1.89	1.0610	0.5
Sandy Clay Loam		0.100	0.39	5.9	1.48	0.3144	0.5
Sandy Clay		0.100	0.38	2.7	1.23	0.0288	0.5
Silty Clay		0.070	0.36	0.5	1.09	0.0048	0.5
Biomat[1]		0.050	0.32	3.0	2.22	0.0140	0.5

[1] parameters presented by Finch et al. (2008)

3. Results and discussion

The calculations were conducted for cross section A-A according to the line in Fig. 1 where three observations points were set at the same place where piezometers PJ1, PJ6 and PJ4 were installed. For the analyzed blanket composite of sandy, sandy loam or sandy clay loam groundwater levels are very high, which is why the building floor is wet. The results of numerical calculations for sandy soil (without blanket) are convergent with the observed groundwater level and condition of the building (Fig. 6).

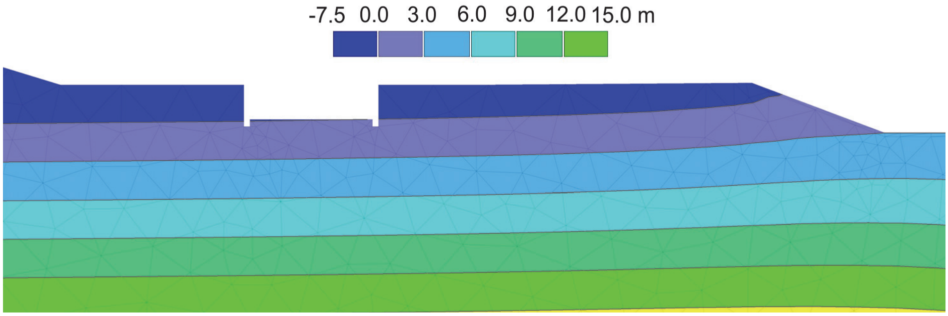

Fig. 6. Piezometric pressure level without blanket (only permeable sandy soils)

Using the blanket with lower permeability material -biomat causes the groundwater level to be distant from building elements. In that case the building floor will be dry (Fig. 7).

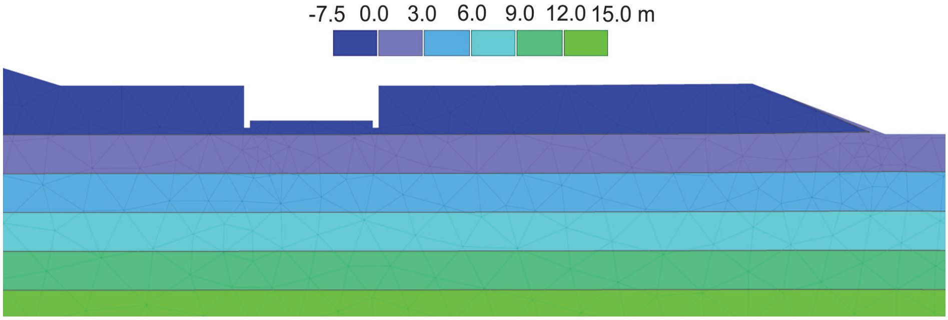

Fig. 7. Influence of low-permeability blanket (biomat) on changes of hydrostatic pressure

The influence of kind of soils or material used as the blanket on groundwater level was particularly important for observation point PJ6 located under the building. Only in the case of using low-permeability materials with hydraulic conductivity lower than Ks < 0.03 m/d is the groundwater level drop significant and with a distance greater than 1 m. The building fundaments and floor will be out of reach of capillary rise. The results of changes of groundwater level under the building – level zero (for PJ6) – are presented in Figure 8.

The results of calculations confirmed the influence of blanket permeability on groundwater level. The measured groundwater level at PJ6 and PJ1 was about 2.5 cm and 15 cm higher in comparison to numerical solutions. The result of calculations using the two-dimensional numerical model gave the best convergence with field measurements in the case where the bottom blanket consists of material with hydraulic conductivity of approximately 1 m/d. Based on the above, a simplified three-dimensional model was constructed to simulate seepage from the reservoir to Strużyna Channel. These calculations take into account the existing (designated for demolition) abutment wall, which directed groundwater flow to the warehouse building. The abutment wall was modelled as 1.0 m width no permeability structure. The result of HYDRUS 3D simulation are similar to field measurements. The steady state conditions were achieved after 5 days. The changes of seepage pressure during 4 days are presented in Figure 9.

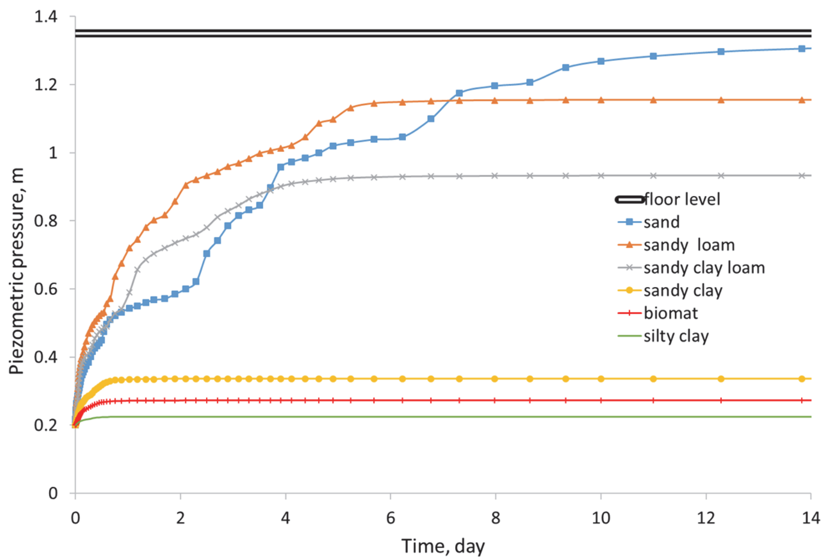

Fig. 8. Changes of groundwater level at observation point PJ6 for different kinds of upstream impervious zone.

In three dimensional simulations the observations points were located according to the installed piezometer network. Differences between measured and calculated groundwater levels are presented in Table 2.

Table 2. Results of comparisons obtained using field monitoring data and numerical solutions

Observation points	Piezometers	calculated m asl	Groundwater levels measured m asl	difference m
1	PJ8	56.10	56.30 ± 0.02	-0.20
2	PJ1	57.00	56.88 ± 0.03	0.12
3	PJ2	56.60	56.50 ± 0.05	0.10
4	PJ3	55.20	55.66 ± 0.02	-0.46
5	PJ5	56.20	56.19 ± 0.02	0.01
6	PJ6	56.10	56.04 ± 0.01	0.06

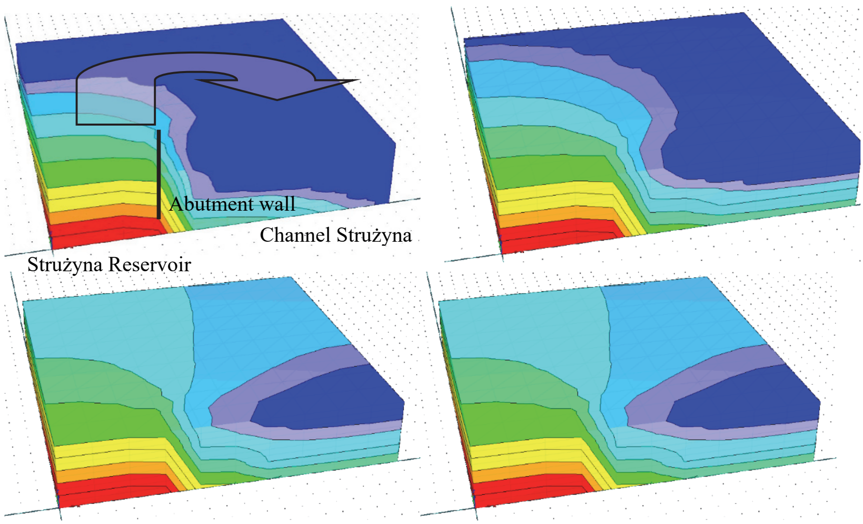

Fig. 9. Visualization of groundwater inflow from Strużyna Reservoir to Strużyna Channel around the abutment wall without biomat

Three dimensional simulations allow one to find the difference between PJ2 and PJ8, which are located close to each other but on two sides of the abutment wall. The influence on the results obtained in PJ3 has appointed boundary conditions due to location of PJ3 on the border of the modelled area. The presented simulations confirmed groundwater flow observed in field measurements.

The Strużyna reservoir is located in the forest, and small organic and mineral particles sediment on the bottom. As a result, a natural low-permeability layer on the bottom of the reservoir was created after many years of operations and the soil bottom became clogged (Nieć et al. 2016b). Spychała & Błażejewski (2004) confirmed that in sand the clogging process can be produced during one year (depending inter alia on hydraulic loading and temperature). Use of HYDRUS software in the analysis of the clogging process was presented in a previous study (Wang et al. 2017).The authors showed the effects of streambed clogging on changes in hydraulic properties. An iteratively increasing total hydraulic resistance during the slug test was considered to correct the estimation of streambed hydraulic conductivity. The mentioned paper suggested the possibility of using one-dimensional coupled water modelling with HYDRUS to quantify the effects of seasonal changes in stream and streambed temperature on streamflow losses. The modelling results for the Strużyna reservoir confirmed the influence of the natural clogging process on water outflow from the reservoir and effects of destruction of the low-permeability layer. In the case of reservoirs, the long-term clogging process occurring at the bottom is very important for water management (including water losses, water quality, supply of aquifers) and the impact on the areas bordering the reservoir (Xanke et al. 2016, Sojka et al. 2019).

The management of groundwater resources directly impacts stream flows through stream-aquifer interactions. A previously presented (Dogrul et al. 2016) example of application to California's Central Valley showed that surrogate models may be insufficient. These approaches may introduce restrictive, sometimes inaccurate, representation of the groundwater flow dynamics and additional modelling steps. Other authors (Fienen et al. 2016, Li et al. 2017) similarly as in our case, have presented the advantages of a non-linear, three-dimensional, finite element groundwater model.

In the filtration studies through the earth dam, as in our work, the effect of the piezometers' location on the analysis of groundwater levels was verified. The exact dependence of water levels in the reservoir on groundwater levels in the work is confirmed by the process of interaction between the reservoir and areas adjacent to the reservoir observed in the article (Shawet al. 2013). This also affects the quality of groundwater and water in the reservoir (Kidmose et al. 2013).

4. Conclusions

During modernization of the overflow structure the natural low-permeability layer was removed. Probably that was the reason for flooding of neighbouring buildings. Using numerical solutions it was easy to predict groundwater level according to many different blankets (differing in permeability) installed on the reservoir bottom.

The conducted research allows us to draw the following conclusions:

1. HYDRUS 3D software can be used to calculate engineering seepage for both design and assessment of reasons. A mathematical model can be used to easily predict water seepage, pressure and velocity in different accepted variants of dam construction.
2. The artificial impervious blanket built during modernization probably has two orders higher permeability (hydraulic conductivity) compared to a natural clogging layer. The authors expect in future reduction of seepage water flow due to the phenomenon of clogging.
3. The cause of the high water level under the building was identified as improper executed of the low-permeability layer in the reservoir.
4. The conducted numerical simulations confirmed correct built low-permeability layer prevents fundament flooding.

An additional reason for increased risk of flooding in the vicinity could be the abutment wall, which has never been destroyed and can direct groundwater to the building.

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Abstract

The article presents the results of a simulation of groundwater flow in the near vicinity of a small storage reservoir, Strużyna. The calculations of water flow in the porous area were conducted using HYDRUS 2D/3D software. The extent of the reservoir's influence on the groundwaters in steady flow conditions was determined. The results were compared with field monitoring data. The field measurements confirmed the negligible impact of precipitation on groundwater level. It was found that the permeability of bottom reservoir has a significant impact on the extent of the reservoir influence. Increasing the groundwater level with simultaneously removal of low permeable soil created a flood risk to buildings near the reservoir. As a result the probable cause of fundament inundation in the near vicinity was indicated.

Keywords:
HYDRUS 2D/3D, seepage velocity, low-permeability blanket

Symulacje numeryczne zmian wód gruntowych na przykładzie zbiornika Strużyna

Streszczenie

W artykule przedstawiono wyniki symulacji przepływu wód gruntowych w pobliżu niewielkiego zbiornika retencyjnego Strużyna. Obliczenia przepływu wody w obszarze porowatym przeprowadzono za pomocą oprogramowania HYDRUS 2D/3D. Określono zasięg oddziaływania zbiornika na wody gruntowe w warunkach stałego przepływu. Wyniki zostały porównane z pomiarami terenowymi, wskazały m.in. pomijalny wpływ deszczu na poziom wód gruntowych. Stwierdzono, że poziom uszczelnienia dna zbiornika ma istotny wpływ na wody gruntowe w jego otoczeniu. Zwiększenie poziomu piętrzenia przy jednoczesnym usunięciu z dna i ścian bocznych zbiornika gruntów o niskiej przenikalności stworzyło zagrożenie podtopieniem dla budynków zlokalizowanych w pobliżu zbiornika. W rezultacie wskazano prawdopodobną przyczynę zalania fundamentów w najbliższym otoczeniu.

Słowa kluczowe:
HYDRUS 2D/3D, prędkość filtracji, warstwa uszczelniająca

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The Use of a Camera Trap System for Monitoring the Movement of Forest Animals Through the Wildlife Crossing in Napchanie

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1. Introduction

In recent years, the intensive development of road infrastructure, particularly expressways and motorways, has resulted in a high-scale fragmentation of landscape. The desire to move the infrastructure away from human settlements and sights of high natural value has led to a situation in which new road projects separate elements of landscape and prevent free migration of animals for feeding and mating purposes. One crucial element considered when planning new infrastructure facilities is environmental compensation. In order to compensate for the fragments of landscape they irrevocably seized control over, investors carry out actions aimed at restoring migration routes and wildlife corridors. An example of such action is designing and constructing overpasses and wildlife crossings along line investments. This is quite common in Poland, were wildlife crossings have been constructed in numerous locations across the country. A given crossing can be considered well-designed only after its use has been verified. Such verification can be performed through studies carried out with PIR sensors, continuous monitoring systems or systems that record on detecting movement. Such tools, however, require a considerable amount of financing and conducting additional construction work. This paper describes how a monitoring system based on inexpensive portable camera traps was designed and applied. The monitoring performed with the use of this system allowed to determine behaviour patterns of animals passing through the lower wildlife crossing (Iwiński et al. 2019).

2. Literature overview

Monitoring the environment and its phenomena with the use of portable video cameras is a scientific method that appeared in the literature as early as in the 1960s. First attempts to record images were made in 1956 (Cutler, Swan, 1999). Technological progress together with lower costs of the equipment resulted in a very intensive development of this method between 2009 and 2016. Over that period, portable camera traps started to be used on a mass scale. (Stachowicz et al. 2017). Simple cameras with built-in memory, powered by integrated or replaceable batteries, made monitoring animal behaviour much easier (Rovero et al., 2013). Stationary devices require a permanent power source. Data they record need to be transferred or stored on external carriers. But first of all, the installation process of stationary devices or their whole systems has an impact on the environment. Portable camera traps have an unquestionable advantage – their installation is non-invasive and they can be mounted on any element that belongs to the infrastructure or to the environment. They do not require to be permanently connected to any power source. The installation process of such devices can help to avoid problems that may arise from changes in the environment e.g. results of vegetation or overgrowing of the monitored area Camera traps do, however, have some disadvantages – they are easy to steal and they easily suffer damage caused by animals. It is also problematic to gather material from more than one device. Portable devices are an optimal solution for monitoring animal behaviour in problematic areas such high mountains, glaciers (Sangay et al., 2014) or forests located far from power sources.

When monitoring animals with camera traps, the key issue is to place the devices properly. Jackson and others (2013) suggest that for animals using narrow crossings (with a width of < 2.5 m), the optimal solution would be to place two cameras mounted at an angle of 45° opposite to each other, pointing to the direction of migration. Such position was indicated as the one ensuring the highest efficiency of the system. Cameras should be placed in a way that corresponds to the to features of the area that is monitored. Installation should be preceded by initial tests. Weather conditions and the type of populations monitored should be taken into consideration on selecting the proper equipment (Noss et al., 2013, Stratford, Naholo 2017).

Applying devices that record material after detecting movement may cause problems with interpreting data. A high number of observations made in a short period of time may be misinterpreted. Dividing animals into groups may be incorrect, as animals moving one after another often do not constitute separate populations. Therefore, in order to interpret the results correctly, it is necessary to adopt an appropriate methodology and apply it consistently to avoid errors (LaFleur et al. 2017). A well-designed and well-operated system of camera traps is invisible to animals and allows to record more objects than an observer. It also allows to learn secrets about species, as animals do not feel constrained when they cannot see the devices (Stratford, Naholo 2017). Cameras, especially the PIR sensor and IR illuminators can be noticed by forest animals (Rovero et al. 2013).

3. Aim, scope and methodology of the study

The aim of the study was to determine the possibility of using a monitoring system designed according to an original concept. This system consists of portable recording devices – camera traps. They allow to determine the behaviour of animals that pass through the wildlife crossing in wintertime. As it is difficult to use constant power supply and there is no way to send data in real time, the system designed consists of several recording devices that were able to cover the whole width of the wildlife crossing in Napchanie.

The monitoring system is based on ScotGuard HC-SG520 cameras that were selected at the stage of initial tests from three types of camera traps, the two other being Hunting Trial Camera HC-300M and Redleaf 1006. The type selected allows to record sound and image at any time of the day or night thanks to a built-in pyroelectric sensor. The built-in IR illuminators allow to record grayscale images during periods of day with insufficient sunlight and at night. Each camera is equipped with 4 IR diodes that emit light with a wavelength range of 940 nm (invisible for humans). According to the technical specification, the diodes can illuminate the area with a maximal length of 36.57 m and with a visibility radius of circa 60°. Camera traps react in less than one second to movement detected in the field of view of the pyroelectric sensor that is placed just under the lens of a 5 Megapixel CMOS image sensor. The pyroelectric sensor operates on 5 sensitivity levels. According to the information provided by the manufacturer, it is able to detect movement in a distance of 25 m from the device and within a radius of 55°. The cameras are powered by AA batteries (4 x 1.5 V). The images recorded are stored on memory cards (maximum 32 GB), which ensures that the device can operate without maintenance for the time required to take 3000 pictures and 3 months. The operating time of the device depends on the number of activities, the duration of the IR diodes illumination and the air temperature.

The first stage of the study involved a comparison of 3 camera types in order to select the optimal device that would carry out research on location in Napchanie. The testing process included a verification of data provided in the technical specification of the cameras. HC-300M and RL1006 cameras were rejected at the initial stage due to higher operating costs (both types require 8 batteries in each device). Moreover, it was problematic to set appropriate frames in HC-300M (the camera is operated with an infrared remote control). On the other hand, the RL1006 camera trap had problems with the PIR sensor, which did not react to a clear crossing of the camera's field of vision. It is worth to mention that both RL1006 and HC-300M have better image sensors than the SG520 type, however, due to the nature of research, they were rejected. The next stage was to verify the ability of the SG520 camera trap to register image. The device's operating time (and standby time), the visibility of angles and distance of the lense, the PIR sensor, the illuminator and weather resistance were all verified in test conditions. The results of the verification differed from the data included in the technical specification of the device. The radius of movement detection was much wider than mentioned in the specification, while the distance of effective detection was shorter. It is also worth mentioning that that the visibility level of the lens, as well as the level of illumination, are much higher than included in the specification. It was possible to effectively illuminate objects located nearly 40 m from the device, however, it is worth to point out that such distance could have been achieved due to the nature of the test location (tests carried out in the structure located in Napchanie indicated that the maximum distance of effective illumination was 32 m). The last parameter analyzed was the period the device can operate in maintenance-free and on battery power supply. In test conditions, the result was 35 days. The optimal operating period, however, should be 4 weeks – considered as a period when the device takes more night pictures and operates without any power shortage or the lack of storage space on the portable disc. Angles and distances were verified with a portable laser rangefinder in a closed area located within the premises of the Poznań University of Life Sciences.

SG520 cameras were installed in the lower wildlife crossing under the Expressway S11 in the village of Napchanie. The crossing is located under a two-part flyover suspended over the riverbed of the Sama river and is designed for large and medium-sized animals. The crossing is 30-meter wide. It is divided by the river and two rows of concrete pillars that support the flyover. The crossing is not equipped with natural infrastructure guiding forest animals. Instead, there are safety nets that protect the expressway and the junction from the intrusion of forest animals. The crossing features many elements of technical infrastructure such as a drainage ditch protected by stones and nets, as well as absorptive wells. This is against the principles of designing wildlife crossings. The river divides the crossing into 2 fragments with a width of 12 m and 14 m respectively. Both fragments are divided into smaller parts by pillars with a diameter of 1 m. The sizes of those parts are: 12 m, 2 m, 10 m and 2 m. The crossing is 4 metres high. There is a gap between the lines of the expressway, which startles animals that pass through this crossing. The crossing is surrounded by concrete retaining walls. At the entrance, there are strips of vegetations made of densely planted bushes. The floor is covered with a mixture of sand and humus. This corridor joins two parts of the forest separated by the Expressway S11.

The devices were installed with the use of straps and cable ties in a non-invasive manner on the elements of infrastructure of the crossing. The support of the crossing was selected to be the main monitoring point as it ensured visibility in all directions and allowed to identify the species and the number of animals moving through the structure.

In the course of tests carried out in the structure and according to the methodology suggested by Noss and others (2014), it was established that placing 3 devices at 120° intervals will allow to correctly monitor the whole wildlife crossing. To ensure the correct operating of the devices and to protect them against theft, the crossing was equipped with an additional device whose field of view covered the entire object. The cameras were programed to record 30-second videos with a minimal delay of 1 second between the PIR sensor detection and the beginning of the recording. The sensitivity of the sensor and the power of IR illuminators were adjusted to the prevailing conditions (the amount of vegetation cover). Camera traps recorded videos with a resolution of 720 px, which was a balance between the size of the recorded file and the ability to read and analyze the image. Animals were monitored continuously throughout the winter period i.e. from 21 December 2018 till 23 March 2019. Battery exchange and data collection took place every 21 days. Videos were transferred to a separate collective disc and were subject to further analysis. It focused on the following elements:

- species,
- number of animals,
- pace of movement and behaviour,
- exact time of passage,
- route selected to pass through the structure.

Data were compiled in a spreadsheet in order to identify a typical behaviour each species demonstrates on using the wildlife crossing.

4. Results

The seasonal monitoring resulted in 752 unique images of animal migrating through the wildlife crossing (Table 1). 77% of videos were recorded at night with the use of IR illuminators. Wild boars were recorded 280 times, which made them the species that used the crossings most frequently. They were followed by roe deer (102), deer (84) and the category of farm animals and humans (83). 67 foxes and 4 racoon dogs were also recorded. It should be noted that the group of farm animals included birds. They were, however, impossible to identify due to the the fast pace of migration.

Table 1. List of images recorded with the use of the monitoring system

Observation		1	2	3	4	5	Total
Number of videos:		83	0	208	100	211	752
At daytime		3	9	37	3	67	169
At nighttime		50	1	171	7	144	583
Empty		4	1	27	9	41	132
Successful		49	9	181	1	170	620
Species	Wild boar	1	7	101	4	67	280
	Roe deer	2	4	33	8	15	102
	Deer	1	8	15	2	18	84
	Fox	7	0	13	6	31	67
	Rackoon dog	0	0	3	1	0	4
	Others (humans, pets)	8	0	6	0	9	83

The number of migrations depends on weather conditions and the time of day. By analyzing the daily distribution of usage and the images recorded, it is possible to identify behaviour patterns of 3 animal species that pass through the structure most frequently. Moreover, the video material collected indicates that different parts of the crossing are used depending on the time of day and on the species of user. Regardless of the time of day, wild boars migrate through the entire width of the crossing, without paying attention to any possible danger. They usually move in tight groups, running at high speed, slowing down only when they leave the crossing and approach the drainage ditch located next to the vegetation strip in front of the crossing. An opposite behaviour pattern can be observed among migrating deer. They seem to be extremely consistent as they move through the crossing. They migrate in groups, one after another. One deer enters the crossing only when the other starts to leave it. One interesting phenomena is the fact that deer use specific fragments of the crossing depending on the time of day. During daytime, they use the main migration route that leads between the widest supports. They move quickly, without paying attention to any danger. At night, however, they use the narrow fragments of the crossing located between the supports and the riverbed, as well as the narrow fragment located on the northern side of the Sama river. Those fragments are somehow sheltered from the rest of the passage and can be a form of protection for the animals. Another of the groups analyzed were roe deer. They used the crossing as if it had been their place of feeding. They were frequently spotted playing and relaxing in the main part of the crossing. This was particularly evident during snowfall, when most of the roe deer fed under the expressway on grass that was not covered with snow. Roe deer were mostly observed during daytime. They migrated fast only when startled. Under such circumstances, roe deer run into the direction opposite to the startling factor, without paying attention to any other danger.

Due to the proximity of houses and to the fact that the object is located in the valley of the Sama river, a large group recorded in the videos were humans and farm animals. The wildlife crossing is frequently used by pets (cats and dogs spending time or playing in the crossing) and people taking walks or walking their dogs. Many of the people recorded were photographers that carry out outdoor sessions in the valley of the river. It is worth to mention that human presence does not significantly affect the migration of animals. There was a decrease in the number of animal migrations immediately after humans passed through the crossing. However, in a perspective of 24 hours, the number of migration did not change.

5. Discussion and conclusion

In recent years, studies on the inventory and the behaviour of forest animals have been closely connected with minimizing costs and making use of the rising mobility of equipment. Disadvantages and problems of applying camera traps in scientific research have not prevented them from becoming one of the basic measuring devices used for inventorying mammals (Meek et al. 2012). This is confirmed by the analysis of the number of research carried out with the use of portable cameras conducted by Stachowicz in several scholarly publications (Stachowicz et al. 2017). It indicated a huge increase in the use of camera traps that began after 2009. Low maintenance costs and low prices make camera traps an interesting alternative to permanent monitoring systems connected to power lines and to monitoring conducted by qualified personnel. Studies have indicated (De Bondi et al. 2010) that the level of species identification achieved by camera traps was the same as the one achieved by qualified personnel. Therefore, camera traps can be an economical alternative applied in research not involving animal tagging. The difficulties of using ready-made cameras can be compensated by the use of modular solutions based on Raspberry Pi computers that can be fully regulated by users and easily adapted to environmental need (Nazir et al. 2017). The application of the aforementioned devices shall be and extension of this study. The high efficiency of ready-made recording devices has been demonstrated in this study. It is worth to mention that the operating costs of camera traps, excluding the cost of purchase, are almost 9 times lower than the costs of traditional inventory methods (De Bondi et al. 2010, Meek, Pittet 2012).

The lower crossing in Napchanie is used by big game (wild boars, roe deer, deer) and is a corridor joining forest complexes that enables migrations between different habitats.

An inexpensive monitoring system allows to record the migration of forest animals with an efficiency of over 82%. It can be successfully applied in wildlife crossings with a width up to 30 m. HC-SG520 devices can operate successfully throughout the period of 21 days, and provide continuous observation.

Migrating animals show specific behaviour patterns and, depending on the species and the time of day, use different part of the crossing. Information about they behaviour obtained through monitoring can be used for securing traffic routes or as training materials for drivers.

The presence of anthropogenic elements does not cause a decrease in the number of animal migrations. However, since the crossing is located in the vicinity of settlements, it is frequently used by humans and pets, which may startle forest animals.

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Abstract

The development of road and railway infrastructure leads to landscape fragmentation. Environmental compensation is an important aspect developing communication networks. It can be achieved through designing and constructing green infrastructure that joins habitats separated by human activity. This article describes an attempt to create a system of monitoring forest animals with the use of portable devices (camera traps) in a wildlife crossing located under the line of Expressway S11 near the riverbed of Sama in the Wielkopolska Voivodeship. The crossing for large animals was created there to join habitats located within Poznan city limits with the forest complexes outside of Poznań. The system proposed in this article is intended to evaluate the use of the crossing by animals and to identify behavioural patterns of animals passing through the structure. Authors proved that it is possible to create an economical and efficient monitoring system of forest animals without electrical supply and without any data transmission system. In addition, authors manage to identify some behaviour patterns of migrating forest animals, different of each species. This can be helpful in designing and maintaining wildlife crossings. The system consisted of 4 cameras that monitored the whole crossing; 3 of them were recording videos from the central point while the one was used for control purposes. It was established that using even 1 device is enough to successfully monitor the animals migrating through the crossing. The monitoring process was carried out with the use of HC-SG520 cameras, which allowed to record image after triggering the pyroelectric detector. It was also possible to monitor animal movement in nighttime, thanks to the illumination provided by IR diodes Cameras recorded 30-second videos and saved them on SD cards that were replaced every 21 days.

HC-SG520 cameras were selected in the course of tests that involved 2 other types of devices. The efficiency of the equipment used was 82%, only 17% of videos recorded did not feature any migrating animals. It was observed that the crossing is used mostly by wild boars, roe deer and deer. Due to the proximity of human settlements, the crossing is used by humans and pets, which can affect the functionality of the structure and the freedom of migration. Most migrations (78%) take place during the night. The behavioural patterns of forest animals identified throughout the study, can be later applied in ways of protecting roads from animal intrusion or can serve as educational material for drivers.

Keywords:
camera trap, environmental monitoring, wildlife crossing.

Wykorzystanie systemu fotopułapek do monitoringu ruchów zwierzyny leśnej przez ekodukt Napachanie

Streszczenie

Rozwój infrastruktury drogowej i kolejowej powoduje zjawisko fragmentaryzacji krajobrazu. Ważnym aspektem rozbudowy sieci komunikacyjnych jest kompensacja przyrodnicza. Jednym z narzędzi realizacji tych zadań jest projektowanie i budowa zielonej infrastruktury służącej do łączenia siedlisk, które zostały rozdzielone ze względu na bariery liniowe. W artykule podjęto próbę wykonania systemu monitoringu zwierzyny leśnej przy wykorzystaniu przenośnych urządzeń rejestrujących (camera trap) na ekodukcie pod nitką drogi ekspresowej S11 w ciągu koryta rzeki Samy w województwie wielkopolskim. Przejście dla zwierząt dużych powstało w tym miejscu w celu połączenia siedlisk leżących w granicach miasta Poznania z kompleksami leśnymi powiatu poznańskiego System ten służyć ma ocenie wykorzystania przejścia przez zwierzęta oraz wskazania wzorców zachowania zwierząt w trakcie korzystania z tego typu infrastruktury. Autorzy wskazali, że istnieje możliwość wykonania taniego i skutecznego systemu monitorowania zwierzyny leśnej bez konieczności doprowadzenia energii elektrycznej oraz systemu przesyłu danych. Dodatkowo wskazane zostały wzorce zachowania zwierzyny w zależności od gatunku migrujących osobników, co może być pomocne przy projektowaniu jak i pielęgnacji tego typu rozwiązań. Zaprojektowany system monitoringu składał się z 4 kamer monitorujących całą powierzchnie przejścia dla zwierząt, 3 z nich realizowały nagrania z centralnego punktu, natomiast 4 z niech pełniła funkcję kontrolną. Zauważono, że wykorzystanie już jednego urządzenia pozwala na skuteczne monitorowanie zwierząt na ekodukcie.

Do monitoringu wykorzystano urządzenia HC-SG520, które umożliwiały rejestrowanie obrazu po wybudzeniu czujnika piroelektrycznego i monitorowanie ruchu również po zmroku zw względu na wykorzystywanie oświetlania za pomocą diod IR. Kamery rejestrowały 30 sekundowe materiały video i zapisywały je na kartach SD, które wraz z bateriami wymieniane były co 21 dni. Kamery HC-SG520 zostały wybrane po przeprowadzeniu testów wykorzystujących 2 inne tego typu urządzenia. Skuteczność zastosowanego sprzętu wyniosła ponad 82%, urządzenia zarejestrowały zaledwie 17% filmów pustych, na których nie można było zauważyć migrującej zwierzyny. W wyniku monitoringu zwierząt zauważono, że z przejścia korzystają przeważnie dziki oraz sarny i jelenie. Ze względu na bliskość zabudowy mieszkaniowej – przejście jest intensywnie wykorzystywane zarówno przez ludzi jak i przez zwierzęta domowe – co może mieć wpływ na funkcjonalność ekoduktu i ograniczać swobodę migracji. Większość migracji (78%) odbywa się w ciągu nocy. Zaobserwowane wzorce zachowania zwierzyny leśnej mogą być wykorzystane do szeroko pojętej tematyki zabezpieczania dróg przed wtargnięciem zwierzyny jak i służyć jako materiały edukacyjne dla kierowców.

Słowa kluczowe:
fotopułapki, monitoring środowiska, przejścia dla zwierząt

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The Use of a Standardized Runoff Indicator for Hydrological Characterization of Selected Rivers of Poland and Slovakia

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1. Introduction

Knowlede of the hydrologic regime of rivers comprises the basis for water resources assessment in river basins. For last several years, a number of studies on variability of river runoff under the influence of climate changes (Stahl et al. 2010) and anthropogenic changes have barchieen conducted (Lv et al. 2018). Determination of runoff change trends is remarkably important to strategic management of water resources (Húska et al. 2017). Therefore, numerous studies discuss the issue of uneven distribution throughout the year, in regional extent, caused by seasonality of climatic factors (Parajka et al. 2009). Such research was conducted by Kļaviņš et al. (2008) on the rivers of Latvia, Stonevičius et al. (2014) in Lithuania. The runoff studies on the area of Poland were conducted by Gutry-Korycka & Rotnicka (1998), Michalczyk & Głowacki (2008), Pociask-Karteczka (2011), Jokiel & Stanisławczyk (2012), Gądek & Tokarczuk (2015), Niedzielski & Miziński (2017), Wrzesiński & Sobkowiak (2018), Mostowik et al. (2019). The studies of Pekárová et al. (2006) revealed that the analysis of runoff of main European rivers throughout last 150 years did not indicate significant increasing or decreasing trend. Contrary results have been achieved in small river basins, where the runoff reacts quicker to the changes that take place in the basin, which causes significant changes to the runoff (Song et al. 2012). The assessment of river discharge reaction to precipitation depends on physiographic features of the catchment, among others they are geological structure, fall of the ground, plant cover (Banasik & Hejduk 2012, Osuch et al. 2015, Wałęga et al. 2016, Čanjevac & Orešić 2018, Dunca & Bădăluţă-Minda 2018). Van Loon & Laaha (2015) claim that over 30 factors may be distinguished in a catchment, which may have influence to the river runoff. Interactions between the mentioned factors vary temporally and spatially (Bažatová & Šimková 2015).

The aim of this paper is to investigate how the data collected from 2 selected basins with diverse physically-geographical parameters talks about the frequency of floods and droughts in the last three decades. Two basins have been selected for the case study: lake district basin in Poland (Gwda) and mostly the mountain basin in Slovakia (Laborec). The areas of Poland and Slovakia have been included by Spinoni et al. (2015) in common region of Europe – Eastern Europe. Based on the data regarding discharge and precipitation in the years 1981-2010, there have been analyzed long-term and seasonal trends of runoff changes. On the basis of average monthly precipitation and runoff, the appearance and duration of wet and dry periods as well as their intensity have been compared. The comparison of the results was possible thanks to application of standardized hydrological indices.

Standardized Runoff Index (SRI) was developed on the basis of the Standardized Precipitation Index (SPI) concept for hydrological drought characteristics (Nalbantis & Tsakiris 2009). It is a simple and efficient index of hydrological droughts assessment. It was applied to assessment of dry and wet period forecasts in various climate zones. The proposed approach bases on the assessment of water resources in various hydro-climatic conditions and on determination of various intensity classes of hydrological drought.

2. Study area

Two basins located in Central Europe, which reflect different climate and physio-georaphic conditions, have been selected for the analysis (Table 1). Hydrological characteristics of the rivers Gwda and Laborec have been presented in the Table 2. The River Gwda, located in northern part of Poland, is a 4th order tributary, which flows into the River Noteć. Total length of the river is 139.95 km. Gwda's basin is a lake district basin, built of sands and fluvioglacial gravels, with numerous endorheic depressions and large share of lakes and forests. Forest area (afforestation index) comprises 30% of total area, while lakes area (lake density index) is 2.5% (Kubiak-Wójcicka & Kornaś 2015). Arable area accounts for 44.4 % of the Gwda River basin. The basin represents the agricultural-forest type. The River Laborec is a tributary of Bodrog. It is mostly a mountain river. Its length is 135.5 km. The basin's surface area is 4522 km^2 and is characterized by large river network density (1.01 km$\cdot$km^{-2}). The most important tributaries of Laborec include rivers Uh and Cirocha. The basin is asymmetric, left-side tributaries prevail over the right-side ones. In the basin of River Laborec there are located artificial water reservoirs, which have influence on the discharge of the River Laborec.

Table 1. Physio-geographical parameters of basins of the Rivers Gwda and Laborec

Characteristics	Gwda River	Laborec River
Basin area (km^2)	4947.27	4522.70
Average altitude (m a.s.l.)	128.1	657.5
Forest cover (%)	30	40
Denivelation (m)	160.5	580
River network density (km·km^{-2})	0.31	1.01

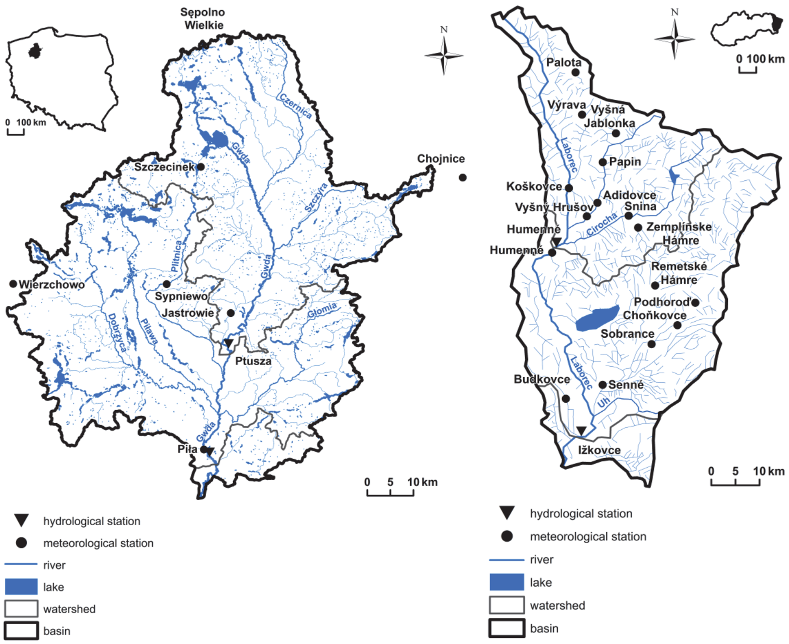

Fig. 1. Study area

Table 2. Hydrological characteristics of the Rivers Gwda and Laborec

River	Gauging station	Basin area in km^2 (% of total area)	Precipitation 1981-2010 (mm)	Average discharge 1981-2010 ($m^3 \cdot s^{-1}$)
Gwda	Ptusza	2042.00 (41.3%)	659	11.91
Gwda	Piła	4713.11 (95.3%)	634	27.80
Laborec	Humenne	1321.63 (29.2%)	816	12.74
Laborec	Izkovce	4350.86 (96.2%)	799	51.55

3. Materials and methods

In order to characterize the runoff regime, the data pertaining to discharge and precipitation in basins of Gwda and Laborec was used. On the basis of daily values,there have been calculated the average monthly and average annual values in multiyear period of 1980-2010. The data comes from Institute of Meteorology and Water Management – National Research Institute (data pertaining to Gwda's basin) and from Slovak Hydrometeorological Institute (SHMI) (data pertaining to Laborec's basin).

The runoff in River Gwda basin was analyzed on the basis of the discharge at gauging stations in Piła and Ptusza, and in the River Laborec basin – Izkovce and Humenne. Average monthly and annual precipitation consist of averaged precipitation recorded on several meteorological stations located in particular catchments. The precipitation data for the River Gwda basin come from 7 precipitation stations closing the water gauging station in Piła, while the Ptusza gauging station encloses 5 meteorological stations. In the Laborec river basin there were 16 meteorological stations, while in the Humenne profile there were 10 stations. Location of the stations have been presented on Fig. 1.

The analysis has been focused on the trends of average annual and monthly runoff and on occurrence of dry and wet periods. The 30-year measurement period assumed for the analysis is considered as reliable for creation of a credible characteristics of volume, regime and variability of the runoff (Ljubenkov & Cindrić Kalin 2016). The assumption of the beginning of study at the 1980s is important because that decade is considered a turning point in development of hydro-climatic variables (Blahušiaková & Matoušková, 2015).

Because the basins under analysis are similar in their surface area but different in physio-geographical conditions, the runoff variability has been analyzed with use of the standardized meteorological indices – SPI (Standardized Precipitation Index) (Mc Kee et al. 1993), which are SRI (Standardized Runoff Index) (Shukla & Wood 2008, Lorenzo-Lacruz et al. 2013, Kubiak-Wójcicka &

Bąk 2018). As a normalizing function, a 2-parameter logarithmic function was adopted (Vicente-Serrano et al. 2012). The calculation details have been presented in the work by Bąk & Kubiak-Wójcicka (2017). In order to calculate the SRI values in various time scales (*n* months), it is necessary to use accumulation of discharges for each month and for *n* months. Five different time series have been analyzed: 1, 3, 6, 9 and 12 months. Based on the achieved SRI values, classification of drought intensity has been carried out (Table 3). The main advantage of the SRI index is the fact that it allows for estimation of beginning and end of a drought as well as its intensity. Hydrological drought beginning is assumed when the SRI is less than -1.0 while wet periods – when the SRI > 1.0. The range between -1.0 and 1.0 has been defined as regular.

Table 3. The classification scale for SRI values (McKee et al. 1993, Bąk & Kubiak-Wójcicka 2017)

SRI value	**Category**
SRI≥2.0	Extremely wet
2.0>SRI≥1.5	Severely wet
1.5>SRI≥1.0	Moderately wet
1.0>SRI>-1.0	Normal
-1.0≥SRI>-1.5	Moderately dry
-1.5≥SRI>-2.0	Severely dry
SRI≤-2.0	Extremely dry

To understand present and future water resources sustainability and developments, it is necessary to consider the existence of a trend in hydro-meteorological variables. The most common for trend analysis is non-parametric Mann-Kendall (MK) statistical test. The Mann-Kendall test follows statistics based on standard normal distribution (Z), using Eq. (1) (Mann 1945, Kendall 1975).

$$Z = \begin{cases} \frac{S-1}{\sqrt{Var(S)}} & \text{if} \quad S > 0 \\ 0 & \text{if} \quad S = 0 \\ \frac{S+1}{\sqrt{Var(S)}} & \text{if} \quad S < 0 \end{cases} \tag{1}$$

in which,

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} \operatorname{sgn}(x_j - x_k) \tag{2}$$

where x_j and x_k are data values at times *j* and *k* (*j* > *k*) respectively.

$$\mathrm{sgn}(x_j - x_k) = \begin{cases} +1 & \text{if } (x_j - x_k) > 0 \\ 0 & \text{if } (x_j - x_k) = 0 \\ -1 & \text{if } (x_j - x_k) < 0 \end{cases} \tag{3}$$

$$\mathrm{Var}(S) = [n(n-1)(2n+5) - \sum_{i=1}^{m} g_i(g_i - 1)(2g_i + 5)]/18 \tag{4}$$

where:
n – the number of data points,
m – the number of tied groups
(a set of g_i of sample data having the same value).

The null hypothesis H0 (no trend) is accepted if $Z<Z_{\alpha/2}$ and rejected (hypothesis H1) if $Z>Z_{\alpha/2}$ where α is the significance level and $Z_{\alpha/2}$ the standard normal distribution for $\alpha/2$. The applications carried out considered $\alpha=0.05$ and $Z_{\alpha/2}=1.645$. The trend magnitude in time series is expressed by Sen's method (Sen 1968):

$$\beta = \mathrm{Median}\left((x_j - x_k)/(j-k)\right) \tag{5}$$

where:
x_j, x_k – data values at times j and k ($j > k$) respectively.

A positive value of β indicates an upward (increasing) trend and a negative value indicates a downward (decreasing) trend in the time series. Both the MK test and Sen's method require time series to be serially independent, which can be accomplished using the pre-whitening technique. In this paper, the authors used a trend-free pre-whitening method before applying the MK test to detect significant trends (Khaliq et al. 2009).

4. Results and discussion

4.1. Annual precipitation and discharge in the years 1981-2010

Annual precipitation in the Laborec river basin reach on the average approximately 800 mm in the years 1981-2010. In the basin area, the precipitation ranges from 560 to 1020 mm. Maximum precipitation has been recorded in 2010, when it reached approximately 1113 mm. The lowest precipitation has been recorded in 1986 (620 mm). Due to the location of Gwda river basin in a lake district and in a so called rain shadow, annual precipitation is lower when compared to the precipitation in the Laborec river basin by approximately 180 mm. In the Gwda basin area, the precipitation ranges from 550 to 730 mm. The highest values of precipitation have been recorded in 2010 (821.7 mm) and 2007 (808.3 mm), and the lowest – in 1982 (377.4 mm). The amount of precipitation translates into annual average discharge. In the estuarial section of Gwda river in Piła the discharge value on the average was 27.8 $m^3 \cdot s^{-1}$ (specific runoff 5.9 $dm^3 \cdot s^{-1} \cdot km^{-2}$), while for the river Laborec in Izkovce it was 51.55 $m^3 \cdot s^{-1}$ (specific runoff 11.4 $dm^3 \cdot s^{-1} \cdot km^{-2}$).

The trend course analysis reveals statistically significant increase of annual precipitation sum on all the analyzed meteorological stations in the analyzed multi-year period. The results achieved in the Laborec river basin coincide with studies carried out on the area of whole Slovakia (Labudová et al. 2015, Zeleňáková et al. 2017). However, precipitation increase does not imply annual discharge increase on all gauging stations. Only in the river Laborec, weak upturn trend of discharge in gauging station Izkovce, while in gauging station Humenne the trend was upturn but statistically insignificant (less than 0.05). In the Gwda river basin, despite the upturn trend of precipitation, a downturn trend of discharge has been recorded. It was especially noticeable in Piła gauging station, where a statistically significant downturn discharge trend was recorded (Fig. 2-3).

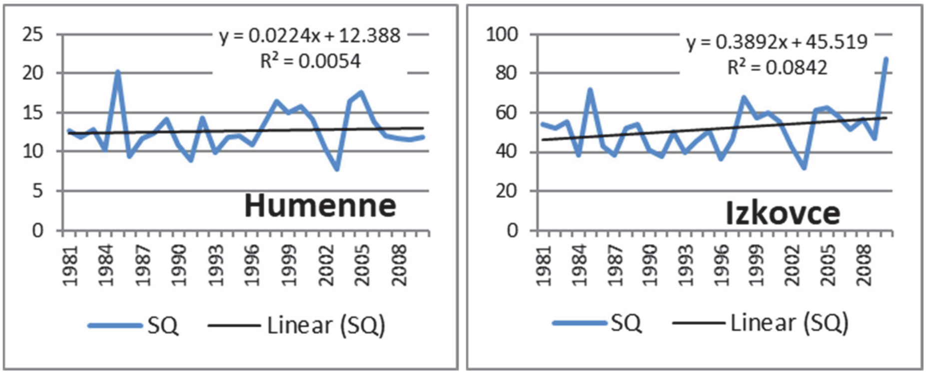

Fig. 2. Average annual discharge (SQ in $m^3 \cdot s^{-1}$) of Laborec at gauging station Humenne and Izkovce in the years 1981-2010

Despite different precipitation and discharge distribution throughout a year, their seasonal distributions in both basins are similar (Table 4). The largest average monthly precipitation occurred in July while largest average monthly discharges were recorded in March and April. In the Gwda river basin, the precipitation in summer months predominated and consisted about 58% of the annual precipitation, while river discharge was higher in winter months and also consisted approximately 58% of the annual discharge. The situation is similar in the Laborec river basin. In the summer months, the precipitation consisted of 60-62% of annual precipitation, while the discharge in winter months was significantly higher than in the case of River Gwda and consisted 64-67% of annual discharge.

The studies of Štefunková et al. (2013) indicated that in long-term periods, average runoff will be decreasing in summer months and increasing trend will appear in winter and early spring periods. It results from air temperature increase and shifting snow thawing from spring to winter months.

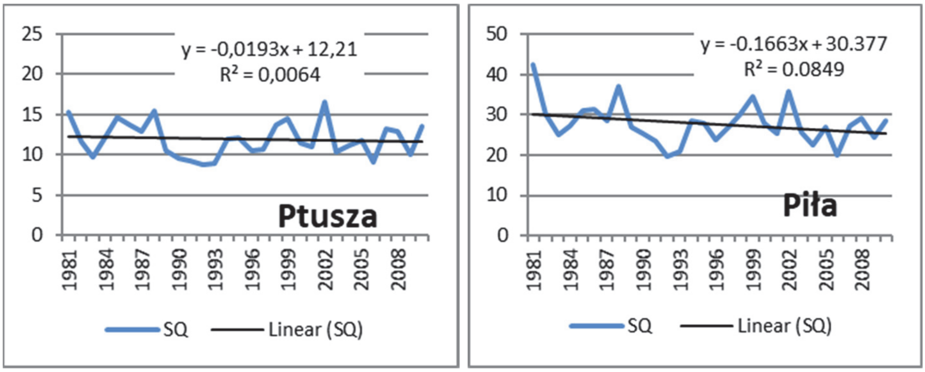

Fig. 3. Average annual discharge (SQ in $m^3 s^{-1}$) of Gwda at gauging station Ptusza and Piła in the years 1981-2010

4.2. Seasonal distribution of precipitation and discharge in the years 1981-2010

Table 4. Precipitation and discharge in the years 1981-2010

Month	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
River Gwda, gauge Ptusza												
P (mm)	49.7	37.3	48.5	37.1	57.2	72.7	**75.4**	72.8	58.1	47.3	50.7	55.5
Qmean($m^3 s^{-1}$)	13.55	14.85	**16.39**	15.00	13.06	11.22	9.71	8.89	9.04	8.91	10.35	11.97
Qmax ($m^3 s^{-1}$)	21.38	27.76	**28.31**	20.85	18.91	17.59	14.81	14.43	15.33	13.08	19.14	18.44
Qmin ($m^3 s^{-1}$)	9.13	8.92	9.45	**9.50**	7.72	6.81	6.02	5.77	6.01	4.93	6.52	8.14
River Gwda, gauge Piła												
P (mm)	48.2	36.0	47.2	35.0	58.1	67.8	**71.5**	70.1	56.2	43.6	47.7	52.3
Qmean($m^3 s^{-1}$)	32.56	35.12	**38.12**	34.88	28.74	24.05	21.97	21.17	21.57	22.27	24.58	28.83
Qmax ($m^3 s^{-1}$)	49.50	63.10	**63.30**	48.80	41.30	39.30	35.90	33.40	34.10	31.20	44.80	40.50
Qmin ($m^3 s^{-1}$)	22.40	22.40	**25.20**	21.80	16.50	12.30	11.00	11.00	11.60	12.20	14.30	19.50
River Laborec, gauge Humenne												
P (mm)	46.9	45.1	46.5	56.2	83.2	94.1	**107.2**	83.9	79.8	58.2	56.1	58.7
Qmean($m^3 s^{-1}$)	12.09	14.90	**30.78**	22.17	14.72	9.47	10.35	5.34	5.80	6.57	10.28	13.80
Qmax ($m^3 s^{-1}$)	24.77	38.79	**63.17**	59.56	51.06	35.53	33.93	15.52	18.58	19.99	31.20	37.53
Qmin ($m^3 s^{-1}$)	1.35	2.75	**11.00**	5.53	3.83	2.66	1.74	1.14	1.61	1.41	1.84	1.21
River Laborec, gauge Izkovce												
P (mm)	49.0	45.5	45.7	55.3	81.3	89.2	**98.3**	79.8	75.7	58.6	58.3	62.1
Qmean($m^3 s^{-1}$)	49.44	55.43	**98.10**	90.75	56.54	39.32	36.69	29.58	29.45	33.28	45.08	54.95
Qmax ($m^3 s^{-1}$)	106.88	146.77	185.72	**230.05**	178.98	169.57	82.40	66.54	48.93	90.26	123.04	169.13
Qmin ($m^3 s^{-1}$)	8.50	19.84	**26.88**	26.06	13.73	16.88	14.98	13.66	11.98	18.49	10.06	7.08

The course of average monthly discharges of Gwda and Laborec is balanced over a year with maximum occurring usually in March or April and minimum in Spetember or October. The years, in which the highest and the lowest annual average discharge values were recorded, the seasonal distribution changed. In case of the River Laborec, the most wet year was 2010, which had 2 high river flows – in June and December – caused by heavy precipitation (Fig.

4). The lowest annual discharge was recorded in 2003, in which a single maximum, related to spring thaw, occurred in April. The highest discharges of the analyzed period in River Gwda basin took place in 1981 and the lowest – in 1992. In wet year 1981, 2 high river flows were recorded: in March and November, while in 1992 just one – in April (Fig. 5).

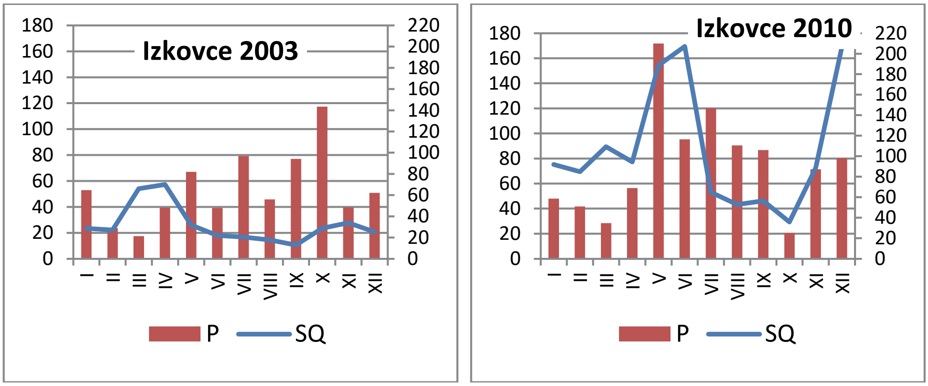

Fig. 4. The course of average monthly discharge (SQ in $m^3 \cdot s^{-1}$) of River Laborec at gauging station Izkovce in dry year 2003 and wet year 2010 against precipitation (P in mm)

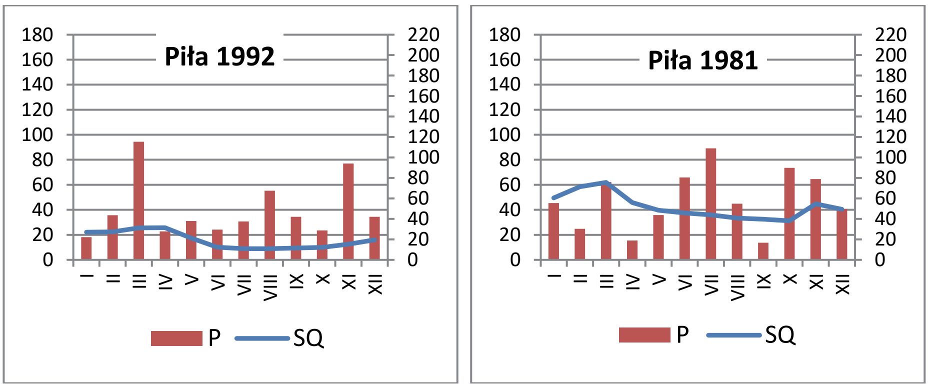

Fig. 5. The course of average monthly discharge (SQ in $m^3 \cdot s^{-1}$) of River Gwda at gauging station Piła in dry year 1992 and wet year 1981 against precipitation (P in mm)

4.3. Standardized Runoff Index (SRI) utilization in hydrological analyses

The analysis of course and occurrence of wet and dry periods in the basins being discussed is possible with use of the Standardized Runoff Index. The course of the SRI's values in particular months has been presented in various time scales on 2 gauging stations. The highest amplitude of the SRI value has been achieved in the case of 1-month interval and at gauging station Izkovce it was 6.35, Piła – 5.31. Based on the SRI values there can be identified periods of occurrence of wet and dry months.

The frequency of dry and wet periods' occurrence in the basin of River Laborec is significantly higher than in the case of River Gwda. It results from higher susceptibility of the basin to course of precipitation. River Gwda basin is much more hydrologically inert and does not react that suddenly to precipitation volume. The SRI index has been presented on the basis of the following parameters: number of months (duration of drought/wetness in months) and maximum intensity, in Tables 5-6.

Table 5. Parameters of the SRI in various time scales for River Gwda at gauging station Ptusza and Piła

	SRI-1	SRI-3	SRI-6	SRI-9	SRI-12
Ptusza					
Number of wet months (SRI>1.0)	62	64	62	66	76
Number of dry months (SRI<-1.0)	62	61	74	75	65
Index maximum value	2.44 (II 2002)	2.25 (IV 2002)	2.05 (VII 2002)	2.05 (III 1981)	1.93 (XII 2002)
Index minimum value	-2.68 (V 1993)	-2.36 (VI 1993)	-2.11 (VIII 1993)	-1.99 (VI 1993)	-2.11 (VI 1993)
Piła					
Number of wet months (SRI>1.0)	57	58	56	64	67
Number of dry months (SRI<-1.0)	62	55	51	47	45
Index maximum value	2.57 (II 2002)	2.31 (II 1981)	2.24 (IV 1981)	2.40 (IX 1981)	2.55 (XI 1981)
Index minimum value	-2.74 (VII 1992)	-2.73 (VII 1992)	-2.60 (XI 1992)	-2.28 (I 1993)	-2.34 (V 1993)

Table 6. Parameters of the SRI in various time scales for River Laborec at gauging station Humenne and Izkovce

	SRI-1	SRI-3	SRI-6	SRI-9	SRI-12
Humenne					
Number of wet months (SRI>1.0)	64	59	57	47	54
Number of dry months (SRI<-1.0)	61	63	59	59	59
Index maximum value	2.54 (VI 2010)	2.16 (VII 2010)	2.32 (X 2010)	2.32 (XII 2010)	2.35 (III 1981)
Index minimum value	-3.05 (XII 1986)	-3.41 (I 1987)	-3.16 (I 1987)	-3.00 (IV 1984)	-2.80 (V 1984)
Izkovce					
Number of wet months (SRI>1.0)	59	62	57	56	56
Number of dry months (SRI<-1.0)	44	53	56	61	63
Index maximum value	3.48 (VI 2010)	2.63 (X 1998)	2.53 (X 2010)	2.64 (XII2010)	2.48 (XII2010)
Index minimum value	-2.87 (I 1987)	-3.34 (I 1987)	-2.76 (II 1987)	-2.65 (V 1984)	-2.44 (V 1984)

Maximum value of the SRI index recorded at gauging station Ptusza is lower than that recorded at the station Piła. That may be caused by water retention in the basins located by the hydropower plants. In case of River Laborec, maximum values of the SRI index are higher at the station Izkovce than Humenne. Possible cause is River Uh estuary which is located close to the gauging station Izkovce. Hydrological droughts are more gentle at gauging station Izkovce than at gauging station Humenne. The delay is approximately 1 month. During the wet periods, drought intensity is also higher at gauging station Izkovce than at Humenne. Duration of dry periods extends and the number of wet months stabilizes. Frequency of dry and wet periods' occurrence is higher in case of the mountain river than the lake district one. The lowest SRI values for River Gwda were recoded in 1992, which is related to the one of the lowest precipitation throughout the analyzed period (481 mm) and low precipitation in the preceeding year 1991 (553 mm). The highest values of the SRI for River Laborec were in 2010, in which annual precipitation sum in the basin was the highest over the analyzed period and its value was 1113 mm. The lowest SRI values were recorded in 1987 – annual precipitation sums were 771 mm – and it was preceeded by the year 1986 with the lowest recorded precipitation sum of 620 mm. The share of particular drought classes in River Laborec and River Gwda basins varies. Noteworthy is higher frequency of extremely wet months (SRI >=2.0) and extremely dry months in the basin of River Laborec. Moreover, there are the years in which in the River Laborec basin the extremely wet and extremely dry periods occur simultaneously at the same year, e.g. 2007. Normal years (-1.0<SRI<1.0) in the estuarial parts of both rivers comprise approximately 67-71% of the analyzed period.

Table 7. Monthly trend analysis of discharge in the years 1981-2010

month	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
River Gwda, gauge Ptusza												
Z	-0.1779	0.0593	0.2075	0.2965	-0.1779	-0.4447	-0.9191	0.2372	0.0296	0.2075	0.1779	0.3558
β	-0.0193	0.0078	0.0110	0.0193	-0.0072	-0.0181	-0.0316	0.0127	0.0007	0.0065	0.0177	0.0186
River Gwda, gauge Piła												
Z	-0.6226	0.7412	0.0889	0.0593	-0.0889	-0.7116	-1.5121	**-2.2533**	**-1.7493**	-1.3935	-1.4528	-1.4824
β	-0.0683	0.0696	0.0037	0.0044	-0.0210	-0.0894	-0.1398	**-0.2501**	**-0.1733**	-0.1204	-0.1432	-0.1324
River Laborec, gauge Humenne												
Z	1.3342	0.7709	-1.0081	0.2286	-0.3261	-0.1186	0.6523	0.7412	-0.2668	-0.8302	-0.2668	-0.4744
β	0.1383	0.1307	-0.3098	0.0168	-0.0319	-0.0186	0.0421	0.0590	-0.0140	-0.0393	-0.0169	-0.0702
River Laborec, gauge Izkovce												
Z	1.1613	0.6774	0.0968	-0.5565	-0.7258	-1.0645	-1.4758	0.0000	-1.3548	-1.3065	0.9194	-0.2419
β	0.3064	0.2908	0.0409	-0.4087	-0.3070	-0.2455	-0.2011	-0.0032	-0.2067	-0.1927	0.2277	-0.1024

*bold values in grey mean significant trend

Tables 7 and 8 summarize the results from the trend analysis based on the Mann-Kendall non-parametric statistical test for a critical probability level of 5% coupled with the Sen approach applied to the discharge datasets. The results of trend analysis show mainly decreasing trends of discharges in evaluated gauges. Significant decreasing trends were proved in Ptusza station at River Gwda in Poland and in Izkovce station at River Laborec in Slovakia. These decreasing trends are obvious mainly in summer months (August and September). The obtained values are usually not statistically significant.

Table 8. Trend analysis of discharge in summer and winter months

Station	winter (I-III, X-XII)	summer (IV-IX)	year (I-XII)
River Gwda, gauge Ptusza			
Z	0.4216	-0.8299	-0.3899
β	0.0018	-0.0032	-0.0006
River Gwda, gauge Piła			
Z	-1.3449	**-2.0938**	**-2.3404**
β	-0.0113	**-0.0214**	**-0.0081**
River Laborec, gauge Humenne			
Z	0.4257	-0.0728	0.2845
β	0.0042	-0.0005	0.0008
River Laborec, gauge Izkovce			
Z	0.6366	**-2.2039**	-1.0156
β	0.0174	**-0.0393**	-0.0080

*bold values in grey mean significant trend

5. Conclusions

The periods of drought and flood occurrence overlap with other authors' studies for the analyzed basins. The slow rise in air temperature had been lasting since the mid-nineteenth century. At the turn of the 1980s and 1990s, an intensive increase in air temperature and reduction of precipitation started, which contributed to the formation of droughts (Żmudzka 2009). Those droughts were reflected not only in Poland but also throughout Central and Eastern Europe (Kliment & Matoušková 2008, Spinoni et al. 2015, Somorowska 2016). In the basin of River Laborec, droughts were occurring much more often than in the River Gwda basin at the same time. The strongest droughts in the River Laborec basin occurred in 1987 in shorter cumulation periods (SRI-1, 3 and 6) and in 1984 in longer cumulation periods (SRI-9 and 12). What is worth of mentioning, is an intense hydrological drought in 2003, which occurred in both short (SRI-1) and in long (SRI-12) cumulation period. That drought was also recorded by Fendeková et al. (2018) in other Slovak river basins. In the River Gwda basin, the strongest droughts occurred in 1992 (SRI-1, 3, and 6) and in 1993 (SRI-9 and 12). Year 2010 in most of the area of Europe, was an extremely wet year. Large precipitation which took place in May and June resulted in floods in both Poland and Slovakia (Bissolli et al. 2011, Kundzewicz 2012). In 2010 in the Gwda River basin, the precipitation was one of the largest in the analyzed multi-year period. However, it did not result in an increased river discharge (Kubiak-Wójcicka & Kornaś, 2015).

The study of influence of selected river basin parameters on river runoff has been conducted in 2 river basins in the area of Poland and Slovakia. The influence, in the analyzed river basins, depends on precipitation. The index method (SRI) that was applied, allowed for relatively simple identification and, at the same time, assessment of drought intensity in appropriate classes.

In order to assess runoff variability, there was used the SRI index (Standardized Runoff Index), which was calculated in several time scales, i.e. 1, 3, 6, 9 and 12 months. The analysis of drought duration and intensity with the SRI index in short time intervals revealed that hydrological droughts (SRI<-1.0) on River Gwda were longer and less intensive than in the case of River Laborec, in which hydrological droghts were shorter and more intensive. Duration of wet periods (SRI>1.0) was similar in case of both rivers, however, the phenomenon intensity was higher in the mountain river. The analysis of longer cumulation periods revealed that for River Gwda, wet periods extended while hydrological drought periods' duration decreased. In case of River Laborec, wet periods slightly shortened, while drought periods got significantly longer. The trend analysis of discharges proved significant decreasing trends, which can be a sign of drought hazard in the end of summer period.

Hydrological droughts in River Laborec basin occurred more frequently but were brief and more intensive than in case of River Gwda. River Laborec is characterized with higher sensitivity of water downflow than the basin of River Gwda, which is considerably inert to precipitation.

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Abstract

This study compares river discharge of two catchments in Central Europe. The catchments' areas are similar while their geological structure differs significantly. The River Laborec (Slovakia) is an example of a mountain river, draining hardly permeable land. The River Gwda (Poland) is a lowland river, draining mainly sandy formations. The study used average monthly flows in the period of 1980-2010 measured on water gauges Humenne and Izkovce on the river Laborec and water gauges Piła and Ptusza on the river Gwda.

The aim of the study is a review of hydrological drought course in two catchments that differ in their structure. The analysis was conducted on the basis of the SRI (Standardized Runoff Index), which was calculated in various time scales, i.e. 1, 3, 6, 9 and 12 months. It is a dimensionless index, which allows determination and comparison of dry and wet periods for rivers in various regions. The analysis of duration and intensity of the SRI in short time periods revealed that hydrological droughts on the river Gwda lasted longer and were less intense than in case of river Laborec. The duration of the wet periods (SRI > 1.0) was similar on both rivers, however the phenomenon intensity was higher on the mountain river. The analysis of longer accumulation periods revealed that on the river Gwda wet periods got longer, while hydrological drought periods were shortened. In case of the river Laborec, wet periods were slightly shortened, while drought periods have extended significantly.

Keywords:
discharge, hydrological drought, Standardized Runoff Index (SRI), Poland, Slovakia

Wykorzystanie znormalizowanego wskaźnika odpływu do charakterystyki hydrologicznej wybranych rzek Polski i Słowacji

Streszczenie

W niniejszym opracowaniu porównano odpływ rzeczny w 2 zlewniach centralnej Europy o podobnej powierzchni zlewni i zróżnicowanej budowie geologicznej. Rzeka Laborec (Słowacja) jest przykładem rzeki górskiej, odwadniającej tereny trudno przepuszczalne, natomiast rzeka Gwda (Polska) reprezentuje zlewnie pojezierną, zbudowaną głównie z utworów piaszczystych. W opracowaniu wykorzystano średnie miesięczne wartości przepływów w okresie 1980-2010 na posterunkach wodowskazowych Humenne i Izkovce na rzece Laborec oraz Piła i Ptusza na rzece Gwdzie.

Celem niniejszego opracowania jest ocena przebiegu suszy hydrologicznej w dwóch zlewniach o zróżnicowanej budowie. Analizę przeprowadzono w oparciu o wskaźnik SRI (Standardized Runoff Index), który obliczono w różnych skalach czasowych tj. 1, 3, 6, 9 i 12 miesięcy. Jest to bezwymiarowy wskaźnik, który umożliwia wyznaczenie i porównanie okresów suchych i mokrych dla rzek z różnych regionów. Analiza czasu trwania i intensywności wskaźnika SRI w krótkich skalach czasowych wykazała, że susze hydrologiczne (SRI < -1.0) na rzece Gwdzie trwały dłużej i charakteryzowały się mniejszą intensywnością niż w przypadku rzeki Laborec. Czas trwania okresów wilgotnych (SRI > 1.0) był podobny w obu rzekach, jednak większą intensywność zjawiska notowano w rzece górskiej. Analiza dłuższych okresów kumulowania wykazała, że dla Gwdy okresy wilgotne uległy wydłużeniu, natomiast skróceniu uległy okresy suszy hydrologicznej. W przypadku rzeki Laborec okresy wilgotne uległy niewielkiemu skróceniu, natomiast okresy suszy zdecydowanie uległy wydłużeniu.

Słowa kluczowe:
przepływ, susze hydrologiczne, Standaryzowany Wskaźnik Odpływu (SRI), Polska, Słowacja

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Characteristic of Fulvic Acids Extracted from the Wastewater by Different Methods

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1. Introduction

Humic substances (HSs) are a major form of natural organic matter (NOM). They have different compositions and properties vary with the source of origin and the method of extraction (Litvin et al., 2015). Regardless of their origin and place of occurrence they always consist of: carbon, oxygen, hydrogen, nitrogen and sulphur. HSs are macromolecular compounds with a very complex and heterogeneous structure (Casassas et al., 1995). Their main functional groups are: carboxylic, phenolic, carbonyl, hydroxyl, amine and aromatic moieties, among others (Pena-Mendez et al. 2005). Discussed substances play many important roles in the environment, mostly in soils, although they are also uptaking toxic metals, anthropogenic organic chemicals and other contaminations from water (Pena-Mendez et al., 2005; Manzak et al., 2017). As reported by (Pena-Mendez et al., 2005; Manzak et al., 2017) ion modifiers based on the calcium humate could remove cadmium, iron, nickel, copper and mercury from water. HSs constitute a high percentage of total dissolved organic carbon (DOC) in the natural environment, they appear to be one of the most popular organic components of water (Boggs et al. 1985). Fulvic acids (FAs), as dissolved form of HSs are soluble in water under all pH conditions. There are many different methods of FAs extraction and it is difficult to compare the data reported by researchers (Kuwatsuka et al., 1992). Kuwatsuka et al. (Kuwatsuka et al., 1992) compared two methods of humic and fulvic acids isolation: IHSS Method and NAGOYA Method.According to the International Humic Substances Society (IHSS), it is not possible to define which one is the most effective. It may be the reason why the inconsistency of isolation methods hindered the development of humus studies. HSs are mainly extracted from soils, surface and groundwater and there is a shortage of information on the humification process taking place during wastewater treatment. According to Nissinen et al., (2001) chemical composition of wastewater indicated that they could affect forms of trace metals, salt and organic substances (including xenobiotics) concentrations which is higher in treated wastewater than in surface water. Also, humic acids (HAs) originated from the wastewater treatment had better complexing abilities than naturally occurring HSs. The authors (Polak et al., 2009) compared the humification processes at wastewater treatment plants (WWTPs) with different technological processes. The results showed that the sequence of wastewater treatment processes had a significant influence on the humification of sewage sludge and properties of extracted HAs. The next important thing was the order in which they were carried out at treatment plants. A lot of publications confirmed that HAs extracted from sludge were weakly humificated and they had low free radical concentrations (Polak et al., 2009). HSs stimulate biological processes, mainly nitrification. The authors (Yabing et al., 2019) investigated the potential influence of bio-refractory HSs on the reactor performance and a functional structure of microbial communities within anammox bioreactors. The results showed that the presence of HSs in wastewater did not significantly limit nitrogen removal in the anammox reactors. According to (Kochany & Lipczyńska-Kochany, 2008) the use of HAs would be beneficial for wastewater treatment plants supplied with leachate from landfills or industrial wastewater with inhibiting agents. This would allow improving their efficiency (mostly ammonia and phosphorus removal) without major modifications. On the other hand, HSs are generally considered to be irreplaceable or difficult to degrade during the wastewater treatment process, instead of biodegradation, the biosorption process is considered for their removal (Feng et al. 2008). Therefore, humification during wastewater treatment is a very important and interesting issue. It can determine the suitability of sludge for agricultural purposes and indicate changes that are needed to achieve this goal (Pajączkowska et al., 2003). Since large amounts of HSs can be found as by-products of different human activities (wastewater treatment plants and waste landfills) the authors (Anielak & Łomińska-Płatek, 2017) compared FAs extracted from the raw wastewater, sewage sludge and waste landfill leachates. The detailed analysis of the infrared spectrum (IR) indicated that discussed substances extracted from landfill leachates and treated wastewater had a convergent chemical structure. The degree of FAs aromatization depends on the time of their humification and a place of generation. In the environment, they undergo dynamic biochemical and chemical transformations and may have different content of inorganic matter (ash) depending on their origin (Anielak & Łomińska-Płatek, 2017).

Maximum use of treated wastewater e.g. to irrigation or in modern technologies purifying wastewater to drinking water standards is a very important problem.

In the work, the authors examined the content of FAs in the primary and secondary effluents. The main aim of the research was to compare isolated FAs using two different extraction methods.

2. Materials and methods

The samples were collected directly from the primary and secondary effluents at the WWTP and the obtained results were averaged. The WWTP treats mainly wastewater from individual users and industrial plants. The WWTP comprises mechanical and biological wastewater trains as well as sludge processing and biogas trains. The plant works as a three-stage Bardenpho system and operates five identical biological reactors.

2.1. Extraction of FAs with the NH_4OH and NaOH methods

Isolation of FAs was carried out using two methods: 1) with NH_4OH, according to the work (Pempkowiak et al., 2008) and 2) with NaOH following the method presented by International Humic Substances Society (IHSS) with a small modification. Samples were acidified with HCl to pH = 1. After 24 hours, wastewater was filtered on a medium thickness filter with glass beads of diameter < 0.5 cm and then passed through a glass column (ϕ = 25 mm, h = 1000 mm) filled with polymeric adsorbent resin - Amberlit XAD 1180 at a rate of about 1 L/hr. In the first method, FAs were eluted with 0.5 mol /L NH_4OH (Fig. 1a) while in the second 0.5 mol/L NaOH (Fig. 1b) and then FAs eluent with an excess of NaOH from the first column was directed to the II-nd ionic column (Lewatit SP112 cation H^+). Next, FAs eluent from the II cation exchange column and from the I column with an excess of NH_4OH were concentrated in a vacuum evaporator at 85°C under a vacuum of 350 mbar. After evaporation bath at 85°C, the sample was dried to obtain a dry FAs residue.

2.2. Analysis of FAs properties

The analysis of carbon, hydrogen and nitrogen contents was performed using combustion technology with a chromatographic detection of evolving gas products (elemental analysis). The determinations were made on an elemental analyzer Flash 2000 Thermo. Oxygen was determined via mass balance 100% –(C% + H% + N%+ S%) for FAs on the ash-free basis (Łomińska & Anielak, 2017).

Analysis of the trace element content was performed using X-ray fluorescence (XRF), model S8 Tiger, Bruker apparatus. Discussed technique involves the excitation of characteristic X-rays using radiation from an X-ray tube or currently a synchrotron. X-ray fluorescent radiation has the same nature and wavelengths as the characteristic X-ray radiation of the corresponding element. The analysis was carried out in a vessel for analyzing powders on a 4 μm Prolen film. Elements such as Cl, Si, Ca, K, Mg, P, Br, Mn, Ce, Ti, I, Al, B and Sr were analyzed.

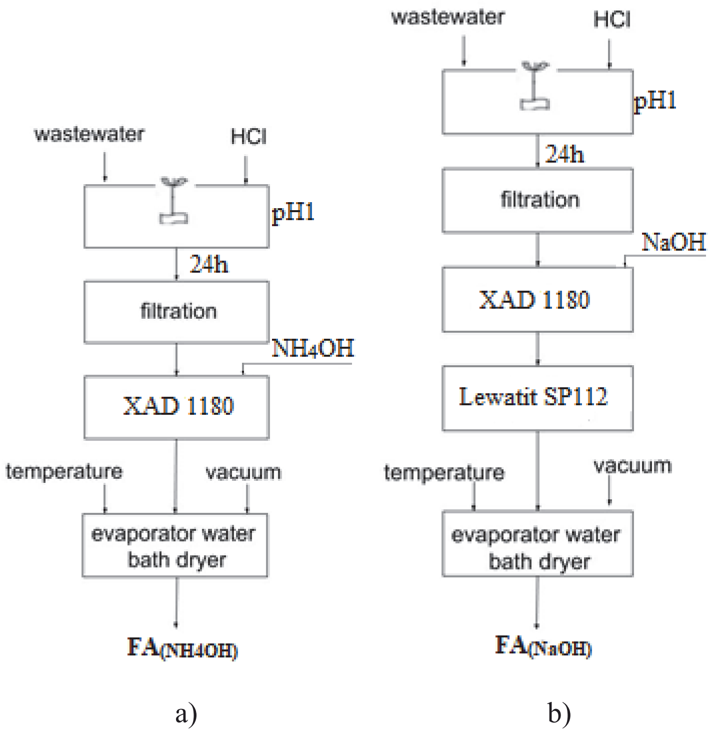

Fig. 1. Elution of FAs with NH_4OH (a) and NaOH (b) method

Fourier transform infrared spectra of FAs were obtained in a Thermo Nicolet FTIR-is10S spectrophotometer. The spectral range was: 650-4000 cm^{-1} at a resolution of 1 cm^{-1}, the number of scans was 32. The IR absorption spectra were run to analyse the structure of extracted substances. FTIR spectroscopy allows determining characteristic vibrations for groups occurring in FAs. This method provides valuable information on oxygen-containing functional groups. Since there are many deforming and stretching vibrations within one molecule the full analysis of the IR spectra for FAs is quite difficult (Zhu & Ryan 2016).

3. Results and discussion

All measurements were carried out in three repetitions and then averaged. The concentration of the FA is given as dry residue.

Table 1. Concentration and ash content of FAs isolated from primary (FA1) and secondary (FA2) effluent

Samples*	FA concentration ash free [g/m^3]	Ash content [%]
$FA1_{(NH4OH)}$	13.09	11.55
$FA1_{(NaOH)}$	15.20	41.53
$FA2_{(NH4OH)}$	4.69	9.74
$FA2_{(NaOH)}$	2.78	14.77

* primary effluent NH_4OH - $FA1_{(NH4OH)}$, primary effluent NaOH - $FA1_{(NaOH)}$, secondary effluent NH_4OH - $FA2_{(NH4OH)}$, secondary effluent NaOH - $FA2_{(NaOH)}$

The concentration of $FA1_{(NH4OH)}$ was 13.09 g/m^3 and $FA2_{(NH4OH)}$ was 4.69 g/m^3 for primary and secondary effluent, respectively. In the samples obtained using the NaOH method concentration was 15.20 g/m^3 for the primary effluent ($FA1_{(NaOH)}$) and 2.78 g/m^3 for the secondary effluent ($FA1_{(NaOH)}$) (Table 1). The highest amount of FAs was detected in the primary effluent sample isolated with the NaOH method. The results indicate that in the secondary effluent in $FA_{(NH4OH)}$ solution (I method) obtained in little more fulvic acids than in the method with NaOH. This may be caused by the application of a two-stage ion exchange, where more FAs remained absorbed by the ion-exchange grains resulting in their larger mass losses. Some differences in the isolated substances were observed in the primary effluent ($FA1_{(NH4OH)}$ - $FA1_{(NaOH)}$ = 2.11 g/m^3), which was richer in organic and inorganic constituents than the secondary effluent.

Regardless of the chosen method, the FAs concentration decreased in each subsequent stage of wastewater treatment:

$$FA1_{(NH4OH)} > FA2_{(NH4OH)}$$
$$FA1_{(NaOH)} > FA2_{(NaOH)}$$

The concentration of FAs extracted from biologically treated wastewater was similar to the data obtained previously (Pempkowiak et al., 2008). The concentration of HAs in the treated wastewater was 2.8 g/m^3 (Jamno WWTP) and 3.2 g/m^3 (Unieście WWTP). During the treatment process in selected WWTP the amount of FAs decreased over 2 times (in I method) and over 5 times (in II method). It can be concluded that the investigated WWTP discharges secondary effluents with a smaller concentration of discussed substances compared to primary effluents. This is particularly important because the secondary effluent is discharged directly to surface waters, serving as a water source to the water treatment plant. That is why their quality and composition is particularly important.

The ash content was much higher in the NaOH method ($FA1_{(NaOH)}$ = 41.53% and $FA2_{(NaOH)}$ = 14.77%), it may be related to the fact that sodium hydroxide is a stronger base than NH_4OH, therefore during ion exchange more cations were extracted together with FAs. The amount of isolated FAs in both methods were quite similar.

3.1. Elemental composition

A study of the elemental composition provided indications regarding a structure of isolated acids, an origin of their organic matter as well as a degree of aromatization and condensation. The results of the elemental composition were converted to the ashless mass. The analysis of the extracted FAs reveals that they are built primarily of carbon, oxygen, hydrogen and nitrogen, this is a characteristic feature for all of them, regardless origin (Łomińska & Anielak, 2017).

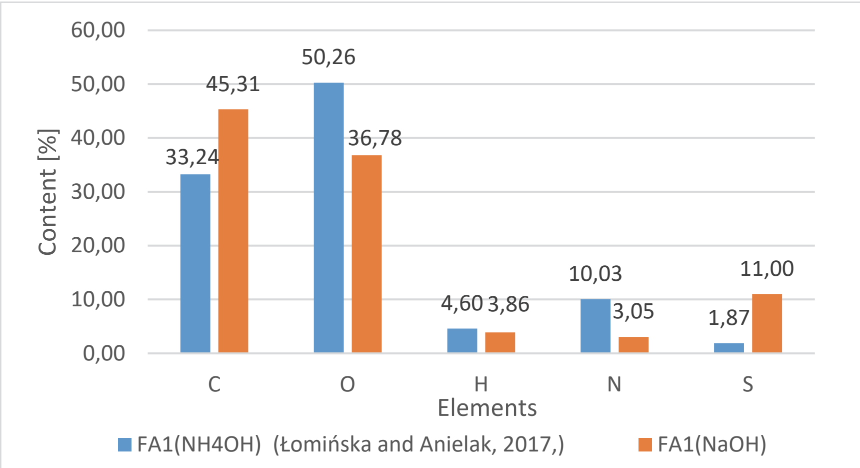

Fig. 2. Elemental composition of FAs extracted from the primary effluent by different methods

Carbon and Oxygen were the main elements found in the extracted FAs (Fig. 2 and Fig. 3). The content of C for $FA1_{(NaOH)}$ was bigger and amounted to 45.31% while in the $FA1(_{NH4OH})$ it was 33.24%. According to (Gomółka and Szaynok, 1997) FAs contain 43% to 52% of C. A higher content of this element means that the NaOH method resulted in the isolation of substances characterized by a higher degree of humification. The content of O for the first method was 50.26% while for the second one it was 36.78% and it is typical for FAs which usually contain from 42% to 51% (Litvin et al., 2015). High content of this element in their structure in the NaOH method may indicate a presence of carboxyl, carbonyl, methoxy, hydroxyl, alcohol, ester and eter groups (Grzegorczuk-Nowacka & Anielak, 2017). The content of H was similar for both samples (4.60% and 3.86%) and was typical 3.3-6.0%. Usually, FAs contain from 1.0% to 6.0% of N (Gomółka & Szaynok, 1997), since nitrogen compounds are removed as a result of biological nitrification and denitrification. It should be noticed that the content of N varied with the methodology used, the NH_4OH method generated more N (10.03%) than the NaOH method (3.05%). High nitrogen content is attributed to a large number of amino acids in the FAs structure (Łomińska & Anielak, 2017). FAs extracted by the I method had 1,87% of sulphur and it was almost 6 time less than by the II method.

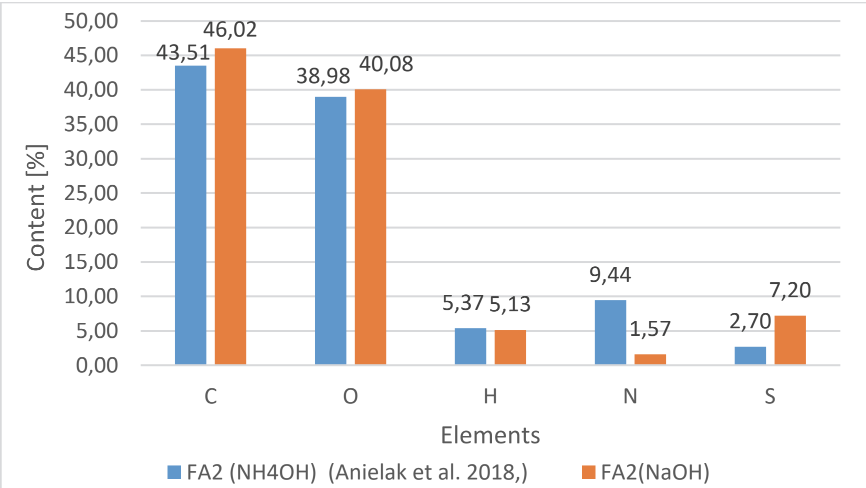

Fig. 3. Elemental composition of FAs extracted from the secondary effluent by different methods

The content of C in the secondary effluent (Fig. 3) was similar for both samples as it was 43.51% (NH_4OH) and 46.02% (NaOH), both values are characteristic for FAs (Gomółka & Szaynok, 1997). Slightly higher content of C in the NaOH method can indicate a higher degree of humification, but the difference is quite small. The same was true for O, its content was 38.98% and 40.08% for the first and the second method, respectively. Both these values are also characteristic of FAs (Gomółka & Szaynok, 1997). The content of H was similar for both samples (5.37% and 5.13%). As previously, the N content varied with the methodology. The NH_4OH method generated more N (9.44%) than the NaOH method (1.57%).

FAs extracted by the NaOH method had much more S in their structure - 11% and 7.20% (Figure 2) than the ones with using the NH_4OH method - 1.87%

and 2.7% (Figure 3). The content of S was similar in samples isolated with the same method. According to (Pempkowiak et al., 2008) various organic compounds like proteins and urea of natural origin are found in a primary effluent during biological treatment process, simple organic compounds (including monomer derived from proteins, such as amines) and others with nitrogen and sulphur in their structure are created (Pempkowiak et al., 2008). It can explain the high content of N and S in the isolated FAs. The high level of N and S (Fig. 2 and 3) may be attributed to the incorporation of protein decomposition products and sulphur-containing surfactant residues in the macromolecules (Senesi et al., 1996). Another source of N can be the aqua ammonia, which is used in FAs extraction. NH_4OH is easily broken down into water molecules and ammonia and is released into the atmosphere, in particular at elevated temperatures. However, small amounts of nitrogen may contaminate the extracted FAs (Pempkowiak et al., 2008). The remaining elements constituted a small percentage of the sample content.

Comparing the elemental compositions of extracted FAs with literature it can be seen that they have a similar structure.

3.2. Atomic ratios

Based on the elemental composition atomic ratios: C/O, C/H, C/N and O/H have been determined. Atomic percentages were calculated from the averages of the weight percentages determined from the elemental composition.

Table 2. Atomic ratios of FAs extracted from the different samples

Samples	Atomic ratios [-]			
	C/O	C/H	C/N	O/H
$FA1_{(NH4OH)}$	0.88	0.60	3.30	0.68
$FA1_{(NaOH)}$	1.64	0.98	14.86	0.60
$FA2_{(NH4OH)}$	1.49	0.68	4.61	0.45
$FA2_{(NaOH)}$	1.53	0.75	29.31	0.49

The C/O ratio provides information on carbohydrate content and acid hydrophobicity (Table 2). FAs with a lower C/O have a lower content of carbohydrates. The more carbon, the greater the ratio and hydrophobicity of acids. The value of the ratio can result from biodegradation of protein, which are strongly present in both primary and secondary effluent. This fact is confirmed by a significant amount of nitrogen and sulphur in the structure of extracted acids (Fig. 4 and 5). Discussed atomic ratio determines the degree of oxidation, a high value indicates a low degree of oxidation and humification. It may be concluded that FAs from the primary effluent (NH_4OH), was the most hydrophilic and had many functional groups, such as hydroxyl and carboxyl. The atomic ratio was quite similar for all samples. An increase in the C/O value was observed in the following sequence:

$$FA1_{(NH4OH)} < FA2_{(NH4OH)} < FA2_{(NaOH)} < FA1_{(NaOH)}$$

The C/H ratio describes the aromatization and condensation of FAs (Table 2). A lower C/H value means an aliphatic characteristic of acids, while a higher one – their aromatic form. An atomic ratio was relatively small for all samples what means a low degree of aromatization. For $FA1_{(NH4OH)}$ it was 0.60 while for $FA2_{(NH4OH)}$ it was around 0.68, next for $FA1_{(NaOH)}$ 0.98 and for $FA2_{(NaOH)}$ 0.75. FAs extracted with the NaOH method were more aromatic. The differences between the samples were quite small.

$$FA1_{(NH4OH)} < FA2_{(NH4OH)} < FA2_{(NaOH)} < FA1_{(NaOH)}$$

The C/N ratio determines the degree of maturity (Table 2). It establishes direction and intensity of transformation of organic matter and nitrogen compounds, as well. The C/N ratio was quite small for 2 samples: $FA1_{(NH4OH)}$ 3.31 and $FA2_{(NH4OH)}$ 4.61 and it can be correlated with the extraction method (ammonia water). The higher the value of N, the lower the C/N atomic ratio according to the following sequence:

$$FA1_{(NH4OH)} < FA2_{(NH4OH)} < FA1_{(NaOH)} < FA2_{(NaOH)}$$

The O/H ratio determines the degree of humification (Table 2), this indicator is directly proportional to the atomic ratios. The higher O in the O/H ratio the higher the amount of oxygen-containing groups and a lower degree of humification. The O/H ratios were quite large for all samples. They were: $FA2_{(NH4OH)}$ 0.45, $FA2_{(NaOH)}$ 0.49, $FA1_{(NH4OH)}$ 0.68 and the biggest one $FA1_{(NaOH)}$ 0.60. It may be concluded that FA extracted from different samples had many oxygen groups. The higher loss of hydrogen than oxygen was observed in the NaOH method due to the humification process. An increase of the O/H value was observed in the following sequence:

$$FA2_{(NH4OH)} < FA2_{(NaOH)} < FA1_{(NaOH)} < FA1_{(NH4OH)}$$

3.3. The degree of inside oxidation

The degree of inside oxidation was based on the Żdanow formula (Becher et al., 2013; Boguta et al., 2016):

$$\omega = [(2O+3N)-H]/C \tag{1}$$

where:
O – the oxygen content, N – the nitrogen content, H – the hydrogen content, C – the carbon content.

Samples	ω
$FA1_{(NH4OH)}$	1.51
$FA1_{(NaOH)}$	0.40
$FA2_{(NH4OH)}$	0.51
$FA2_{(NaOH)}$	0.07

Table 3. The degree of inside oxidation of FAs extracted from the primary and secondary effluents by different methods

According to the Table 3 ω was bigger for the primary and secondary effluents in the NH_4OH method. For primary effluent it was 1.51 $FA1(_{NH4OH})$ and 0.40 for $FA1_{(NaOH)}$. FA extracted from the secondary effluent had ω = 0.51 – $FA2_{(NH4OH)}$ and 0.07 for $FA2_{(NaOH)}$. The parameter is closely related to oxidation and degradation reactions. The degradation process involves the loss of CH_3 groups and partial oxidation, thus decreasing the number and length of aliphatic chains in HSs (Litvin et al., 2015). The high degree of oxidation means a high level of humification (Łomińska & Anielak, 2017; Pena-Mendez et al., 2005). Based on the results, it can be concluded that the extraction with a NaOH solution and a two-stage ion exchange process (hydrophobic ion-cation exchanger – H+) reduce internal oxidation of FAs. Soluble HSs extracted from the primary effluent had a higher level of humification in both methods. An increase in ω value was observed as below:

$$FA2_{(NaOH)} < FA1_{(NaOH)} < FA2_{(NH4OH)} < FA1_{(NH4OH)}$$

3.4. Trace elements content

The highest Cl content was found in the $FA1_{(NaOH)}$ (26,58%) while the other samples had the Cl content below 15%, in $FA2_{(NH4OH)}$ Cl was not found. The content of Si was similar for all samples, but in $FA2_{(NH4OH)}$ the element was not found. The lowest Na content was detected in the $FA1_{(NH4OH)}$ sample while all other samples had similar content of Na. The Na content was correlated with the extraction method, a higher content of this element could be related to the fact that NaOH was introduced to the column in the second method. The content of Ca and K was similar in three samples ($FA1_{(NH4OH)}$, $FA1_{(NaOH)}$ and $FA2_{(NaOH)}$) while for $FA2_{(NH4OH)}$ the content of these elements was much higher (Ca – 8.8% and K – 2.5%). The content of Mg and P were similar (below 0,5%) in three samples ($FA1_{(NH4OH)}$, $FA1_{(NaOH)}$ and $FA2_{(NaOH)}$) although in $FA2_{(NH4OH)}$ it was 1,6%. The highest content of Fe was in the $FA1_{(NaOH)}$ sample (18,76%), the other samples ($FA1_{(NH4OH)}$, $FA2_{(NH4OH)}$, $FA2_{(NaOH)}$) had the Fe content below 0,7%.

3.5. Infrared spectroscopy IR

The results of IR were compatible with the analyses of elemental composition and functional groups. The IR analysis showed some similar as well as different bands.

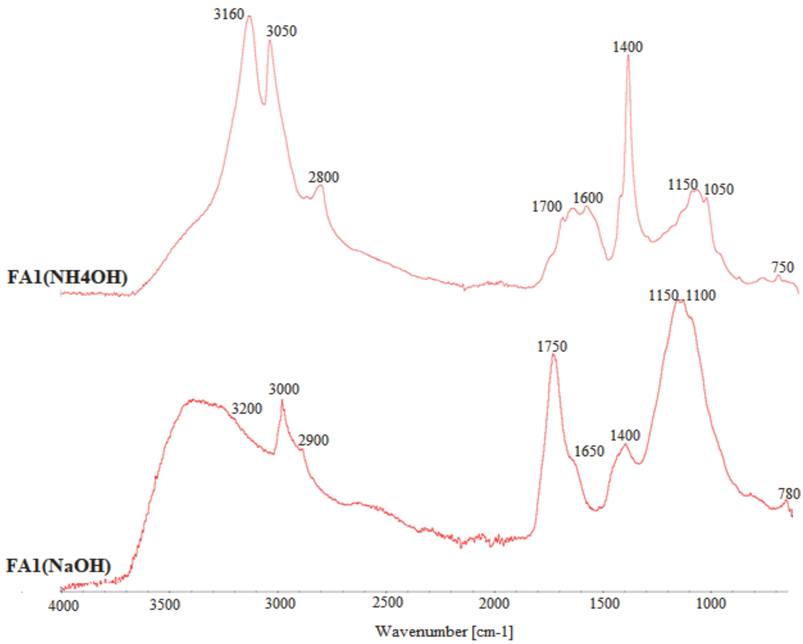

Fig. 4. The IR absorption spectra of FAs extracted by NH_4OH (Łomińska and Anielak, 2017) and NaOH method from the primary effluent

Quite broad peaks appeared around 3200^{cm-1} (FA1$_{(NaOH)}$) and 3160^{cm-1} FA1($_{(NH4OH)}$) (Fig. 4). They are usually attributed to O-H stretching from alcohols, phenols and carboxylic related groups and also to N-H stretching from amide and amine functional groups. The next quite intense peaks around 3050 $^{cm-1}$ (FA1$_{(NH4OH)}$) and 3000^{cm-1} (FA1$_{(NaOH)}$) are caused by C-H asymmetric and symmetric stretching of aromatic compounds. Peaks around 2900^{cm-1} (FA1$_{(NaOH)}$) and 2800^{cm-1} (FA1$_{(NH4OH)}$) may indicate the presence of alkanes stretching bonds C-H. Peaks around 1750 (FA1$_{(NaOH)}$), 1700^{cm-1} (FA1$_{(NH4OH)}$) and 1650^{cm-1} (FA1$_{(NaOH)}$), 1600^{cm-1} (FA1$_{(NH4OH)}$) can be attributed to the C=C and C=O stretching vibrations, coming from aromatic rings and carboxylic, ketone or ester groups, respectively. Peaks from 1400^{cm-1} to 1000^{cm-1} are probably due to C-O stretching and -CH_3 deformation vibrations (Zhu & Ryan 2016, He et al., 2011; Huo et al., 2008; Zieliński & Rajca. 2000; Huan et al., 2017).

Quite broad peaks (Fig. 5) appeared around 3200^{cm-1} (FA2$_{(NaOH)}$) and 3150^{cm-1} (FA2$_{(NH4OH)}$) .They are usually attributed to O-H stretching from alcohols, phenols and carboxylic related groups and also to N-H stretching from amide and amine functional groups. The next peaks around 3000^{cm-1} – only for FA2$_{(NH4OH)}$ samples are caused by C-H asymmetric and symmetric stretching aromatic compounds. Peaks around 2970^{cm-1} ($FA2_{(NH4OH)}$) and 2950^{cm-1} ($FA2_{(NaOH)}$) may indicate the presence of alkanes stretching bonds C-H. Peaks around 1750^{cm-1} ($FA2_{(NaOH)}$), 1700^{cm-1} ($FA2_{(NH4OH)}$) and 1650^{cm-1} ($FA2_{(NaOH)}$ and $FA2_{(NH4OH)}$) can be attributed to the C=C and C=O stretching vibrations, coming from aromatic rings and carboxylic, ketone or ester groups respectively. Peaks from 1400^{cm-1} to 1050^{cm-1} are probably due to C-O stretching and $-CH_3$ deformation vibrations (Zhu & Ryan, 2016; He et al., 2011; Huo et al., 2008; Zieliński & Rajca, 2000; Huan et al., 2017).

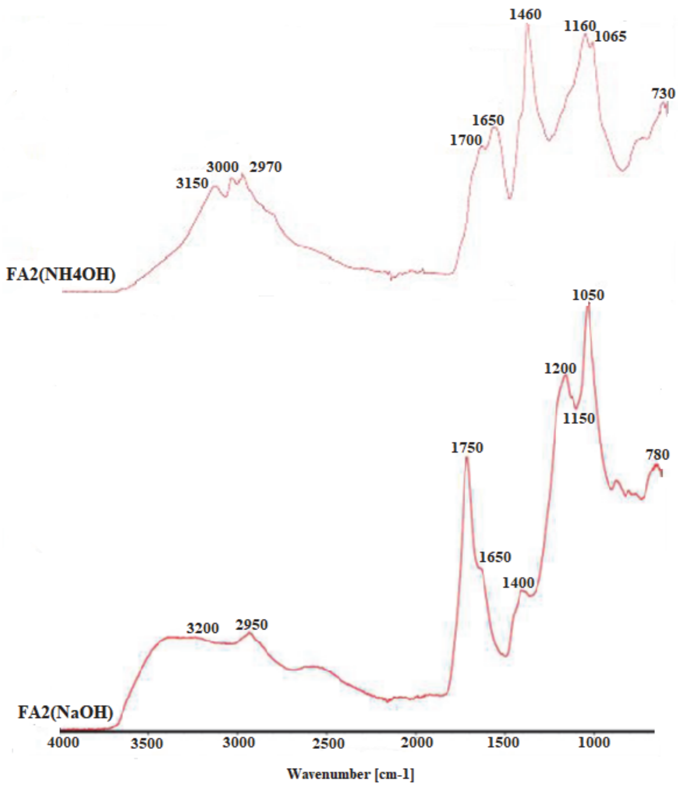

Fig. 5. The IR absorption spectra of FAs extracted by NH_4OH and NaOH methods from the secondary effluent

The bands of $FA1_{(NaOH)}$ and $FA2_{(NaOH)}$ (Fig. 4,5) were broader than those of $FA1_{(NH4OH)}$ and $FA2_{(NH4OH)}$, it could indicate that H-bonded OH groups were formed during a wastewater treatment process.

4. Conclusions

The main objective of the study was to balance and assess the amount of FAs extracted by two different methods from the primary and secondary effluent. The studies have shown that the biggest concentration was received from the primary effluent using the NaOH method, moreover less inorganic impurities were removed in the secondary effluent. Based on the results, it can be concluded that the extraction with a NaOH solution with a two-stage ion exchange process (hydrophobic ion-cation exchanger – H^+) reduces the degree of internal oxidation of FAs. Discussed substances isolated from the primary effluent had a higher level of humification in both methods. Comparing an elemental composition of four samples, it can be noticed that a structure of FAs extracted with the same method is very similar for both primary and secondary effluent. But when two different methods are compared some small differences can be found. The content of C, O and H was similar in the secondary effluent, regardless of the chosen method. The significant difference was observed in the N content, which was in both methods higher for the primary effluent. FAs obtained from the primary effluent (NH_4OH) were the most hydrophilic and had many functional groups, such as hydroxyl and carboxyl. The C/H atomic ratio for all samples was relatively small and indicated a low degree of aromatization. The C/N ratio was quite small for $FA1_{(NH4OH)}$ – 3.31 and $FA2_{(NH4OH)}$ – 4.67. It can be correlated with the method of extraction using ammonia water. FAs isolated from different samples had many oxygen groups. The higher loss of oxygen than hydrogen was observed in the NaOH method due to the humification process. The IR absorption spectra showed that bands of $FA1_{(NaOH)}$ and $FA2_{(NaOH)}$ (Fig. 4 and 5) were broader than those of $FA1_{(NH4OH)}$ and $FA2_{(NH4OH)}$, it could indicate the formation of H-bonded OH groups during the wastewater treatment process.

Based on the research, it can be stated that the WWTP discharged less FAs compared to the input pollution load, regardless the method of extraction.

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Abstract

Fulvic acids (FAs) were isolated from the wastewater by two different extraction methods. The first one with ammonia water (NH_4OH) and the second with an ion exchange using a hydrophobic ion exchanger and desorbed using aqueous sodium hydroxide (NaOH). The samples were collected directly from the primary and secondary effluents at the WWTP and the obtained results were averaged. The WWTP treats mainly wastewater from individual users and industrial plants. The selected plant comprises mechanical and biological wastewater trains as well as sludge processing and biogas trains. The plant works as a three-stage Bardenpho system and operates five identical biological reactors. The main objective of the study was to conduct a mass balance and assess the amount of FAs in the primary and secondary effluent. The extracted acids were subjected to an analysis of their elemental composition, trace elements content and IR spectrum analysis. Based on elemental composition, atomic ratios: C/O, C/H, C/N and O/H, as well as a degree of inside oxidation, have been determined. The studies have shown that the highest amount of FAs was extracted from the primary effluent with the NaOH method and in the secondary effluent less inorganic impurities were removed. Based on the results, it can be concluded that extraction with NaOH solution and a two-stage ion exchange process (hydrophobic ion-cation exchanger-H+) reduces the degree of internal oxidation of FAs. Soluble HSs extracted from the primary effluent had a higher level of humification in both methods. Comparing an elemental composition of four samples, it can be noticed that a structure of FAs extracted with the same method is very similar for both primary and secondary effluent, but when two different methods are compared some small differences can be found.

Based on the research, it can be stated that the WWTP discharged less FAs compared to the input pollution load, regardless of the extraction method used.

Keywords:
humic substances, fulvic acids, wastewater treatment plant, extraction of fulvic acids, elemental analysis, spectroscopic characteristics

Właściwości kwasów fulwowych wyekstrahowanych ze ścieków za pomocą różnych metod

Streszczenie

Kwasy fulwowe (KF) zostały wyekstrahowane ze ścieków z wykorzystaniem różnych metod ekstrakcji. Pierwsza metoda z użyciem wody amoniakalnej (NH_4OH) natomiast druga oparta na procesie wymiany jonowej na hydrofobowym wymienniku jonitowym przy użyciu wodnego roztworu wodorotlenku sodu (NaOH). Próbki zostały pobrane bezpośrednio z mechanicznie oraz biologicznie oczyszczonych ścieków z wybranej oczyszczalni ścieków a podane wyniki zostały uśrednione. Oczyszczalnia ścieków (OŚ) odprowadza głównie ścieki od indywidualnych użytkowników, ale i również z zakładów przemysłowych. Wybrana OŚ składa się z części mechanicznej i biologicznej oraz osadowej i gazowej. W skład części mechanicznej wchodzą: kraty rzadkie, pompownia, kraty gęste, piaskowniki, osadniki wstępne, pompownia II stopnia. Część biologiczna składa się z reaktorów i osadników wtórnych. OŚ pracuje w układzie 3 stopniowym Bardenpho i składa się z 5 identycznych biologicznych reaktorów. Z kolei część osadowa to: zagęszczarki mechaniczne, stacja dezintegracji osadu, zagęszczanie grawitacyjne, prasy taśmowe, wydzielone komory fermentacji oraz ciąg generowania gazu. Oczyszczone ścieki trafiają do rzeki poprzez wylot kaskadowy.

Głównym celem badań był bilans masy oraz określenie ilości KF w mechanicznie i biologicznie oczyszczonych ściekach. Wyekstrahowane KF poddano analizie ich składu elementarnego, zawartości pierwiastków oraz przeprowadzono badanie absorbancji widma IR w podczerwieni. Na podstawie składu elementarnego określono ilorazy atomowe: C/O, C/H, C/N i O/H oraz wyliczono stopień utlenienia wewnętrznego. Wyniki badań pokazały, że największe stężenie KF wyekstrahowano przy użyciu metody z wykorzystaniem NaOH z mechanicznie oczyszczonych ścieków. Przy użyciu tej samej metody mniej zanieczyszczeń nieorganicznych usunięto z KF wyekstrahowanych ze ścieków biologicznie oczyszczonych. Na podstawie wyników badań można wnioskować, że ekstrakcja KF z użyciem roztworu NaOH podczas dwu stopniowej wymiany jonowej (hydrofobowy wymiennik jonitowy H^+) zmniejsza stopień utlenienia wewnętrznego (ω). KF wyekstrahowane ze ścieków mechanicznie oczyszczonych miały wyższy stopień humifikacji, w obu metodach. Porównując skład elementarny czterech próbek można zauważyć, że budowa KF wyekstrahowanych tą samą metodą jest bardzo zbliżona, ale kiedy porówna się ze sobą KF wyekstrahowane z tych samych ścieków jednak różnymi metodami zauważalne są małe różnice.

Badania wykazały, że wybrana OŚ odprowadza mniejszy ładunek KF w porównaniu do wprowadzanego, bez względu na rodzaj zastosowanej metody ekstrakcji.

Słowa kluczowe:
substancje humusowe, kwasy fulwowe, oczyszczalnia ścieków,
ekstrakcja kwasów fulwowych, analiza elementarna, charakterystyka spektroskopowa

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Content of Cd, Cu, Cr, Fe Mn, Ni and Pb in Water and Selected Organs of Blotched Picarel *Spicara maena* L. and Mezgit *Merlangius euxmus* L. from Karantinna Bay and Balaklava Bay in the Region of Sevastopol

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1. Introduction

Accumulation of trace elements in water organisms is an important problem related to contamination of the environment and their use for food purposes (Zhong et al., 2018). Due to a specificity of biogeochemical circulation of trace elements, we often observe their increased amounts in water reservoirs. Chemical elements emitted to atmosphere together with gas and dust contaminations in consequence of dry and wet deposition fall into the surface of water reservoirs or land from where they are washed away (Sikora et al., 2018). In water reservoirs most of elements precipitates in the form of soluble salts or because of absorption and adsorption processes, they link to bottom deposits. Bottom deposits constitute an integral part of water ecosystems. Organic matter decomposition and accumulation of mineral and organic compounds introduced to reservoirs from the area of drainage basin, takes place. Raised amounts of trace elements of organic contaminations in bottom deposits are often observed, even in the conditions of their low concentration in water (Qiu et al. 2011). Those deposits are also a place of living for many water organisms, which constitute an alimentary base for higher animals, including fish. Heavy metals accumulated in fish bodies are collected together with food or directly from water through gills or skin. The increased content of trace elements in water organisms results in numerous negative changes at the level of a population, biocenose or the entire ecosystem. At the level of a population, embryotoxic and mutagenetic impact is observed, which induces problems related to the reduction of the reproductive success of water organisms and mutations leading to degeneration of particular specimens (Kong et al., 2013). Heavy metals influence reduction of the amount of spawn, disorders of movement of sperm cells leading to the limitation of fertilization, death of embryos and reduce the survival rate of larvae (Arambourou et al., 2014). Seaside ecosystems are more exposed to negative effects of environmental pollution due to a considerable impact of land to shaping of their ecosystem. Particularly sensitive are estuaries where considerable amounts of pollution brought with river waters, and bays, with city centres (Van Praet et al., 2014; Ordog et al., 2004). Estuarine and bay areas are significant from the point of view of obtaining food. A great amount of organic matter and nutrients introduced to the sea from land, low depths of reservoirs and higher temperatures cause that the seaside has an enormous potential of primary production. It is also a place of living and reproduction of many species of fish. Due to closeness of densely populated areas and a considerable production potential, on estuarine areas and shallow bays often aquaculture units are located. Fish, seafood obtained from the area with a raised level of antropopression often have an increased content of trace elements even in the conditions of their low content in particular elements of the marine ecosystem (Boalt et al., 2014, Bonsignore et al., 2018). Monitoring of the trace elements content in water organisms enables, on one hand assessment of a threat for consumers and on the other hand, determination of the level of contamination of the ecosystem in the context of biocenose impact (Niemiec et al., 2016). Assessment of the trace elements content in biotype elements such as water of bottom deposits does not allow for a full evaluation of the condition of the environment since the content of trace elements does not translate into the level of accumulation in living organisms which is emphasised by many authors (Kong et al., 2013, Niemiec et al., 2015, Niemiec et al., 2018a). Except for the total content of elements in environment, their collection by living organisms is influenced by the conditions and properties of environment such as salinity and water reaction and content of organic matter as well as content of other elements which may synergistically or antagonistically influence the collection of elements. The level of bioaccumulation of trace elements also depends on the species of an organism, its age, physiological condition, and properties related to the individual variability. Monitoring of the environment of marine ecosystems is incredibly significant from the point of view of planning and evaluation (Jia et al., 2018). Due to great volumes of salty water reservoirs, their variable depth and considerable territorial differences in xenobiotic accumulation, monitoring is very difficult and obtaining credible results leading to appropriate conclusions must be preceded with a suitable approach to collection of samples for their chemical analysis and correct interpretation of results (Van Praet et al., 2014). One of the most dangerous effects of contamination with heavy metals is reduction of the reproductive success of fish through mutagenic and embryotoxic potency (Kong et al., 2013). Heavy metals influence reduction of the amount of spawn, disorders of movement of sperm cells leading to limitation of fertilization, death of embryos and reduce the survival rate of larvae (Arambourou et al., 2014).

The goal of the study was to evaluate a content of Cd, Cu, Cr Ni, Fe, Mn and Pb content in water and in selected organs (gills, tissue, gonads, and liver) blotched picarel *Smaris smaris* L. and mezgit *Merlangius euxmus* L. from Krarantinna and Balaklava Bay in the region of Sevastopol. The second aim was to determine the level of bioaccumulation of those elements in organisms used in the studies.

2. Material and methods

Studies were carried out in 2017 in two bays of Sevastopol: Balaklava and Karantinna. Samples of water were collected from the surface layer from the depth of 1 m. A laboratory sample had a volume of 1 dm^3. The collected water was preserved in the place of collection by addition of the nitrous acid (V) in the amount of 2 cm^3 for each 100 cm^3 of water and then samples were transported to a laboratory. *Spicara maena* L. and Mezgit *Merlangius euxmus* L. were caught in June 2017. Fish were caught with the use of a net. From each bay 15 fish of each specimen were caught. The mass of fish caught in the tests was within the range 15-31 g and their length was 11-18 cm. Fish came from the last year spawning and were not mature and their age was established as 1 year. From fish organs were prepared (muscles, gills, gonads. liver). The choice of those organs was justified with their usefulness in the assessment of environment with bioindicative methods and analytical possibilities (Łuczyńska et al., 2018). Water samples were collected from the same places. A laboratory sample with the volume of 1 dm^3 consisted of approximately 10 original samples. A group samples constituted a sum of original samples.

Table 1. Statistical parameters of elements analysis

Parameter	Cd	Cr	Cu	Fe	Mn	Ni	Pb
Length of waves, nm	228,802	267,707	327,393	238,204	257,608	231,604	220,353
Limit of detection, $\mu g \cdot dm^{-3}$	0,021	0,061	0,045	0,032	0,014	0,0105	0,046
Content in the attes, $mg \cdot kg^{-1}$	0,189	0,73	3,28	146	3,52	0,6	0,12
Measured, $mg \cdot kg^{-1}$	0,179	0,71	3,38	154	3,37	0,567	0,126
Retrieved, %	94,71	97,26	103,05	105,48	95,74	94,56	104,59

The collected water was preserved in the place of collection by addition of the nitrous acid (V) in the amount of 2 cm^3 for each 100 cm^3 of water and then samples were transported to a laboratory. In a laboratory, water samples were condensed tenfold by evaporation. Laboratory samples were subjected to mineralization when wet in the closed system with the use of microwave energy with the use of a microwave system by Anton Paar Multivawe 3000. Analytical portion was 0.5 g per dry mass. Biological material was solved in the mixture of HNO_3 and H_2O_2 in a proportion 5:1 (v/v). Concentration of the investigated elements in the obtained solutions and in water was determined with the element method of absorption spectrometry with electronic atomisation in the apparatus M6 by Thermo. Uncertainty of measurement of the use methods was 8%. For control of the correctness of analysis a certified material of liver reference was applied IAEA-407, from IAEA Reference Materials. Statistical parameters of analysis of certified materials and waves lengths and limits of detection (LOD) were placed in Table 1. The obtained results of average element content were compared with T test at the level of significance p=0.05. Based on the obtained results a coefficient of bio-accumulation of particular elements was calculated. Coefficient of bio-accumulation was calculated by division of the element concentration in dry mass of organs used in the experiment by the content of these elements in water, using a formula

$$BF = Cl / Cw,$$

where:
BF – bioaccumulation factor,
Cl – element concentration in organs dry matter,
Cw – element content of in water.

3. Results and discussion

Results show a higher average content of chromium, iron, manganese, and nickel in water collected from Balaklava Bay compared to the samples collected from the region of Karantinna Bay. The copper content was comparable in samples from both locations, while water from Karantinna Bay included twofold more lead and threefold more cadmium in comparison to the sample from Balaklava Bay (Table 2).

Table 2. Content of selected elements in water collected from the investigated bays (average of 5 samples)

Region	Cd	Cr	Cu	Fe	Mn	Ni	Pb
	($\mu g \cdot dm^{-3}$)						
Balaklava	0,172a	3,891a	16,55a	885,6b	12,32b	3,787b	14,56a
± SD	0,048	0,896	2,523	46,69	2,596	0,458	3,985
Karan-tinna	0,511b	3,056a	17,85a	625,5a	6,488a	2,454a	11,23a
± SD	0,089	0,423	3,011	51,06	1,896	0,328	2,196

Different letters at mean values indicate the statistically significant differences between the samples from each of the bays at $p = 0.05$.
SD – standard deviation

In case of all the investigated elements, except for iron, their concentration on the level that indicates anthropogenic enrichment, was reported. A natural content of cadmium, copper, chromium, and zinc in sea water is respectively 0.02; 0.1; 0.2; 0.1 $\mu g \cdot dm^{-3}$ (Bandara et al., 2010; Liang et al.., 2018; Kahle and Zauke, 2003). Sanders et al., (2012) provide that a concentration of manganese in water of Sepetiba Bay in Brazil in the region of anthropogenic influence at the level of ca. 2.5 $\mu g\ Mn \cdot dm^{-3}$.

Table 3. Arithmetic average content of investigated elements in organs of fish from Balaklava Bay (average of 15 samples)

Blotched picarel	Cd	Cr	Cu	Fe	Mn	Ni	Pb
	(mg·kg^{-1})						
Gills	**0.425**	**3.494**	**11.34**	**222.2**	**15.07**	**13.24**	**1.804**
± SD	0.322	1.91	8.085	80.65	4.885	1.885	0.998
tissue	**0.360**	**4.822**	**5.465**	**47.35**	**2.644**	**7.301**	**1.300**
± SD	0.102	0.675	1.583	15.00	1.766	3.749	0.742
GM	**0.208**	**5.008**	**14.31**	**71.46**	**1.418**	**7.853**	**1.040**
± SD	0.011	1.463	4.049	26.85	0.332	5.581	0.882
GF	**0.682**	**4.915**	**17.46**	**98.04**	**4.343**	**8.340**	**1.009**
± SD	0.282	1.516	2.187	32.52	0.272	5.293	0.741
Liver	**3.238**	**2.925**	**21.60**	**236.6**	**4.434**	**4.647**	**0.867**
± SD	1.145	1.016	12.98	64.59	0.505	1.549	0.356
Mezgit							
Gills	**0.852**	**6.284**	**12.48**	**182.8**	**15.08**	**7.261**	**1.585**
± SD	0.429	1.668	5.931	88.95	0.617	2.772	0.628
tissue	**0.595**	**5.331**	**4.230**	**91.20**	**4.239**	**6.958**	**1.488**
± SD	0.211	1.202	1.918	26.98	0.711	3.485	0.544
GM	**0.462**	**5.9569**	**13.27**	**81.36**	**1.789**	**7.125**	**0.985**
± SD	0.182	1.563	4.231	34.72	0.328	3.110	0.529
GF	**0.896**	**4.8965**	**18.65**	**113.6**	**2.156**	**8.652**	**0.911**
± SD	0.357	1.056	5.296	41.09	0.411	1.008	0.663
Liver	**3.326**	**3.125**	**23.26**	**244.3**	**3.885**	**5.231**	**1.235**
± SD	1.655	1.028	9.615	86.32	0.423	2.538	0.618

SD – standard deviation

Table 4. Arithmetic average content of investigated elements in organs of fish from Karantinna bay (average of 15 samples)

Blotched pica-rel	Cd	Cr	Cu	Fe	Mn	Ni	Pb
	(mg·kg^{-1})						
Gills	**0.206**	**9.319**	**9.194**	**250.7**	**16.97**	**13.98**	**1.764**
±	0.015	1.435	1.896	28.96	2.213	1.332	0.236
Tissue	**0.409**	**4.371**	**7.587**	**41.24**	**2.694**	**6.293**	**1.070**
±	0.049	0.512	0.912	6.229	0.311	0.811	0.123
GM	**0.105**	**4.966**	**11.53**	**83.08**	**1.948**	**5.130**	**0.804**
±	0.011	0.596	1.965	10.89	0.253	0.621	0.0962
GF	**1.067**	**5.715**	**8.704**	**125.9**	**4.094**	**8.908**	**1.580**
±	0.096	0.689	1.59	15.98	0.543	1.266	0.205
Liver	**2.158**	**2.533**	**19.23**	**244.9**	**4.142**	**4.632**	**1.229**
	0.259	0.198	3.19	36.89	0.509	0.563	0.182
Mezgit							
Gills	**0.524**	**5.849**	**9.644**	**142.5**	**1.281**	**9.545**	**1.281**
±	0.046	0.511	2.085	19.56	0.150	1.326	0.163
tissue	**0.369**	**5.578**	**7.252**	**44.33**	**14.52**	**11.22**	**1.050**
±	0.042	0.688	1.931	5.235	1.536	1.463	0.112
GM	**0.223**	**5.116**	**13.65**	**92.33**	**2.245**	**8.756**	**0.775**
±	0.029	0.462	1.658	11.06	0.268	1.236	0.089
GF	**0.986**	**6.235**	**7.986**	**103.7**	**4.652**	**7.685**	**1.326**
±	0.106	0.698	1.44	14.56	0.596	0.896	0.209
Liver	**2.236**	**2.896**	**21.52**	**268.4**	**3.885**	**5.162**	**1.445**
±	0.289	0.315	2.963	34.23	0.423	0.623	0.209

SD – standard deviation

Copper and cadmium content in water from Baya Bay in the region of the increased anthropopression was determined at the level of respectively 2.4 and 0.2 $\mu g \cdot dm^{-3}$ (Qiu et al., 2011). The research area (Balaklava and Krantinna Bay) includes areas with the increased anthropopression. Niemiec et al., (2018) carried out research related to bioaccumulation of heavy metals in fish larvae in several bays of Sevastopol. Those authors found the content of nickel in water from Karantinna Bay in 2012 at the level of ca. 4 $\mu g \cdot dm^{-3}$, of lead at the level of ca. 19 $\mu g \cdot dm^{-3}$ and zinc 55 $\mu g \cdot dm^{-3}$. Those authors reported a great variability of content of the investigated elements in various bays in the region of Sevastopol. The authors' own research shows slight differences of concentration of the tested elements in waters from both investigated bays. The content of elements in water and other elements of a biotype is not a credible source of information related to a threat to the ecosystem and for consumers of aquaculture products. Fish constitute a principal element of a diet in many regions of the world and macroelements and trace elements include there may negatively influence people (Bonsignore et al., 2018).

The average content of cadmium in tested water organisms was from 0.105 to 3.326 $mg \cdot kg^{-1}$. The content of chromium was within 2.533 to 9.319 $mg \cdot kg^{-1}$. Amount of copper in particular organs of tested fish was within 4.23 to 21.523 mg·kg-1, of iron from 41.2 to 268.4 $mg \cdot kg^{-1}$, manganese from 1.418 to 16.97 $mg \cdot kg^{-1}$. Nickel content was reported within 4.647 to 13.98 $mg \cdot kg^{-1}$ (Table 3 and 4). Results of the research show a slightly higher, average for all organs cadmium content in blotched picarel fish in comparison to fish from the whiting species. In case of the remaining elements, no differences of concentration of the content of elements between both fish species were reported. Both species belong to benthos eating fish. They live in similar ecological niches, in seaside regions where they cover underwater meadows. They eat similar organisms living on the bottom. A type of the food they eat, and a living strategy of fish is one of the main elements that influence the level of bioaccumulation of trace elements. Velusamy et al., (2014) concluded a strong dependency between the place of living of fish and the type of the collected food and the level of bioaccumulation of trace elements in them. Those authors concluded in majority of cases a higher concentration of trace elements in benthos fish in comparison to the fish species that live in the pelagic zone. Similar relations were reported by El-Moselhy et al., (2014) in case of several fish caught in the Red Sea.

The highest content of cadmium and copper in case of both fish species were found in liver. The content of cadmium in those organs was more than 3 $mg \cdot kg^{-1}$ for fish caught in Balaklava Bay and ca. 2 $mg \cdot kg^{-1}$ in fish from Karantinna Bay. In case of copper no differences in the content of this element in fish liver from particular locations were reported. The content of this element was ca. 20 $mg\ Cu \cdot kg^{-1}$. Cadmium content in gills and muscles was ca. eightfold lower in comparison to the content of this element in liver. Content of this element in ovaries was ca. half lower than in testicles of the investigated fish. In case of copper, its content in gills and testicles was considerably lower than in liver. El-Moselhy et al., (2014) show similar relations of the amount between the copper content in liver, muscles, and gills. The highest content of chromium and copper in all investigated locations was found in gonads of the investigated fish (Table 2 and 3). In the authors' own research, a higher impact of the location in comparison to a fish species used in the tests was confirmed. In general, cadmium content in liver of the investigated fish was high which indicates a threat for water organisms. El-Moselhy et al., (2014) observed lower cadmium content in liver of various species of fish from the Red Sea in comparison to the results obtained in own research, the amount of copper provided by those authors was comparable to the results of own research. A comparable content of copper was reported by Anandkumar et al., (2018) in muscles and gonads of several pelagic fish species from Borneo. The highest concentration of nickel, lead, iron, and manganese was reported in gills of the investigated animals (Table 2 and 3). The amount of nickel in gills was on average twofold higher than in other organs. Anandkumar et al., (2018) et al., say that the content of nickel in gills of several fish species from Borneo was at a higher level than in the content of this element in gonads, muscles, and liver. The average amounts of the investigated elements from the lowest were as follows: Pb<Cd <Cr<Mn<Ni<Cu<Fe. In gonads these relations were as follows Cd<Pb<Mn<Cr<Ni<Cu<Fe, while in muscles and gills Cd<Pb<Cr<Mn<Cu<Ni<Fe and Cd<Pb<Cr<Cu<Ni<Mn<Fe. Cadmium, copper, and iron content in particular organs of the investigated fish were from the lowest in particular fish organs. On average more of this element was found in fish caught in Balaklava Bay than in Karantinna Bay.

It was also concluded that the content of elements is high and characteristic for polluted environments. In no case, however, critical values for fish muscles for food purposes were not exceeded (WHO 1989). According to Rahman et al., (2012) the content of cadmium in muscles of various fish species from the polluted regions of Bangladesh are within 0.09 to 0.87 mg Cd·kg^{-1} s.m. Qiu et al., (2011) concluded that the content of copper and lead in predatory fish muscles from Baya Bay in China in the region of an increased anthropopression was at the level of respectively 4.4 and 1.2 mg·kg^{-1}. The content of copper, lead, cadmium and manganese of Sargocentron spiniferum fish liver caught in the polluted regions of the Red Sea were respectively: 10 mg·kg^{-1}; 0.6 mg·kg^{-1}; 1.8 mg·kg^{-1}; 550 mg·kg^{-1} and 4.5 mg·kg^{-1} (El-Moselhy et al., 2014) say that the content of copper in gills of various species of fish from the Red Sea was at the level of approximately ca. 3 mg·kg^{-1} per dry mass. The content of this element in muscles was determined at the level of ca. 1 mg·kg^{-1}. Moreover, they observed the highest content of copper, cadmium, and iron in liver of the investigated fish. In case of lead and manganese the highest content was observed in fish gills. Yousuf et al., (2000) provide the content of copper in fish muscles from the family of Lethrinidae caught in the region of Arabian Bay in the places of the increased anthropopression at the level of ca. 0.8 mg $Cu \cdot kg^{-1}$ per dry mass. Canli and Atli (2003) provide the content of copper, lead and chromium in fish muscles caught in the Mediterranean Sea at the coast of Turkey within the range of 19-30 275 mg $Fe \cdot kg^{-1}$; 2.19-4.17 mg $Cu \cdot kg^{-1}$; 2.98-6.12 mg $Pb \cdot kg^{-1}$ and 1.24-2.42 mg $Cr \cdot kg^{-1}$. The content of these elements in gills and liver were also lower than the ones concluded in the own research. The location of Sevastopol in the region of several bays influenced formation in each of them of ecosystems with specific conditions shaped mainly by the level and directions of anthropopression (Kuzminova et al., 2014), Karantinna Bay is located in the region of the strongest anthropopression in the region of Sevastopol. While, in the Balaklava Bay a raised anthropogenic pression related to sailing is observed. (Pavlova et al., 2007). The direct disposal of sewage to their waters is lower than in Karantinna Bay.

The value of the bioaccumulation coefficient was expressed as a relation of the content of the element in dry mass of particular organs and in water. Values of the bio-accumulation ratios in organs used in the tests were within 53.47 to 19337 (Fig. 1-5). The lowest value of this parameter was observed in case of lead and iron, for which the average values of this parameter were respectively 96.85 and 190.1 due to a relatively high content of these elements in water. The highest values of the bio-accumulation ratio were observed in case of cadmium and nickel, respectively 4040 and 2668. The value of the bio-accumulation ratio of chromium in muscles of Acanthurus blotched caught in coast regions of Iran was 185 (Alhashemia et al., 2012).

Qiu et al., (2011) Provide values of the bio-accumulation ratio of copper at the level of 4000, while lead at the level of ca. 2000 in fish in Baya Bay in the region of the increased anthropopression. Rajeshkumar et al., (2018) found that the value of the bio-accumulation ratio in muscles of goldfish from Taihu lake in China at the level of ca. 2000 for chromium, while for copper the value of this parameter was ca. 1000. Those authors carried out the research in the regions of the low level of anthropopression.

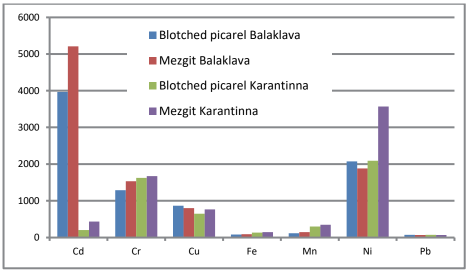

Fig. 1. Bioaccumulation ratio in fish gills

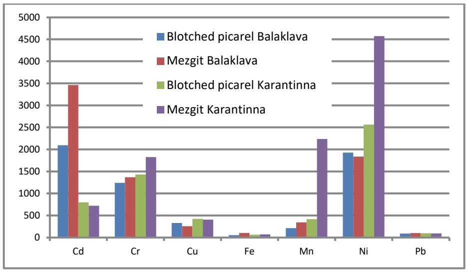

Fig. 2. Bioaccumulation ratio in fish muscles

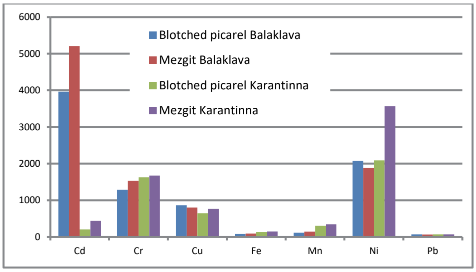

Fig. 3. Bioaccumulation ratio in fish testicles

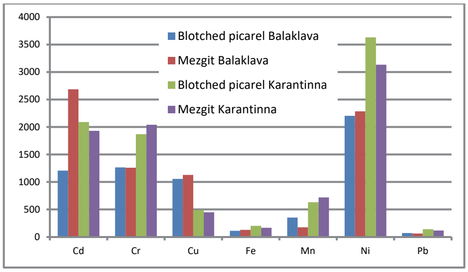

Fig. 4. Bioaccumulation ratio in fish ovaries

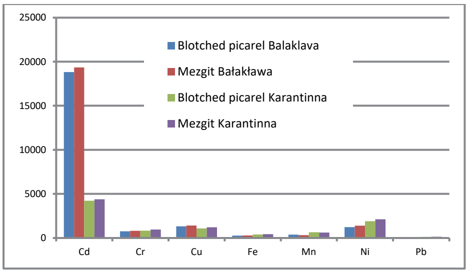

Fig. 5. Bioaccumulation ratio in fish liver

The bio-accumulation ratio is an important ratio of the environmental threat of xenobiotics. The coefficient of bio-accumulation of cadmium in Cyphocharax voga muscles, sweet water benthic eating fish living in not-cleaned region was 778 in relation to the content of this element in water. In the polluted environment, the value of this parameter was 428.4. On the other hand, the bio-accumulation ratio of this element in muscles of Oligosarcus sp., of the fish living in the contaminated region was 667, while in the polluted region this value was at the level of 111.1 (Weber et al., 2013). Those authors pay attention to a higher value of the bio-accumulation ratio in fish from polluted regions. The value of the bio-accumulation ratio of iron and manganese in *Centropomus parallelus* fish muscles from the estuary in Brazil was respectively*:* 57.93 and 40.68 (Souza et al., 2013). These are lower values than the ones obtained in own research. *Even lower values of the bioaccumulation ratio of manganese are provided by* Adhikari et al., (2009), at the level of ca. 8.03.

4. Conclusions

1. Water from the investigated bays of Sevastopol included the investigated elements in the amounts that indicated anthropogenic enrichment in these elements.
2. Higher contents of manganese iron and nickel were reported in water of Balaklava Bay. Only in case of cadmium, its content was statistically higher in water from Karantinna Bay. There were no differences in the content of the remaining elements in water.
3. Higher differences of the content of the investigated elements in particular organs of fish due to the location in comparison to the species. The highest content of cadmium, chromium and manganese in fish larvae were found in samples collected from Karantinna Bay, copper from Omega Bay, while iron in organisms caught in Gałabuja Bay.
4. Concentration of the investigated elements in fish liver was from the lowest Pb<Cd<Cr<Mn<Ni<Cu<Fe. In case of gonads , both testicles and ovaries, these contents were as follows Cd<Pb<Mn<Cr<Ni<Cu<Fe, while in muscles and gills respectively Cd<Pb<Cr<Mn<Cu<Ni<Fe and Cd<Pb<Cr<Cu <Ni<Mn<Fe.
5. The content of all investigated elements in particular organs of fish were high, characteristic for ecosystems changed into anthropogenic.
6. From the point of view of a possibility of using particular fish for consumption, exceeding of the content of the investigated elements was not reported.
7. The value of the bio-accumulation ratio of the investigated elements in tested fish organs was from the highest as follows: Cd>Ni>Cr>Mn> Cu>Fe>Pb.

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Abstract

The objective of the paper was to assess the trace elements content (Cd, Cu, Cr, Fe, Mn, Ni and Pb) in gills, muscles, gonads and liver in two fish species from two bays (Karantinna and Balalaklava) in the region of Sevastopol. Concentration of the investigated elements in the obtained solutions and water were determined with the absorption atomic spectrometry method with electro-thermal atomization. Levels of heavy metals differed in two locations. Differences due to fish species were slight. Water from both locations included the investigated elements in the amounts that indicated anthropogenic enrichment. Concentration of the investigated elements in fish liver was in the order from the lowest Pb<Cd<Cr<Mn<Ni<Cu<Fe. In case of gonads, the content was in the order Cd<Pb<Mn<Cr<Ni<Cu<Fe, while in muscles and gills it was respectively Cd<Pb<Cr<Mn<Cu<Ni<Fe and Cd<Pb<Cr<Cu<Ni<Mn<Fe. The concluded contents of all investigated elements in particular fish organs were characteristic for ecosystems changed into anthropogenic. Critical values of the concentration of the investigated metals in muscles were not exceeded from the point of view of fish use for food.

Key words:
trace elements, bioaccumulation, fish, sea bays, Sevastopol

Zawartość Cd, Cu, Cr, Fe, Mn, Ni i Pb w wodzie oraz wybranych organach ryb z gatunku Pysoń wygrzbiecony *Spicara maena* L. oraz Mezgit *Merlangius euxmus* L. z Zatoki Karantinna i Bałakława w rejonie Sewastopola

Streszczenie

Celem pracy była ocena zawartości pierwiastków śladowych (Cd, Cu, Cr, Fe, Mn, Ni i Pb) w skrzelach, mięśniach, gonadach i wątrobie w dwóch gatunkach ryb pochodzących z dwóch zatok (Karantinna i Bałakława) zlokalizowanych w okolicach Sewastopola. Stężenie badanych pierwiastków w uzyskanych roztworach oraz w wodzie oznaczono metodą atomowej spektrometrii absorpcyjnej z atomizacją elektrotermiczną. Poziomy metali ciężkich różniły się pomiędzy obydwiema lokalizacjami. W mniejszym zakresie zaobserwowano zróżnicowanie ze względu na gatunek ryb. Woda z obydwu lokalizacji zawierała badane pierwiastki w ilościach wskazujących na antropogeniczne wzbogacenie. Concentration of the investigated elements in fish liver was from the lowest Pb<Cd<Cr<Mn<Ni<Cu<Fe. W przypadku gonad, zawartości kształtowały się w kolejności Cd<Pb<Mn<Cr<Ni<Cu<Fe, natomiast w mięśniach i skrzelach odpowiednio Cd<Pb<Cr<Mn<Cu<Ni<Fe i Cd<Pb<Cr<Cu<Ni<Mn<Fe. Stwierdzone zawartości wszystkich badanych pierwiastków w poszczególnych organach ryb były charakterystyczne dla ekosystemów przekształconych antropogenicznie. Nie stwierdzono przekroczenia wartości krytycznych stężenia badanych metali w mięśniach ryb, z punktu widzenia możliwości ich wykorzystania na cele spożywcze.

Słowa kluczowe:
pierwiastki śladowe, bioakumulacja, ryby, zatoki morskie, Sewastopol

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Dewaterability of Digested Sludge Conditioned with Sludge from a Water Treatment Plant

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1. Introduction

Sewage sludge generated in municipal treatment plants is a specific type of waste, which, depending on its properties, can be classified as e.g. waste that needs to be incinerated or a material for fertilizing as well as composting. The specificity of sewage sludge also results from its amount and hydration. The basic technological challenge in the sewage treatment plants sludge management is the need for reduction of water content in the sludge, which reaches over 98% (Skinner et al. 2015, Mowla et al. 2013). Mechanical dewatering is a strategic process used to reduce sludge volume. Due to the structure and properties of sludge, which usually make it difficult to release water, sludge has to be conditioned (Bień et al. 2015). Conditioning means a range of applicable physical, chemical and biological methods and their combinations (Skinner et al. 2015, Mowla et al. 2013). Any factor or substance, including waste, which reduces the bonds between water and solid particles, can be considered a conditioning agent. However, the choice of the conditioner must not be accidental. The qualitative changes in sludge after the addition of a conditioning agent, and technical issues related to the installation and the drainage unit should be taken into account.

Currently, the most popular method of sludge conditioning in sewage treatment plants is the use of polyelectrolytes. One of the examined methods of chemical conditioning is to use sludge from the water treatment process. This sludge is often termed post-coagulation sludge due to the fundamental role of iron and aluminium coagulants in water treatment technology. However, sludge from water treatment plants also contains other streams of liquid waste, e.g. washings from periodic flushing of filtration beds. Post-coagulation sludge can be used in municipal and industrial wastewater treatment plants as a residual coagulant (Ahmad et al. 2016, Jangkorn et al. 2011). The addition of aluminium post-coagulation sewage sludge to wastewater can improve sedimentation in primary settling tanks, including the removal of suspended solids, organic matter, and phosphorus. Removal of these contaminants from wastewater occurs through their sorption on flocs formed during coagulation (Guan et al. 2005, Szerzyna 2013, Totczyk et al. 2015, Bal Krishna et al. 2016). The same effects are caused by the addition of iron sludge (Piaskowski 2005) to wastewater, but it is characterized by lower adsorption capacity (Al-Tahmazi & Babatundea 2016). Iron sludge may find wider applications in wastewater treatment using the Fenton's method (Yoo et al. 2001, Bolobajev et al. 2013). The use of regenerated coagulants allows for more favourable results than in the case of post-coagulation sludge application (Keeley et al. 2014, Keeley et a.l 2016).

Due to potential toxicity (Leszczyńska & Sozański 2009) in biological wastewater treatment, the use of post-coagulation sludge is a problematic issue. In general, the presence of heavy metals, which are disinfection byproducts in sewage sludge or an increase in mass concentration in the biological chamber may limit the effectiveness of biotechnological methods (Asada et al. 2010). However, the simultaneous dosage of the post-coagulation sludge in biological wastewater treatment and waste processing systems is considered in terms of intensification of biogas production (Cimochowicz-Rybicka & Górka 2017), phosphorus reduction (Nair &Ahammed 2015), reduction of hydrogen sulphide and ammonia in biogas (Akgul et al. 2017), as a source of micro and macroelements (Ebrahimi-Nik et al. 2018) and as a mass factor that allows for more efficient further phase separation (Luiz et al. 2018).

It may be advantageous to mix sludge from water treatment plants together with municipal sludge supplied for mechanical dewatering. Post-coagulation sludge can be treated as a physical conditioner due to the presence of inorganic matter acting as a structure-forming factor reducing compressibility. It can also be a chemical conditioner, which results from coagulation properties, including the neutralization of the solids content in sewage sludge and adsorption capacity of the flocs (Guan et al. 2005, Li et al. 2015).

The technology of water treatment, including surface or underground water treatment, has an effect on the quality parameters of the sludge and its application potential. The study analysed sludge from the water treatment plant that uses the denitrification process to remove nitrates from the collected water. The obtained organic water processing sludge was tested as a conditioner of municipal sewage sludge.

2. Substrates and methods

2.1. Substrates

Municipal sewage sludge was collected from a sewage treatment plant located in the Silesian Voivodeship in Poland. The average daily volume of wastewater to the treatment plant is nearly 45,000 m^3/day (People Equivalent 220 000). The plant operates in the UCT (University of Cape Town) technological system. The substrate was municipal digested sludge (MDS) taken from the installation of heat exchangers. After the digested sludge was collected, it was mixed in the laboratory at ambient temperature for 24 hours in order to be degassed.

The equipment in the technological system of the water treatment plant includes: biofilters for denitrification, aerators, double-layer filters, carbon filters, ozonation station and water tank. The sludge from denitrification and washings from the system are supplied to settling tanks. Thickened sludge from settling tanks is pumped to the sludge reservoir and then to the dewatering system. A coagulant in the form of a solution of iron (III) chloride is used in the process of water treatment. The coagulant is dosed to the installation of aerators and settling tanks. The tested organic water processing sludge (WPS) was a mixture of iron post-coagulation sludge and washings from biofilters and filters. WPS was collected from the sludge reservoir.

The dry solids and volatile solids of MDS were 20.7 ± 1.6 g/L and 12.7 ± 1.1 g/L, respectively, and the alkalinity was 5207.0 ± 95 mg $CaCO_3$/L. The concentration of dry solids in the WPS was 10.7 ± 1.5 g/L, volatile solids of 7.9 ± 1.6 g/L, at alkalinity 481.3 ± 195 mg $CaCO_3$/L. Iron content and pH of MDS sludge was as follows: 11,8 % DS, pH 5,8-6,2.

2.2. Conditioners and test combinations

Chemical conditioning of the sludge was performed using medium cationic polyelectrolyte Superfloc® C-494 in the form of an aqueous solution with a concentration of 0.1%. The optimal dose of polyelectrolyte for sludge dewatering was chosen only for digested sludge. The CST test was used to determine the optimal dose, which was 5.16 g/kg $_{DS}$. The study also used a reduced dose of polyelectrolyte, i.e. 25% lower than the optimal dose (4.13 g/kg $_{DS}$). Reduction of the polyelectrolyte dose resulted from the dosage of the second conditioning factor, i.e. water processing sludge (iron post-coagulation sludge).

The research was performed in 5 combinations (A-E), the main process variable was the volumetric fraction of post-coagulation sludge V_{WPS} in the mixture with digested sludge V_{MDS} (Fig. 1). Sludge mixtures (1.0 L) were prepared using a 0.1 m diameter paddle mixer and used for further examinations.

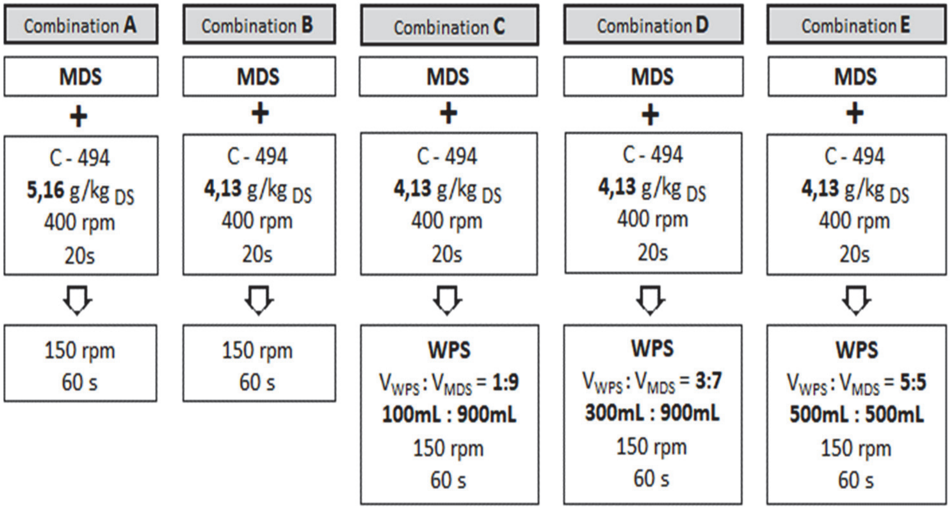

Fig. 1. Combinations of conditioning of municipal digested sludge with polyelectrolyte and water processing sludge

2.3. Analytical methods

Dry solids (DS), volatile solids (VS), pH and alkalinity measured according to standard methods for the examination of water and wastewater (APHA 2005). Technological parameters of sewage sludge, i.e. capillary suction time (CST), specific filtration resistance (r), final hydration of the sludge cake (H_{FC}) and dry solids in supernatant after sludge centrifugation (DS_{CEN}) were determined in accordance to PN-EN 14701-1:2007 (2007), PN EN 14701-2 (2013) and PN-EN 12880:2004 (2004) standards.

Total Kjeldahl nitrogen (TKN) and ammonium nitrogen (NH_4-N) were determined by titration method according to PN-EN 16169:2012 and PN-EN 14671:2007. Dissolved organic carbon (DOC) concentration was evaluated by means of the differential method using a TOC Analytik Jena multi N/C 3100 analyser. A Hach Lange DR 5000 spectrophotometer and cuvette tests were used to determine of chemical oxygen demand (COD). The presence of selected light and heavy metals and phosphorus was tested in accordance with PN-EN ISO 11885:209.

The quality of supernatants after the dewatering process was tested by centrifugation of sludge samples (MDS, WPS, A-E) for 3 minutes with relative centrifugal force of 4500 rcf. DS_{CEN} and COD were determined in these supernatants. Before COD measurement, the samples (50 ml) were homogenized for 60 seconds using an IKA T10 homogenizer.

The centrifugation of sludge samples (15 minutes, rcf = 12 100) and membrane filtration (0.45 um, cellulose acetate) were employed to determine the indices of contaminants occurring in the soluble form (DOC, TKN, NH4-N, metals and phosphorus).

The measurement of shear stresses (τ) and viscosity of the tested sludge samples (η) was performed by means of an RC 20 rheometer. The examinations were conducted at a constant temperature of 20°C using a thermostat, with shear rate of 0-200 s^{-1} and measurement time of 120 s. The flow curves of the tested samples were approximated using the Ostwald de Waele's rheological model:

$$\tau = k \cdot (\gamma)^n \tag{1}$$

where:
τ – shear stresses, Pa
k – consistency coefficient, Pa·s,
n – yield exponent,
γ – shear rate, s^{-1}

The concentrations of selected parameters (in parallel with the analytical procedure) were determined by calculation using the formula:

$$y = WPS(v/v) + B(v/v) \tag{2}$$

where:
y – calculated value – concentration of the selected parameter,
WPS(v/v) – load of the selected parameter in the tested mixture (C, D, E) by adding the appropriate volume of WPS to the mixture,
B(v/v) – load of the selected parameter in the tested mixture (C, D, E) by adding the appropriate volume of B sludge (MDS sludge conditioned with polielektrolite) to the mixture,
(v/v) – volume ratio of WPS and B sludge in the tested 1-liter mixture.

Comparison of calculation result with analytical determination was aimed at determining whether the mixed sludge (WPS, B) react with each other or whether the change in concentration results exclusively from dilution.

3. Results

The basic parameter determining the sludge filtration properties is capillary suction time. The lowest and therefore the most favourable CST values were obtained for digested sludge conditioned with optimal and also reduced dose of polyelectrolyte (combination A and B, Fig. 2). The value of CST = 99 s recorded for a mixture of V_{WPS}:V_{MDS} = 1:9 (combination C) was also beneficial. The increase in the volume of WPS in the mixture with municipal digested sludge resulted in an increase in CST and suggested limited filterability and dewatering of the samples (combination D and E).

CST results confirmed the indications of specific filtration resistance and final hydration of the filtration cake obtained during vacuum filtration of the samples (Fig. 3). The value of $r = 5 \cdot 10^{12}$ m/kg is the threshold value below which sludge is considered susceptible to filtration. This condition was met only for the sludge conditioned in combinations: A ($1.1 \cdot 10^{12}$ m/kg), B ($1.6 \cdot 10^{12}$ m/kg) and C ($3.6 \cdot 10^{12}$ m/kg).

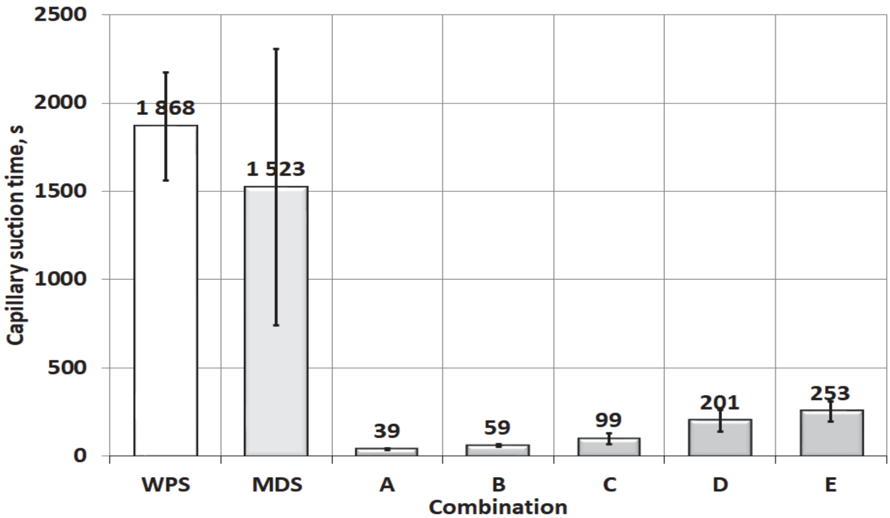

Fig. 2. Capillary suction time of MDS and WPS sludge and A – E mixtures

The lowest hydration of the filtration cake was characteristic of the sludge conditioned with the optimal dose of polyelectrolyte (combination A: 83.8%, Fig. 4). The reduction in the polyelectrolyte dose or the addition of WPS resulted in the filtering cake being significantly hydrated and still present in the liquid state (combination E: 94.3%).

It is worth noting that the susceptibility of the mixtures to dewatering consisted of partial properties of WPS and MDS. This sludge was characterized by a limited susceptibility to dewatering, with the iron post-coagulation sludge being the most difficult substrate for phase separation.

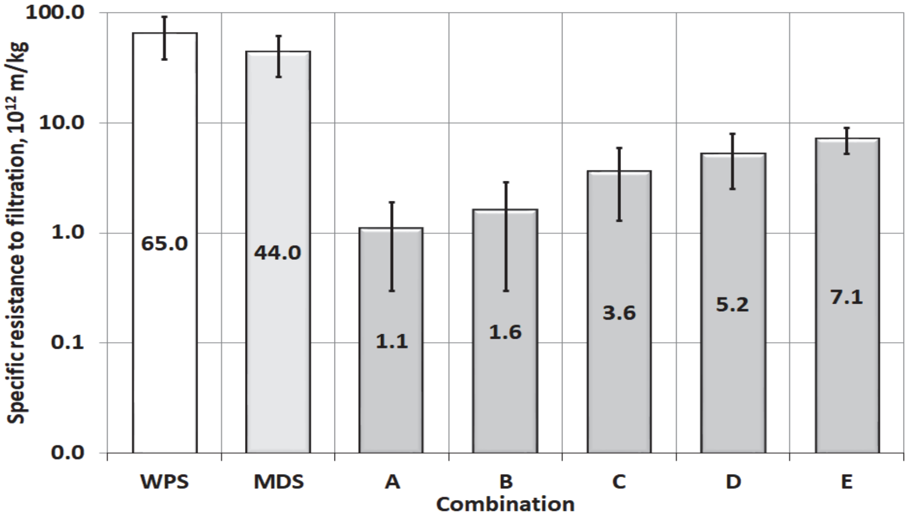

Fig. 3. Specific resistance to filtration of MDS and WPS and mixtures A-E

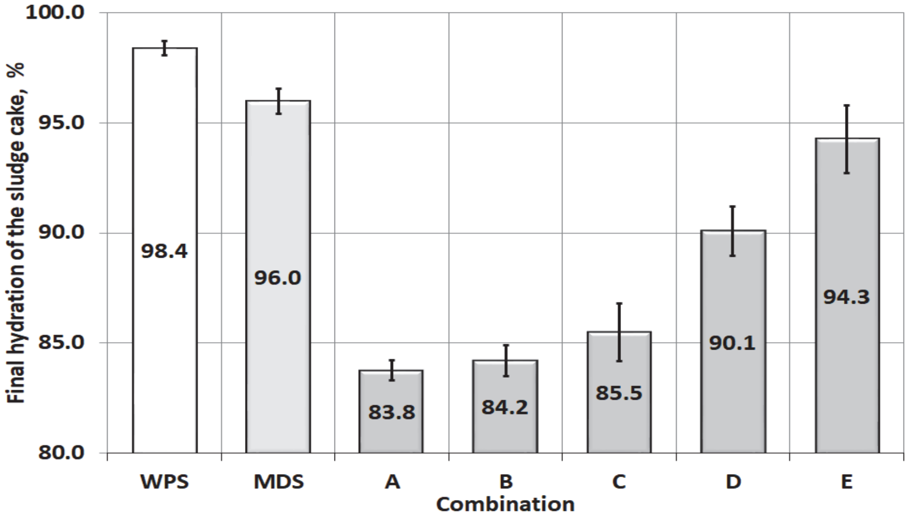

Fig. 4. Final hydration of the filter cake after the vacuum filtration process of tested sludge samples

Evaluation of the parameters of the rheological model allowed for the determination of two basic relationships related to the properties of WPS, MDS, polyelectrolyte and their mixtures (Fig. 5, Table 1).

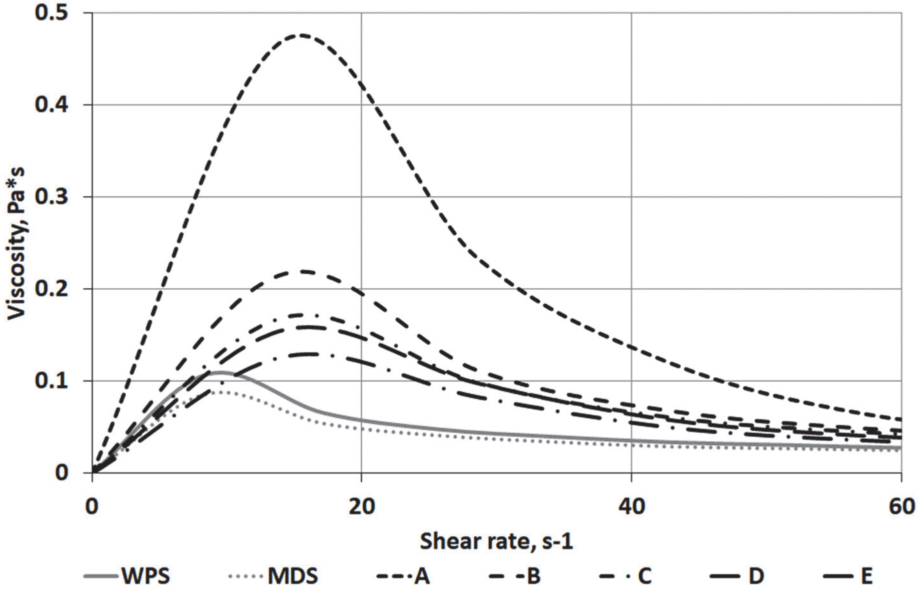

Fig. 5. Viscosity of tested samples of sludge as a function of shear rate

Dosing the polyelectrolyte to the digested sludge caused an increase in the consistency coefficient and, consequently, sludge viscosity (MDS, A, B). Increasing the content of WPS in mixtures C, D and E caused a gradual decrease in viscosity. The flow coefficient had the values $n < 1$, and therefore, all the samples were shear thinned. This was a phenomenon characteristic mainly for mixtures C-E subjected to increasing shear rate (Table 1).

Parameters of supernatant obtained during centrifugation of the samples (180 s, 4500 rcf) also showed a characteristic upward trend. Regardless of the method of sludge conditioning, significant concentrations of suspended solids in supernatant liquid were recorded (Table 2). The lowest concentration of DS_{CEN} equal to 1.3 mg/L was determined for liquor obtained from centrifugation of digested sludge conditioned with polyelectrolyte with the highest dose (A). This value accounted for ca. 6% of the initial dry matter of the MDS sludge. The highest mass of particles which were not subject to centrifugal sedimentation was recorded in supernatant of the centrifuged sample E (w_{WIR} = 1.91 mg/L).

Table 1. Values of rheological parameters of the Ostwald de Waele model

Parameter	WPS	MDS	Combination				
			A	B	C	D	E
k	0,371	0,378	3,950	2,674	1,716	1,578	1,168
n	0,39	0,42	0,35	0,23	0,12	0,12	0,16
r	0,98	0,98	0,83	0,79	0,82	0,83	0,78

Table 2. Quality of supernatant separated in the process of sludge dewatering by centrifugation

Sample	WPS	MDS	Combination				
			A	B	C	D	E
dry solids in supernatant (DS_{CEN}), g/L							
$\bar{x}$	2,06	2,20	1,30	1,37	1,39	1,46	1,91
σ	±1,0	±0,32	±0,04	±0,14	±0,17	±0,27	±1,07
chemical oxygen demand, mg O_2/L							
$\bar{x}$	2790	2256	1198	1297	1453	1661	1869
σ	±846	±443	184	410	145	±40	±163
pH							
x	5,8-6,2	7,3-7,5	7,5-7,7	7,5-7,7	7,5-7,7	7,2-7,6	7,2-7,6
conductivity, mS/cm							
$\bar{x}$	0,7	3,84	3,90	3,98	3,78	2,64	2,17
σ	±0,02	±0,21	±0,35	±0,35	±0,28	±1,10	±0,89
$\bar{x}$ – arithmetic average, σ – standard deviation, x – *range*							

Chemical oxygen demand of sludge liquor also became higher with the increase of OZ in the mixtures C - E. The range of COD values determined was from 1200 mg/L (A) to nearly 1900 mg/L (E). Sludge liquor obtained after centrifugation of the sample E had two times higher concentration of organic matter than the sludge flowing to municipal treatment plants in Poland (910 mg O_2/L).

Dosing polyelectrolyte to digested sludge, both in optimal and reduced doses, did not lead to significant changes in pH and conductance of sludge liquor (MDS, A, B). A gradual decrease in pH and conductance occurred for the cross-section of combinations C - E. Therefore, mixing WPS and MDS (B) allows for neutralization and sorption of dissolved substances (Table 2).

Decreasing the polyelectrolyte dose (B) and increasing the content of WPS in the mixture (C-E) caused a cyclic increase in the concentration of dissolved forms of organic carbon. In combination A, the content of organic carbon was 158 mg/L, whereas for combination E – almost 450 mg/L. Diagram 6 also shows the results of computation for concentration of dissolved organic forms (Fig. 6).

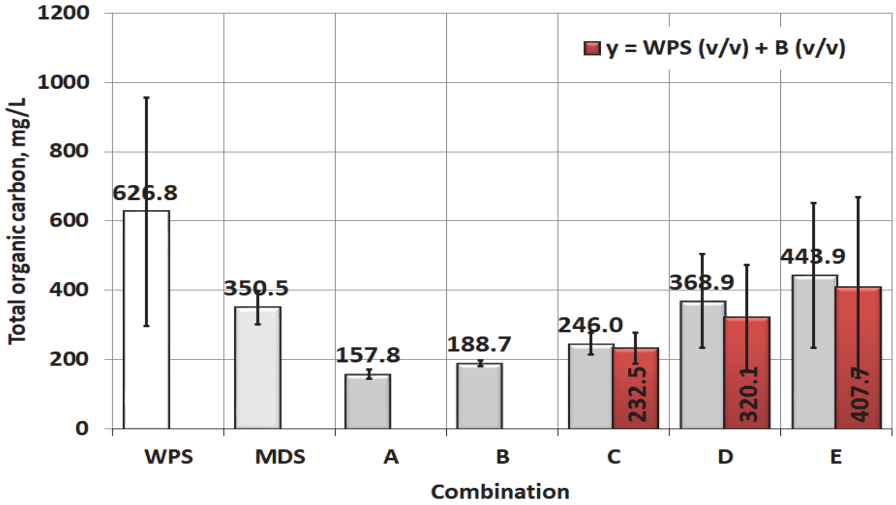

Fig. 6. Empirical and calculated changes in TOC concentration in supernatant

Calculations were based on the values of DOC obtained for MDS (B) and post-coagulation sludge, with consideration for volumetric fraction of WPS in the mixtures tested. The calculated DOC value (y) was by 5 to 15% lower than the empirical value.

Changes in the concentration of total Kjeldahl nitrogen and ammonium nitrogen showed a downward tendency (Table 3). This was due to the increasing content of post-coagulation sludge in the mixture, whose sludge liquor was not concentrated with nitrogen compounds. (TKN = 76.1 mg/L, NH_4-N = 44.8 mg/L). TKN and NH_4-N concentrations in digested sludge liquors were nearly 13 times higher (TKN = 999.6 mg/L and NH_4-N = 922.2 mg/L).

Table 3. Changes in the concentration of Kjeldahl nitrogen and ammonium nitrogen

	WPS	MDS	A	B	C	D	E
total Kjeldahl nitrogen, mgN/L							
$\bar{x}$ σ y	76,1 ±64,9	999,6 ±59,4	840 ±39,6	842,8 ±43,6	800,8 ±39,6 766,1	627,2 ±78,2 612,8	515 ±63,4 459,5
ammonium nitrogen, mg N-NH_4/L							
$\bar{x}$ σ y	48,3 ±44,8	922,2 ±37,1	806,4 ±71,3	823,1 ±39,7	744,5 ±55,9 745,3	613,1 ±59,5 589,6	473 ±83,2 433,9
y – calculated value							

Increasing the volumetric fraction of WPS in the mixture (C-E) resulted in a linear increase or decrease in concentrations of the analysed metals and phosphorus (Table 4).

A cyclical increase in the concentration in the sludge liquor was recorded for Ca, Fe, Mn. This was connected with dosing of larger volumes of WPS sludge to the mixture, which contained higher concentrations of the analysed elements than the digested sludge. However, the determined manganese concentrations were by 14% lower than calculated (mean for C-E combinations); the difference was 380% for iron and 64% for manganese.

Table 4. Changes in concentration of selected elements in supernatant of tested sludge and sludge mixtures

	WPS	MDS	A	B	C	D	E
Al, ppb							
$\bar{x}$ σ y	425 ±338	1490 ±270	60 ±59	68 ±5	**194** ±32 **104**	**43** ±25 **175**	**33** ±145 **246**
Ca, ppb							
$\bar{x}$ σ y	173 330 ±14 024	100 784 ±4 615	77 376 ±3 733	78 375 ±5 002	81 674 ±7 178 87 870	92 801 ±16 249 106 861	103 922 ±16 959 125 852
Fe, ppb							
$\bar{x}$ σ y	208 225 ±147 785	12 255 ±3 863	3 885 ±1 403	4 841 ±1 870	**6 215** ±3 506 **25 179**	**16 264** ±13 037 **65 856**	**31 913** ±25 091 **106 533**

Table 4. cont.

	WPS	MDS	A	B	C	D	E
K, ppb							
$\bar{x}$ σ y	4 589 ±1800	85 755 ±348	76 230 ±29	78 076 ±213	72 220 ±328 70 727	57 448 ±2087 56 030	45 415 ±3151 41 332
Mg, ppb							
$\bar{x}$ σ y	12 594 ±2 615	39 693 ±2 747	32 806 ±1 868	33 217 ±2 786	32 206 ±2 838 31 155	30 877 ±4 811 27 030	27 709 ±4 342 22 905
Mn, ppb							
$\bar{x}$ σ y	720 ±269	136 ±36	47 ±25	53 ±29	76 ±47 120	147 ±111 253	238 ±156 386
P, ppb							
$\bar{x}$ σ y	2 204 ±1 887	20 886 ±1 102	12 989 ±2 165	14 737 ±3 145	**8 805** ±266 **13 483**	**5 454** ±299 **10 977**	**4 951** ±773 **8 470**

A downward tendency, equivalent to the determined and calculated concentrations, was recorded for K and Mg. Mean differences in concentration were 5%, 11%, respectively.

Combinations C, D and E turned out to be effective in removing aluminium, and especially phosphorus, from the mixture. This advantage is confirmed by a linear decrease in P concentrations and calculated concentrations. Interestingly, in the combinations C-E, a decrease in aluminium concentration was observed contrary to the calculation (4-fold difference in concentrations).

The salts of Al, Fe, Ca and Mg play an important role in the removal of phosphorus from sewage or sludge. An increase in the volumetric fraction of iron post-coagulation sludge in the mixture was considered an important factor in phosphorus removal. Similarly, to the study by Li et al. (2013) and Gibbons and Gagnon (2011), an increase in iron concentration led to the increase in sorption capacity of the multiphase system studied. The importance of aluminium in phosphorus removal and the correlation between Al and P concentrations should also be emphasized.

Table 5. Changes in concentrations of heavy metals in supernatant of tested sludge and mixtures

	WPS	MDS	A	B	C	D	E
Cd, ppb							
$\bar{x}$ σ	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cr, ppb							
$\bar{x}$ σ	b.d.	40 ±9	b.d.	b.d.	b.d.	b.d.	b.d.
Cu, ppb							
$\bar{x}$ σ	21 ±14	64 ±1	44 ±39	5 ±2	5 ±2	b.d.	b.d.
Ni, ppb							
$\bar{x}$ σ	b.d.	41 ±5	19 ±4	13 ±4	10 ±7	b.d.	b.d.
Pb, ppb							
$\bar{x}$ σ	29 ±4	27 ±4	14 ±3	18 ±3	15 ±1	23 ±7	b.d.
Zn, ppb							
$\bar{x}$ σ y	1714 ±256	323 ±16	70 ±27	37 ±2	72 ±10 205	71 ±1 540	56 ±8 875
b.d. - below detection limit							

The highest concentration of heavy metals in sludge liquor was recorded for zinc, especially for the sludge from the water treatment plant, i.e. 1714 ppb. In the supernatant of digested sludge, the concentration was only 323 ppb. For this element, only the calculated concentration was determined, with its value almost 9 times higher than empirical (mean combinations C-E). Cadmium and chromium were present in OZ and OP sludge liquors in concentrations below the detection threshold (below 1.56 ppb and 2.65 ppb, respectively). Very low concentrations of copper and nickel, not exceeding 64 ppb and 41 ppb (digested sludge), respectively, were also found.

4. Conclusions

Susceptibility of mixtures tested to dewatering consisted of partial properties of post-coagulation and digested sludge. This sludge was characterized by a limited susceptibility to dewatering, with the organic iron post-coagulation sludge (WPS) being the most difficult substrate for phase separation.

Conditioning of digested sludge from water treatment led to the reduction in susceptibility of the mixtures to dewatering. This method caused a reduction in filtration capacity, including the filtration output over time and increased hydration of the filtering cake.

Dehydration of the mixtures of post-coagulation sludge and digested sludge by centrifugation was also an unfavourable technological solution. A deterioration in the quality of the separated sludge liquors was reflected by an increase in COD and dry residue.

The main conclusions from rheological studies concern the increase in the degree of agglomeration of solids due to polyelectrolyte dosing and the dispersion of this structure and the increasing liquefaction of the tested mixtures due to the dosing of the post-coagulation sludge.

No effect of WP sludge on changes in the concentration of dissolved forms of carbon, Kjejdahl nitrogen and ammonium nitrogen was found. The decrease in concentrations in the tested mixtures resulted from the dilution of digested sludge with water processing sludge.

The use of water processing sludge allowed for sorption of metals and phosphorus, which resulted from the presence of iron in the sludge from the water treatment plant.

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Abstract

Sewage sludge treatment, including dewatering, represents a technological challenge similar to wastewater treatment. It is necessary for the effective sludge dewatering to use conditioning agents, and currently only polyelectrolytes. However, any factor or substance, including waste, which reduces the bonds between water and solid particles can be considered a conditioning agent.

The study verified the possibility of conditioning the digested sludge with sludges from the water treatment plant, mainly produced by coagulation of chlorine iron III and denitrification, was verified. The main process variable was the volumetric fraction of water processing sludges in a mixture with municipal digested sludge amounting to 1:9, 3:7, 5:5.

It was found that the sludge from water treatment plants cannot be used as aconditioner of municipal sludge. Deterioration of filtration and dewatering capacity of the tested mixtures and the quality of the separated sludge liquor was observed. The study confirmed the possibility of the use of post-coagulation sludge in sorption of metals and phosphorus.

Keywords:
municipal sludge, water processing sludge, conditioning, dewatering

Podatność na odwadnianie przefermentowanych osadów ściekowych kondycjonowanych osadami z stacji uzdatniania wody

Streszczenie

Przeróbka osadów ściekowych, w tym ich odwadnianie, stanowi równorzędne wyzwanie technologiczne co oczyszczanie ścieków. Koniecznym dla efektywnego odwadniania osadów jest zastosowanie środków kondycjonujących, a obecnie wyłącznie, polielektrolitów. Niemniej jednak każdy czynnik czy substancja, w tym odpad, który umożliwi zmniejszenie powiązania między cząsteczkami wody i fazy stałej może zostać uznany za środek kondycjonujący.

W przeprowadzonych badaniach zweryfikowano możliwość kondycjonowania osadów przefermentowanych osadami z stacji uzdatniania wody powstałymi głownie w procesie koagulacji zanieczyszczeń chlorkiem żelaza III oraz denitryfikacji. Główną zmienna procesową był udział objętościowy osadów z uzdatniania wody w mieszaninie z osadami przefermentowanymi wynoszący 1:9, 3:7, 5:5.

Stwierdzono, że badane żelazowe osady pokoagulacyjne nie mogą być stosowane jako kondycjoner komunalnych osadów przefermentowanych. Odnotowano pogorszenie filtrowalności i odwadnialności badanych mieszanin oraz jakości oddzielonych cieczy osadowych. Badania potwierdziły możliwość zastosowania osadów pokoagulacyjnych celem sorpcji metali i fosforu.

Słowa kluczowe:
komunalne osady ściekowe, osady pokoagulacyjne, kondycjonowanie, odwadnianie

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Heat and Mass Transfer During Phase Transitions in Liquid Mixtures

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1. Statement of the problem

In many operating processes, gas-to-steam bubbles play a major technological role. As an example, we should mention the following technologies: degassing of water, distillation homogenization of fuel, mixing of colloidal solutions, foam formation in the food industry, etc. Modern technologies for the insulating materials production (Pavlenko 2018), desalination of sea water with the help of isobutane hydrate (Pavlenko et al. 2019a, Takeya et al. 2002, Stem et al. 2003), and obtaining of natural gas hydrate (Pavlenko et al. 2019b, Hashemi et al. 2007) for transportation and storage are also based on heat and mass transfer processes in the gas-liquid systems. Generally, formation and existence of gas-to-steam bubbles are accompanied by intensive heat transfer and mass transfer. The complexity of the "direct" observations (small bubble sizes, high velocity of processes) led to the widespread use of mathematical modeling research methods. Mathematical models allow identifying the most powerful factors and optimizing technological processes. Correctness of the mathematical models of gas-to-steam bubbles is determined by the accuracy of accounting all thermal and physical processes taking place in the liquid and gas.

2. Recent research analysis

To improve the accuracy of simulating heat transfer processes in the gas-to-steam bubble, it is necessary to consider the heat transfer into the liquid medium. A number of authors take the liquid temperature to be constant: when calculating the materials swelling (Pavlenko 2018), when determining the thermodynamic characteristics of steam (Shagapov & Koledin 2013) and cavitation bubbles (Veretel'nik & Difuchin 20108). In (Aktershev & Ovchinnikov 2013), the liquid temperature is described by the exponential function that does not depend on time and the direction of the bubble wall's movement. Some authors (Aktershev & Ovchinnikov 1978) consider the liquid's heat transfer layer to be so thin that the curvature of the bubble's surface can be ignored. However, such assumptions are only possible for a very limited group of tasks. In (Kulinchenko 2007) for cavitation and in (Pavlenko & Koshlak 2015) for steam bubbles, the analytical solution for the problem of non-stationary heat conductivity in a layer of liquid surrounding an oscillating bubble is suggested. As a result of the author's assumptions, the solution of this problem is obtained, and does not depend on thermal and physical characteristics of the liquid. In (Pavlenko et al. 2014), only heat conductivity in a liquid is taken into account, without considering phase transition processes. An overview of the above literature sources shows that phase transition processes in the liquid surrounding the gas-to-steam bubble are not sufficiently studied. The temperature regime of gas inside the bubble can widely vary: from a temperature below the freezing point of the liquid during periods of the bubble's "growth" to a temperature higher than the boiling point of the liquid during the periods of the bubble's compression. Changing the phase state of the liquid causes significant change in heat and mass transfer processes at its boundary.

To expand the limit s of the gas-to-steam bubble's mathematical modeling, it is necessary to consider phase transition processes of heat transfer in the liquid surrounding the gas-to steam bubble. As a result, thermal and physical characteristics of the substance at the bubble's boundary can change considerably. The peculiarity of this task is movement of the bubble's wall, which velocity, at some moments, can reach several tens of meters per second.

3. Identification of previously unsettled parts of the general problem

The aim of the present study was to design a mathematical model of heat transfer in the liquid surrounding the oscillating gas-to-steam bubble. Heat transfer processes in the liquid may be accompanied by a change in the aggregate state and in thermal and physical characteristics. To achieve this aim, the following objectives were set:

- to take into account non-stationary processes of changes in the liquid aggregate state and in its thermal and physical characteristics in the mathematical model,
- to calculate phase transition processes in the liquid surrounding the gas-steam bubble using mathematical modeling,
- to estimate the temperature regime in the liquid under different initial conditions.

4. Statement of assignment and methods of its solving

To develop the mathematical model of heat transfer in the liquid, the following simplifying assumptions are applied:

- the boundary conditions of the second kind are prescribed near the bubble's surface,
- the gas-steam bubble has a spherical shape and is surrounded by an infinite amount of liquid,
- the bubble's center is not displaced relative to the liquid.

To determine the temperature in the column of liquid surrounding the gas-to-steam bubble, it is necessary to consider the process of heat transfer within the liquid. To calculate the heat transfer by means of heat conduction, the Fourier heat transfer equation is normally used, and convection can be considered by applying the efficient thermal conductivity factor. Let us denote by *"x"* the coordinate, where the bubble's radius is changing. To determine the unknown temperature on the surface of the bubble and in the column of liquid ($T_{\tau x}$), a nonlinear Fourier heat conductivity equation for a sphere can be used, with account of its walls mobility and the action of sizable heat sources:

$$\frac{\partial\left(\rho_r c_r T_{(x,\tau)}\right)}{\partial \tau} + \dot{x}\frac{\partial\left(\rho_r c_r T_{(x,\tau)}\right)}{\partial x} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(\lambda_r x^2 \frac{\partial T_{(x,\tau)}}{\partial x}\right) + q_{v(x,T)} \quad (1)$$

where:
ρ_r – liquid density, kg/m; c_r – its heat capacity, J/(kg°C); τ – time coordinate, sec; $\dot{x}$ – velocity of the bubble's radius change, m/sec; λ_r – conductivity factor of the liquid, W/(m°C); $q_{v(x,T)}$ – capacity of sizable heat sources, W/m^3.

As a result of heat transfer processes at the boundary of the bubble, the liquid can change its thermal and physical characteristics, so we will be solving the problem as a non-linear one. The use of heat sources makes the equation (1) heterogeneous. Taking into account that the specific heat flow (***q***) near the surface of the bubble is known, we can write the boundary condition of the second kind:

$$-\frac{\partial \lambda_r T_{(R,\tau)}}{\partial x} = q_{(R,\tau)} \quad (2)$$

Equation (2) takes into account the change in the thermal conductivity factor at the bubble's boundary, for example, in the case of the liquid's freezing. In such a statement, the problem is convenient to solve by the method of finite elements. To describe the thermal conductivity in the liquid surrounding the bubble with radius *R*, let us divide the liquid layer into a series of concentric membranes (***i***), Fig. 1. Let us set the mass distribution of each membrane:

$$m_{r(2)} = 2K_r m_{r(1)}, m_{r(i)} = K_r m_{r(i-1)}, \tag{3}$$

where:
$m_{r(1)}$ – mass of the 1st (internal) layer's membrane, kg; $m_{r(i)}$ mass of each subsequent membrane, kg; K_r – proportionality factor.

This factor allows to "compact" the elements mesh near the bubble's border and to "rarefy" it in the deeper layers of the liquid. The above factor is used to optimize calculations and its typical values are within 1.5-2.

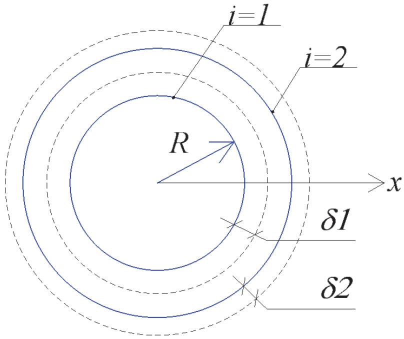

Fig. 1. Diagram of the liquid's division into a series of concentric membranes

Now we shall determine the temperature on the first (internal) membrane's internal surface. To do this, we formulate the equation of the first membrane's thermal balance:

$$Q_{AK} = Q_1 + Q_2 + Q_{\Phi}, \tag{4}$$

where:
Q_{AK} – heat flow that accumulates and causes the temperature increase of the given membrane, W; Q_1 – heat flow from the surface of the bubble into the steam-gas medium, W; Q_2 – heat flow from the second layer of the liquid into the first one, W; Q_{Φ} – heat flow that causes an increase in the solid phase mass (e. g. ice), W. Let us reveal the value of these heat flows.

Heat flow, which is accumulated in the membrane and causes an increase in its temperature, can be determined by means of the known formula:

$$Q_{AK} = m_{r(1)} c_{r(1)} \frac{dT_{(R,\tau)}}{d\tau}, \tag{5}$$

where:

$c_{r(1)}$ – heat capacity of the first membrane's medium, J/(kg°C).

We will write the heat flow from the bubble's surface into its steam-gas medium as a boundary condition of the 2nd kind. Heat removal will reduce the membrane's temperature, therefore this heat flow is negative:

$$Q_1 = -F_R q_{(R,\tau)}, \tag{6}$$

where:

F_R – heat transfer area, m^2.

The heat flow from the outer membrane to the internal one is more convenient to consider within a single layer, for which at the given moment:

$$\lambda_{r(i)} = const: \; Q_2 = \frac{4\pi\lambda_{r(1)}\left(T_{(R+\delta 1,\tau)} - T_{(R,\tau)}\right)}{\dfrac{1}{r_{(1)}} - \dfrac{1}{r_{(1)} + \delta 1}}. \tag{7}$$

The increase in the solid phase mass requires removal of heat energy from the designed membrane and, therefore, is an additional source of the heat energy:

$$Q_{\Phi} = r_{\Phi} \frac{dm_{\Phi(1)}}{d\tau}, \tag{8}$$

where:

r_{Φ} – phase transition heat, J/kg; $m_{\Phi(1)}$ – solid phase mass of the 1st (internal) layer's membrane, kg.

Taking into account the values of individual heat flows, formulas (5)-(8), for the internal membrane can be written as a general differential equation of the thermal balance:

$$m_{r(1)} c_{r(1)} \frac{dT_{(R,\tau)}}{d\tau} = -F_R q_{(R,\tau)} + \frac{4\pi\lambda_{r(1)}\left(T_{(R+\delta 1,\tau)} - T_{(R,\tau)}\right)}{\dfrac{1}{r_{(1)}} - \dfrac{1}{r_{(1)} + \delta 1}} + r_{\Phi} \frac{dm_{\Phi(1)}}{d\tau} \tag{9}$$

The last component of the equation (9) only exists under certain conditions, which need to be specified separately. Within a single iteration step, the membrane's radius remains constant and, for convenience in calculations, it can be designated as:

$$K_1 = \frac{\lambda_{r(1)}}{\frac{1}{r_{(1)}} - \frac{1}{r_{(1)} + \delta 1}} = \frac{\lambda_{r(1)}}{\frac{1}{R} - \frac{1}{R + \delta 1}}. \tag{10}$$

Now, the differential equation determining the temperature on the inner layer's surface of the bubble is written as:

$$\frac{dT_{(R,\tau)}}{d\tau} = \frac{4\pi}{m_{r(1)}c_{r(1)}}\left(-R^2 q + K_1\left(T_{(R+\delta 1,\tau)} - T_{(R,\tau)}\right) + r_\Phi \frac{dm_{\Phi(1)}}{d\tau}\right). \tag{11}$$

In the absence of mass transfer processes, the mass of the 1st layer remains unchanged, therefore:

$$m_{r(1)} = \frac{4}{3}\pi\rho_{r1}\left[(R + \delta 1)^3 - R^3\right] = const \tag{11a}$$

Where the outer radius of the 1st membrane can be determined:

$$R + \delta 1 = \sqrt[3]{r_R^3 + \frac{3m_{r(1)}}{4\pi\rho_{r1}}} = \sqrt[3]{R^3 + \frac{3m_{r(1)}}{4\pi\rho_{r1}}} \tag{12}$$

Similarly, differential equations for all subsequent membranes can be written as:

$$m_{r(i)}c_{r(i)}\frac{dT_{(x,\tau)}}{d\tau} = \frac{4\pi\lambda_r\left(T_{(i-1)} - T_{(i)}\right)}{\frac{1}{r_{(i-1)}} - \frac{1}{r_{(i)}}} - \frac{4\pi\lambda_r\left(T_{(i)} - T_{(i+1)}\right)}{\frac{1}{r_{(i)}} - \frac{1}{r_{(i+1)}}} + r_\Phi\frac{dm_{\Phi(i)}}{d\tau} \tag{13}$$

With account of the problem's non-linearity, the temperature difference between the neighboring layers is more convenient to replace with the temperature difference between the middle of the layer and its edges (boundaries):

$$\frac{dT_{(r_i,\tau)}}{d\tau} = \frac{4\pi}{m_{r(i)}c_{r(i)}}\left(K_3\left(T_{(r_i-\delta i,\tau)} - T_{(r_i,\tau)}\right) - K_1\left(T_{(r_i,\tau)} - T_{(r_i+\delta i,\tau)}\right)\right) + \frac{q_{v(i)}}{\rho_{r(i)}c_{r(i)}} \tag{14}$$

$T_{(r_i+\delta i,\tau)}$ – temperature on the outer boundary of the *i*-th membrane, °C,

$T_{(r_i-\delta i,\tau)}$ – temperature on the internal boundary of the *i*-th membrane, °C.

At every iteration step, these temperatures are determined with account of the thickness and thermal conductivity of the adjacent layers. The temperature at the outer boundary of the *i*-th membrane is:

$$T_{(r_i+\delta i,\tau)} = \frac{K_1 T_i + K_2 T_{i+1}}{K_1 + K_2} \tag{15}$$

$$T_{(r_i-\delta i,\tau)} = \frac{K_4 T_{i-1} + K_3 T_i}{K_4 + K_3}. \tag{16}$$

Factors K_1, K_2, K_3, K_4 are determined by the following formulas:

$$K_1 = \frac{\lambda_{r(i)}}{\frac{1}{r_{(i)}} - \frac{1}{r_{(i)} + \delta_{(i)}}}, \tag{17}$$

$$K_2 = \frac{\lambda_{r(i+1)}}{\frac{1}{r_{(i)} + \delta_i} - \frac{1}{r_{(i+1)}}}, \tag{18}$$

$$K_3 = \frac{\lambda_{r(i)}}{\frac{1}{r_{(i)} - \delta_{(i)}} - \frac{1}{r_{(i)}}}, \tag{19}$$

$$K_4 = \frac{\lambda_{r(i-1)}}{\frac{1}{r_{(i-1)}} - \frac{1}{r_{(i)} - \delta_i}}. \tag{20}$$

Considering the membranes volumes, their radii can be determined:

$$V_{(i)} - V_{(i-1)} = \frac{4\pi}{3}\left(r_{(i)}^3 - r_{(i-1)}^3\right) = \frac{1}{2}V_{(i-1)} + \frac{1}{2}V_{(i)} = \frac{1}{2}\left(\frac{m_{r(i-1)}}{\rho_{r(i-1)}} + \frac{m_{r(i)}}{\rho_{r(i)}}\right) \tag{21}$$

Based on (21), the average radius of the *i*-th membrane is found by the formula:

$$r_{(i)} = \sqrt[3]{r_{(i-1)}^3 + \frac{3}{8\pi}\left(\frac{m_{r(i-1)}}{\rho_{r(i-1)}} + \frac{m_{r(i)}}{\rho_{r(i)}}\right)}. \tag{22}$$

Since the mass of the first membrane is not divisible in half, the 2nd membrane's radius is determined by the following formula:

$$r_{(2)} = \sqrt[3]{R^3 + \frac{3}{4\pi}\frac{m_{r(1)}}{\rho_{r1}} + \frac{3}{8\pi}\frac{m_{r(2)}}{\rho_{r2}}}\,. \tag{23}$$

Considering that the masses of the outer and the internal membrane halves are equal, the radii can also be determined by the analogous formulas. The outer radius of the *i*-th membrane is:

$$r_{(i)} + \delta_i = \sqrt[3]{r_{(i)}^3 + \frac{3m_{r(i)}}{8\pi\rho_{r(i)}}}\,. \tag{24}$$

The internal radius of the *i*-th membrane is:

$$r_{(i)} - \delta_i = \sqrt[3]{r_{(i)}^3 - \frac{3m_{r(i)}}{8\pi\rho_{r(i)}}}\,. \tag{25}$$

At particular moments, in different membranes, favorable conditions to perform phase transition can be created. In this case, it is necessary to consider three components: temperature regime, mass of the solid and liquid phases, the effect of sizable heat sources. The conditions of the first-kind phase transition consist of the two parts: the condition of icing and the condition of ice melting. The condition for icing is:

$$\boldsymbol{T_{(r_i,\tau)} \le T_\Phi} \text{ and } \boldsymbol{m_{\Lambda(r_i,\tau)} < m_{(r_i,\tau)}} \text{ and } \boldsymbol{Q_{\Phi(r_i,\tau)} > 0}, \tag{26}$$

T_Φ – phase transition temperature, °C; $m_{\Lambda(r_i,\tau)}$ – mass of the solid phase in the *i*-th layer at any moment, kg; $Q_{\Phi(ri,\tau)}$ heat flow, which is deduced from the *i*-th layer to erform the phase transition, W.

The condition for ice melting is:

$$\boldsymbol{T_{(r_i,\tau)} \ge T_\Phi} \text{ and } \boldsymbol{m_{\Lambda(r_i,\tau)} > 0} \text{ and } \boldsymbol{Q_{\Phi(r_i,\tau)} < 0}. \tag{27}$$

If the *i*-th layer undergoes a phase transition, then the temperature of this layer does not change, and $dT(r_i,\tau)/d\tau=0$. In this case, the power of sizable heat sources can be determined by the formula:

$$0 = \frac{4\pi}{m_{r(i)}c_{r(i)}}\left(K_3\left(T_{(r_i-\delta i,\tau)} - T_{(r_i,\tau)}\right) - K_1\left(T_{(r_i,\tau)} - T_{(r_i+\delta i,\tau)}\right)\right) + \frac{q_{v(i)}}{\rho_{r(i)}c_{r(i)}}$$

Whence, after simplification, we obtain

$$q_{v(i)}=\frac{4\pi}{V_{r(i)}}\left(K_3\left(T_{(r_i,\tau)}-T_{(r_i-\delta i,\tau)}\right)-K_1\left(T_{(r_i+\delta i,\tau)}-T_{(r_i,\tau)}\right)\right). \tag{28}$$

Similarly, the power of sizable heat sources for the 1-st membrane can be found as follows:

$$q_{v(1)}=\frac{4\pi}{V_{r(1)}}\left(R^2q-K_1\left(T_{(R+\delta 1,\tau)}-T_{(R,\tau)}\right)\right). \tag{29}$$

The sizable heat sources' intensity being known, the change of the solid phase mass can be determined.

$$m_{\Lambda(r_i,\tau+\Delta\tau)}=m_{\Lambda(r_i,\tau)}+\frac{q_{v(i)}\cdot\Delta\tau\cdot V_{r(i)}}{r_{\Phi}}. \tag{30}$$

In the case of a phase transition, a change in the thermal and physical properties will take place in the *i*-th layer of the liquid. Therefore, at each iteration step, the thermal and physical characteristics of the layers need to be specified according to the formulas:

– density

$$\rho_{r(i)}=\frac{\rho_{\Lambda(i)}m_{\Lambda(i)}+\rho_{w(i)}\left(m_{(i)}-m_{\Lambda(i)}\right)}{m_{(i)}}, \tag{31}$$

– thermal conductivity

$$\lambda_{r(i)}=\frac{\lambda_{\Lambda(i)}m_{\Lambda(i)}+\lambda_{w(i)}\left(m_{(i)}-m_{\Lambda(i)}\right)}{m_{(i)}}, \tag{32}$$

– heat capacity

$$c_{r(i)}=\frac{c_{\Lambda(i)}m_{\Lambda(i)}+c_{w(i)}\left(m_{(i)}-m_{\Lambda(i)}\right)}{m_{(i)}}. \tag{33}$$

The density change, with the constant mass, will change the size of the layers, which may complicate the calculation process. Taking into account that the density and heat capacity are used as the product, the density change can be replaced by the equivalent change in heat capacity. With account of the density correction, the *i*-th layer's heat capacity is determined by the formula:

$$c_{r(i)}=\frac{\rho_{r(i)}}{\rho_w}\times\frac{c_{\Lambda(i)}m_{\Lambda(i)}+c_{w(i)}\left(m_{(i)}-m_{\Lambda(i)}\right)}{m_{(i)}} \tag{34}$$

ρ_w – liquid density at the initial temperature, kg/m.

In order to assess the adequacy of the developed mathematical model, a computer software has been developed and a number of mathematical experiments have been performed. The results of the calculation are reflected in the experiments No 2-7.

5. Study results and their discussion

Source data. Let us consider the heat and mass transfer processes in the liquid at the initial stage of the barbotage introducing of bubbles into gas into water. With regard to technology, such processes are characteristic of carbonization, formation of isobutane hydrate (Mosin 2012) and other hydrates (Semenov & Shits 2013, Okutani et al. 2008, Pavlenko & Koshlak 2017). Duration of the estimated time interval is 3-6 μs (microseconds). The time step is 0.005-0.01 ns, the specific heat flow near the bubble's surface (boundary condition of the 2nd kind) is 1 MW/m. The initial diameter of the bubble is 0.1 mm, the initial water temperature is +0.5°C.

The estimated layers are 12 in number, Kr factor equals 1.5. The initial values of heat conductivity, density and heat capacity of water are taken at the temperature of +0.5°C. The heat of the water-to-ice phase transition is 335 kJ/kg. The temperature of the steam-gas medium of the real bubble can vary within a pretty wide range. To study the phase transition processes in water, the bubble with the steam-gas medium temperature below the phase transition temperature will be called "cold". The bubble with the steam-gas medium temperature higher than the phase transition temperature will be called "hot".

Experiment No. 1. Let us consider a bubble in the water formed during the barbotage gas throttling through the narrow nozzle. Due to the Joule-Thompson effect, the gas temperature inside the bubble is lower than the temperature of the surrounding liquid. Considering the gas pressure inside the bubble equal to the pressure of the water (with account of the surface tension forces), we will take the velocity of the bubble walls equal to 0 m/sec. The results of the temperature regime calculation for the liquid surrounding the "cold" bubble, are shown in Fig. 2.

Experiment No. 2. If the gas pressure in the bubble exceeds the pressure of the liquid, the bubble expands. Let us consider the processes in the liquid during the "cold" bubble expansion with the wall movement velocity of 10 m/sec. The calculation results are shown in Fig. 3.

Experiment No. 3. In the process of oscillation, the phase of the bubble's expansion is replaced with the phase of compression. Let us consider the processes in the liquid during the period of the "cold" gas bubble compression with the wall movement velocity of –10 m/sec. The calculation results are shown in Fig. 4.

During the period of the bubble compression, the gas temperature in it increases and favorable conditions are created for melting of the ice crust formed at the previous stages of the bubble's oscillation. As time passes, the movement of the bubble's wall slows down, and the process of expansion starts in the conditions of the high gas temperature. The next series of calculations was performed to study the phase transition processes around the "hot" bubble.

Experiment No. 4. A bubble with "hot" gas is immobile and is surrounded with an ice crust. Let us consider the process of ice melting around the bubble. Based on preliminary calculations, the initial ice temperature will be taken at –0.5°C.

Experiment No. 5. The "hot" bubble expands with the velocity of 10 m/sec. The calculation results are shown in Fig. 6.

Experiment No. 6. Let us consider the ice melting while a "hot" bubble is compressing with the velocity of 10 m/sec (Fig. 7). The initial temperature of ice was taken at -0.5°C.

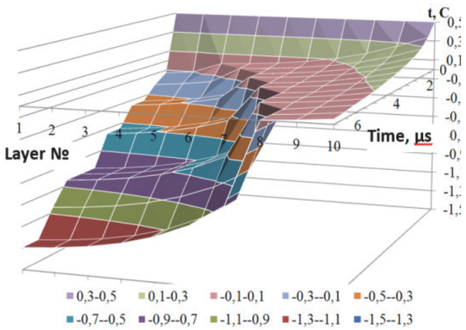

Fig. 2. Diagram of temperature fields in the water surrounding a stationary wall "cold" bubble ($\dot{R} = 0$ m/sec)

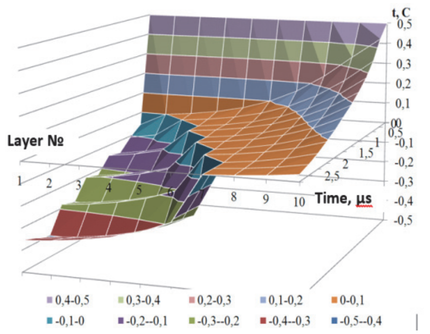

Fig. 3. Diagram of temperature fields in the water surrounding a "cold" bubble expanding with the velocity of *dR/dτ* m/sec

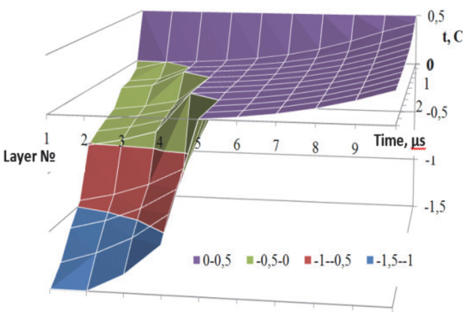

Fig. 4. Diagram of temperature fields

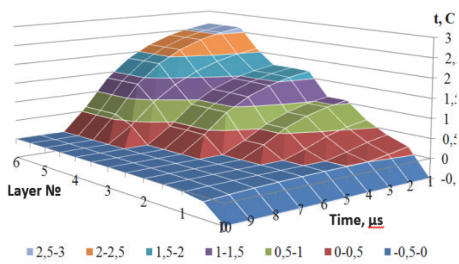

Fig. 5. Diagram of temperature fields in the water-ice system surrounding the immobile "hot" bubble (*dR/dτ=0* m/sec)

in the water surrounding a “cold” bubble compressing with the velocity of $dR/d\tau=-10$ m/sec

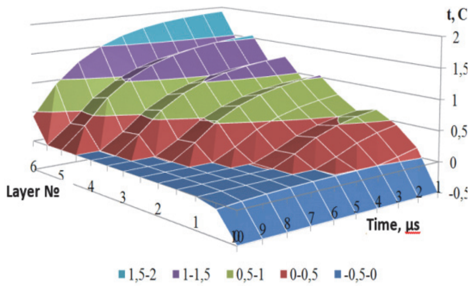

Fig. 6. Diagram of temperature fields in the water-ice system surrounding the “hot” bubble that is compressing with the velocity of $\dot{R}=10$ m/sec

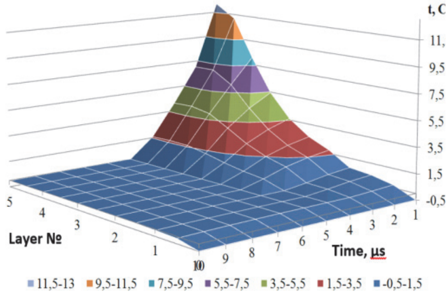

Fig. 7. Diagram of temperature fields in the water-ice system surrounding the “hot” bubble that is compressing with the velocity of $dR/d\tau=-10$ m/sec

6. Discussion of the results of the mathematical modeling of phase transition processes in the liquid

The upper part of Fig. 2 shows a relatively rapid cooling of the liquid to the temperatures close to the phase transition temperature (0°C). The phase transition itself is observed as an almost horizontal platform approximately in the center of the diagram. The left side of the diagram illustrates the process of ice cooling.

The stepped nature of the ice temperature is explained by a small number of the designed layers (12 pcs.). The freezing depth has made 5 layers of the liquid around the bubble for 2.0 ms. As it is seen in Fig. 3, the freezing depth has made 6 layers of liquid for 2.0 ms. Comparison of the frozen layers masses in Experiments 1 and 2 shows that when the bubble expands the liquid freezing is approximately 1.6 times faster. This is due to an increase of the heat transfer surface area when the bubble size is expanding. In the left side of the diagram, the ice temperature is bearing a jagged nature. A slight rise in temperature is observed due to the reduction of thickness and the membranes’ thermal resistance in the process of the bubble expansion.

In general, reducing the solid phase membranes’ thickness leads to the fact that the surface temperature of the bubble is closer to the phase transition temperature than it was in experiment No. 1. The results of the “cold” bubble compression calculation, presented in Fig. 4, demonstrate that in this case, the freezing of the liquid significantly slows down. Namely, the ice thickness was only 60 % of the variant with an immobile bubble wall. This is explained by a reduction of the heat transfer surface area. Due to the freezing layers’ thickness increase, the thermal resistance grows and the internal surface temperature of the bubble reduces more rapidly than in experiments 1 and 2. The results of the immobile "hot" bubble calculation (Fig. 5) show a relatively rapid initial warming of the ice layers to the phase transition temperature. Comparing the results with Experiment No.1, it can be noted that the melting process occurs at almost the same velocity as that of the freezing process.

This is facilitated by the boundary condition of the 2nd kind. Almost four times less than the thermal conductivity of water in comparison with that of ice, causes more intense heating of the interphase liquid-gas surface.

In experiment No. 5, as in experiment No. 2, ice melting is accelerated due to the heat transfer surface expansion. Also, a slower wall temperature rise occurs, and the specific "pulverulent" form of the temperature field is caused by a gradual reduction of the membranes' thickness.

The results of calculating the "hot" bubble compression (Fig. 7) show a significant deceleration of the ice melting process compared with the previous calculation. The temperature of water's internal layers grows much more rapidly than in Experiments 4 and 5. This is facilitated by both the water layers thickness growth when compressing the bubble, and the much less thermal conductivity of water compared with that of ice (approximately 4 times). Reduction in the amount of the melted ice is due to the surface area reduction of the heat transfer, and as a consequence, reduction in the total amount of heat that is brought to the interphase surface of the bubble. Thus, with the help of mathematical modeling, the distribution of temperature fields in the liquid in the conditions of the phase transition processes and the bubble size change (Experiments No. 1-6) was obtained. The study performed demonstrates that the method of finite elements (3)-(34) used for the mathematical model of non-stationary heat transfer in the liquid (1)-(2) surrounding the oscillating gas-to steam bubble correctly displays the physical processes.

It takes into account the change in the thermal and physical characteristics of the liquid (31)-(34), the change in the bubble size (12), (22)-(25), the heat transfer processes at its boundary (9), and the phase transition processes in the liquid column (26)-(30). The designed mathematical model can be used to estimate the thermodynamic parameters of a two-phase liquid in various technological processes. The suggested calculation technique can be used to determine the thermal and physical haracteristics of liquid and steam in various technological processes associated with gases dissolution in liquid, foam hardening and gas hydrates formation.

7. Conclusions

1. A mathematical model of the non-stationary thermal conductivity of the oscillating bubble wall, which takes into account the change in the aggregate state as well as thermal and physical characteristics of the substance, has been developed. It is demonstrated that when applying the finite elements, method, it is a system of nonlinear differential equations of the 1st order. Consideration of the above features in the mathematical model allows obtaining the values of the liquid and solid phases temperatures at any specific time when changing the bubble's size, changing the direction of the heat flow at its boundary.
2. To analyze the correctness of the mathematical modeling of transient processes in a liquid, a series of assessment calculations (experiments) has been performed. They were aimed at testing the reproduction of various thermodynamic conditions and gas-to-steam bubble modes by means of the mathematical model: heating and cooling together with the phase transition processes, compression and expansion. A diagram of temperature fields in the substance surrounding the gas-to-steam bubble was constructed for each experiment.
3. The results of the calculation for an immobile 0.1 mm diameter bubble with a boundary condition of the 2nd kind showed that the icing and ice melting velocities are almost equal, but the temperature on the interphase gas-water surface is approximately four times exceeding the temperature of the gas-ice surface that complies to the ratio of the thermal conductivity of water and ice. The temperature in the liquid-ice phase transition zone is practically constant. Comparison of the frozen layers masses shows that when the bubble is expanding, the liquid freezing and the ice melting are going more than 1.6 times faster than in the immobile bubble. When compressing the bubble, the thickness of the ice formed or melted is approximately 1.7 times smaller than that of the immobile bubble.

   The analysis of the obtained results has demonstrated that they are predictable and completely correspond to the physicists' ideas of the heat transfer and phase transition processes flow in the liquid.

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Abstract

The work is devoted to the study of the transient processes of heat and mass transfer in the volume of a liquid. The method of calculating the temperature field in a liquid takes into account phase transitions, motion of the bubble wall and heat exchange processes near its surface. The method takes into account the change in the thermophysical characteristics of a liquid when its temperature changes. The results of the research can be used to optimize the various technological processes associated with cavitation, boiling and the formation of gas hydrates.

Of particular interest are the processes of spontaneous boiling of superheated liquids under conditions when the liquid is in a non-equilibrium metastable state, since studying the kinetics of metastable state dysfunction can contribute to the creation of new high-intensity technologies for creating gas emulsions, as well as combustion and explosion technologies. The proposed method will allow a numerical analysis of the processes of destruction or the creation of gas hydrates, emulsions, taking into account both thermal and dynamic aspects of the problem.

Keywords:
thermophysical characteristics of a gas-saturated liquid, gas-vapor bubble, heat transfer in two-phase media, phase transitions

Przenoszenie ciepła i masy podczas przemian fazowych w mieszaninach ciekłych

Streszczenie

Praca poświęcona jest badaniu przejściowych procesów przenoszenia ciepła i masy w objętości cieczy. Metoda obliczania pola temperatury w cieczy uwzględnia przemiany fazowe, ruch ściany pęcherzykowej i procesy wymiany ciepła w pobliżu jej powierzchni. Metoda uwzględnia zmianę właściwości termofizycznych płynu w miarę zmian temperatury. Wyniki badań można wykorzystać do optymalizacji różnych procesów technologicznych związanych z kawitacją i tworzeniem się hydratów gazowych.

Szczególnie interesujące są procesy samorzutnego wrzenia przegrzanych cieczy w warunkach, w których ciecz jest w stanie nierównowagi metastabilnej, ponieważ badanie kinetyki dysfunkcji stanu metastabilnego może przyczynić się do stworzenia nowych technologii tworzenia emulsji gazowych, jak również technologii spalania i wybuchu. Proponowana metoda pozwoli na analizę numeryczną procesów niszczenia lub tworzenia hydratów gazowych, emulsji, biorąc pod uwagę zarówno termiczne, jak i dynamiczne aspekty problemu.

Słowa kluczowe:
charakterystyki termofizyczne cieczy nasyconej gazem, pęcherzyk gazowo-parowy, wymiana ciepła w ośrodku dwufazowym, przejścia fazowe

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An Application of Statistical Methods to Compare the Properties of Concretes Produced from Construction Waste

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1. Introduction and aim

Some waste substances, although not directly aggressive towards the environment, cause an increase in the overall amount of matter sent to landfills when not rationally recycled. The group includes construction ceramic materials (bricks, breeze blocks, roof tiles, pipes, wall and floor tiles, taps, sinks, bathroom furnishings, elements of electric wiring and sanitation facilities) (Ciechocki et al. 2014, Halicka et al. 2013). Taking the above facts into account, efficient ways of recycling of the aforementioned materials are sought (Motz & Geisler 2001, Yang et al., 2011). Concrete production is one of recycling methods for construction ceramic products or waste generated during their production (Domski & Głodkowska 2017, Ogrodnik et al. 2017). Their use in concrete mixtures does not require special treatment as they are used as aggregates following crushing in conventional crushing machines widely used in production plants. Concretes made with construction ceramics have different physical, chemical and mechanical properties compared with conventional concretes. The composition of various concrete mixes is altered by selection of cement, aggregate and additives or admixtures. Concretes which gain unique properties are called special concretes and they can be water-resistant, frost-resistant, corrosion-resistant (acidproof, sulphate-resistant); there are also concretes for radiation shielding and insulation concretes (Guerra et al. 2009, Ogrodnik et al. 2012). The array of special concretes has expanded recently to include concretes solely made with recycled aggregates. Demand for environmentally-friendly products is constantly on the increase, which has been confirmed in numerous studies in which concrete production involved using different recycled materials e.g. construction waste (De Brito et al. 2005, Domski et al. 2012, Dowrzańczyk-Krzywiec 2011, Zając 2008), remains of concrete mixture (Gawęda et al. 2013, Gruszczyński 2017), industrial concrete floors and reinforced concrete beams (Węgliński et al. 2017). Usually, concretes made with recycled materials are compared to conventional products in terms of their physical and chemical properties. However, rarely are they compared by means of statistical methods (Gawenda et al. 2005). Thus, the aim of the present work was to carry out statistical analysis and examine variation in properties of concretes with altered composition, compared with conventional concretes. The work is the continuation of the previous research by Zegardło et al. (2018).

2. Materials and methods

The research material consisted of ceramic waste deposited in the building material landfills: red ceramics (mainly crushed bricks, ceramic building blocks, shards of roof tiles), ceramic tiles and sanitary ceramics. The waste materials were crushed using jaw crushers to obtain fine and coarse aggregates (the size of aggregate particles was respectively, 0-4 and 4-8 mm). In order to establish an optimum coarse-to-fine aggregate particle ratio, mixtures of aggregate particles were placed in vessels whose diameter was 1.69 dm^3. The proportions were establish so that the spaces between coarse particles were completely filled with finer particles. In the present research, the coarse-to-fine particle ratio was 1:0.4. Next, using the optimised proportion (1:0.4), mixtures of aggregates of sanitary ceramics, tile ceramics and red ceramics were prepared, and their percentage particle content was determined in accordance with PN-EN 933-1:2012. Moreover, specific density, apparent density, water absorbability and crushing rate were determined for each aggregate type. In order to establish specific density, a standard method was used in accordance with PN-EN1097-7. To that end, aggregates were ground to obtain dust, dried until constant weight was reached, and weighed. The volume of aggregate portions was measured by the pycnometric method. Bulk density and water absorbability were determined by the standard method in accordance with PN-EN 1097-6. Measurements were taken in 10 samples.

Water absorbability of aggregate was expressed as percentage weight of water absorbed by the aggregate to the aggregate dry weight. Aggregate bulk density was the ratio of aggregate weight to aggregate volume. Determination of elemental composition was the final analysis.

The obtained aggregates were used to make concrete samples in which all conventional aggregates were replaced with recycled ceramic tiles, red ceramics and sanitary ceramic aggregates (10 samples of each type). Additionally, for the sake of comparison, samples of standard concretes (gravel- and basalt-based) were prepared using the same proportions of the remaining components (excluding aggregates).

Next, the following concrete properties were determined: tensile strength, compressive strength and compressive strength in a corrosive environment.

In order to statistically compare aggregates (in terms of crushing rate, bulk density, specific density, water absorbability) and concretes (in terms of tensile strength, compressive strength, compressive strength in a corrosive environment, and Al_2O_3 and SiO_2 contents), one-way analysis of variance (ANOVA) was used following the model:

$$y_{ij} = m + a_i + e_{ijl} \tag{1}$$

where:
y_{ij} – value of the examined characteristic,
m − population mean,
a_i – effect of i-th level of factor A (aggregate type, concrete type),
e_{ijl} – random error.

Tukey's test was used for mean separation at $p \leq 0.05$.

The relationships between aggregate characteristics, that is specific density, bulk density, water absorbability and crushing rate, were examined by means of Pearson's correlation coefficient.

As analysis of variance makes it possible to perform multi-trait comparisons but the traits are considered separately, principal component analysis (PCA) and cluster analysis were used because they allow simultaneous comparisons in terms of many characteristics.

As variance analysis makes it possible to compare objects in terms of many characteristics which are viewed separately, principal component analysis (PCA) and cluster analysis were applied to simultaneously compare objects (concretes) in terms of many characteristics (tensile strength, compressive strength, compressive strength in a corrosive environment, Al_2O_3 content, SiO_2 content).

Only the principal components whose eigenvalues, according to the Kaiser's criterion, were greater than 1 were analysed and interpreted. The distance between clusters was estimated by Ward method based on Euclidean distance. The cut-off point (level of cluster similarity) was determined using Mojena rule following the inequality:

$$d_{i+1} > \bar{d} + ks_d; \tag{2}$$

where: $\bar{d}$ and s_d are, respectively, the mean and standard deviation of d_i and k is a constant in the range 2.75 to 3.50 (Mojena 1977). The value k was 1.2 as recommended by Milligan and Cooper (1985).

All the calculations were performed using STATISTICA 12.0.

3. Results and discussion

Statistical analysis demonstrated that aggregates from ceramic waste differed significantly in terms of the analysed characteristics (Fig. 1). Variance analysis revealed significant differences between ceramic tile aggregates in terms of crushing rate ($F = 189.1$, $p = 0.000$), specific density ($F = 75.46$, $p = 0.000$) bulk density ($F = 32.51$, $p = 0.000$) and water absorbability ($F = 47.86$, $p = 0.000$) (Fig. 1).

According to Zając and Gołębiowska (2014), properties of recycled aggregates differ significantly according to their origins.

Aggregates from red ceramics were the most crushed following by aggregates from tile ceramics and basalt grit. The crushing rate of tile ceramic aggregates was statistically the same as that of conventional aggregates. According to Gawenda et al. (2013), resistance to crushing is one of the factors which condition ceramic aggregate suitability for concrete production.

The highest specific density and bulk density were determined for aggregates from basalt grit, it being the lowest for aggregates from red ceramics. Aggregates from tile ceramics had a significantly higher specific density and bulk density compared with red ceramics, it being lower compared with aggregates from sanitary and conventional ceramics as well as from basalt grit. No statistical differences between specific density and bulk density of sanitary ceramic aggregates and conventional aggregates were found.. The specific density and bulk density of these aggregates were significantly lower compared with basalt grit but it was higher compared with aggregates produced from sanitary and red ceramics.

Red ceramic aggregate had the highest water absorbability which differed significantly from that of the other aggregates. Water absorbability of tile ceramic aggregate was also significantly higher compared with sanitary ceramic aggregate, conventional aggregate and basalt grit aggregate. The water absorbability of conventional aggregate and that produced form sanitary ceramics was statistically the same. The lowest water absorbability which differed from the remaining aggregates was determined for basalt grit (Fig. 1). Substantial water absorbability of sanitary ceramics, which was similar to the absorbability of limestone and dolomite, was confirmed in the research by Halicka & Zegardło (2011).

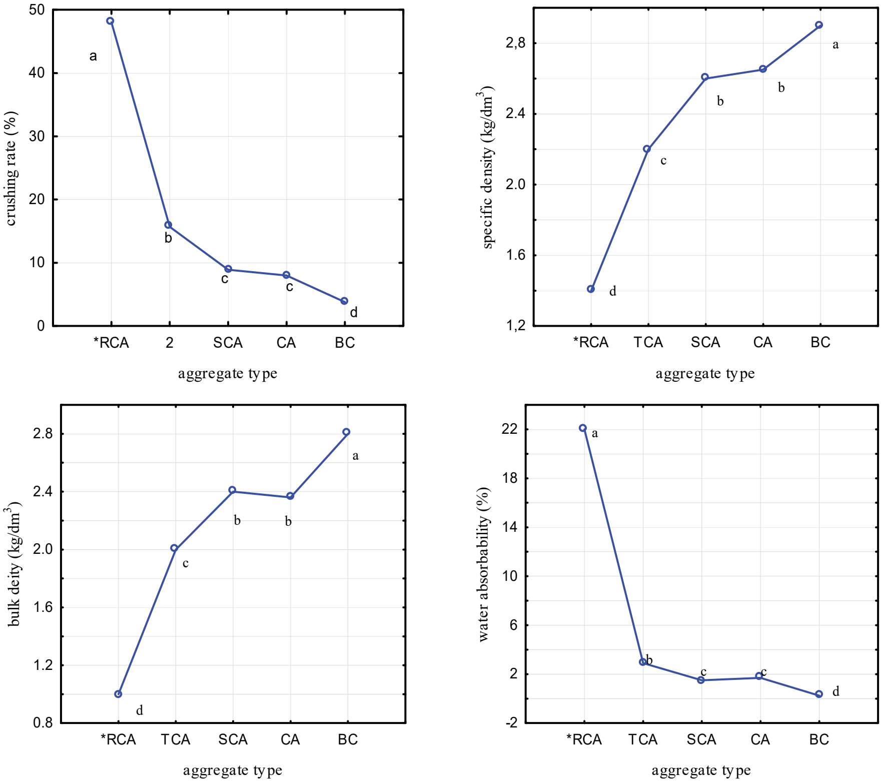

Fig. 1. Comparison of mean values of aggregate properties in terms of the analysed characteristics

Means designated by the same letters differ insignificantly at $p \leq 0.05$.
RCA– Red ceramic aggregate, TCA – Tile ceramic aggregate, SCA – Sanitary ceramic aggregate, CA– Conventional aggregate (gravel), BG – Basalt grit

Correlation analysis revealed a significant positive association between bulk density and specific density of red ceramic aggregate. An increase in specific density was followed by an increase in bulk density (r = 0.710). Water absorbability of aggregate from red ceramics declined significantly (r = -0.807) as specific density and bulk density increased (r = -0.753). Moreover, the more crushed aggregates were, the higher water absorbability was found (r = 0.724). Absorbability of aggregate from tile ceramics declined significantly as bulk density increased (r = -0.719) and crushing rate dropped (r = 0.736). The latter property significantly and positively affected an increase in bulk density (r = 0.738) and water absorbability (r = 0.726) of aggregate produced from sanitary ceramics. Similar relationships were observed for conventional aggregate, although no relationship between its specific density and crushing rate was confirmed. Water absorbability of basalt grit aggregate declined significantly as specific density and bulk density increased (r = 0.729 and 0.811, respectively). Moreover, the absorbability increased as crushing rate increased (r = 0.778) (Table 1).

Table 1. Values of correlation coefficients between the aggregate properties

Items	Red ceramic aggregate (RCA)			
	Specific density	Bulk density	Water absorbability	Crushing rate
Specific density	1.00	0.710*	-0.807*	0.094
Bulk density		1.00	-0.753*	0.036
Water absorbability			1.00	0.724*
Crushing rate				1.00
	Tile ceramic aggregate (TCA)			
Specific density	1.00	0.135	-0.450	0.189
Bulk density		1.00	-0.719*	0.395
Water absorbability			1.00	0.736*
Crushing rate				1.00
	Sanitary ceramic aggregate (SCA)			
Specific density	1.00	0.276	-0.136	0.738*
Bulk density		1.00	-0.605	0.222
Water absorbability			1.00	0.726*
Crushing rate				1.00
	Conventional aggregate (gravel) (CA)			
Specific density	1.00	0.424	-0.606	0.169
Bulk density		1.00	-0.738*	0.369
Water absorbability			1.00	0.802*
Crushing rate				1.00
	Basalt grit (BG)			
Specific density	1.00	0.236	-0.729*	0.089
Bulk density		1.00	-0.811*	0.369
Water absorbability			1.00	0.778*
Crushing rate				1.00

Statistical analysis of concrete strength demonstrated significant differences between the concretes. The highest values of strength parameters were obtained for concrete produced using aggregate from sanitary ceramics. Conventional aggregate replaced with aggregates from tile ceramics and basalt grit significantly increased compressive strength and tensile strength of the remaining concretes. Concrete made with aggregate from red ceramics had significantly lower values of compressive strength and tensile strength compared with concretes made with the remaining types of aggregates (Fig. 2).

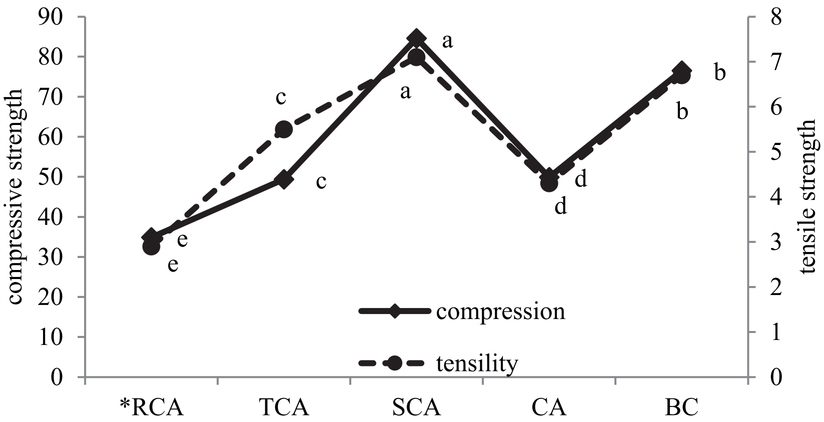

Fig. 2. Mean values of concrete strength
Means designated by the same letters differ insignificantly at $p \leq 0.05$.
RCA – Red ceramic aggregate, TCA – Tile ceramic aggregate, SCA – Sanitary ceramic aggregate, CA – Conventional aggregate (gravel), BG – Basalt grit

As can be seen in Figure 3, concretes containing basalt grit and tile ceramics had the highest silica content, it being significantly higher compared with concretes made with conventional aggregate and that produced from red ceramics. The silica content of concrete containing sanitary ceramics was similar to conventional concrete as well as concrete including tile ceramics. The greatest resistance to a corrosive environment was displayed by concrete made with tile ceramics, the resistance being significantly higher compared with the remaining concretes. The lowest values of the discussed parameter were determined for concrete made with conventional aggregate and aggregate from red ceramics, the differences between these two types being insignificant.

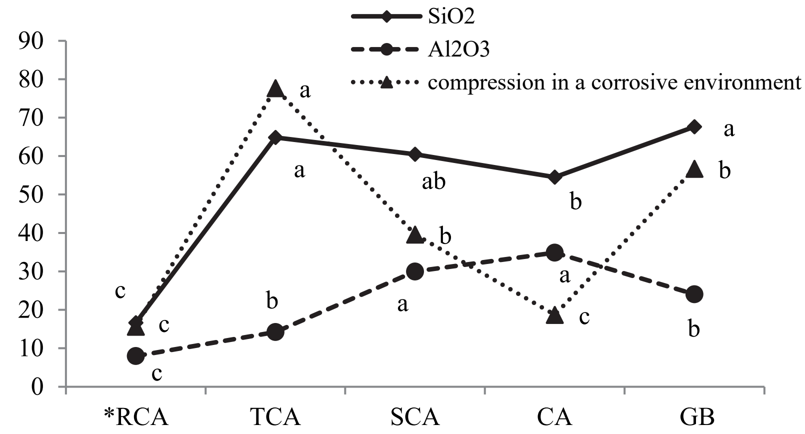

Fig. 3. Mean values of concrete compressive strength in a corrosive environment
Means designated by the same letters differ insignificantly at $p \leq 0.05$.
RCA– Red ceramic aggregate, TCA – Tile ceramic aggregate, SCA – Sanitary ceramic aggregate, CA– Conventional aggregate (gravel), BG – Basalt grit

Due to the fact that analysis of variance makes it possible to compare objects in terms of many characteristics but they are considered separately, principal component analysis and cluster analysis were used to obtain simultaneous multi-trait comparisons of concretes in terms of all the analysed characteristics. Principal component analysis revealed that properties of concretes made with various aggregates had different characteristics associated with the first two principal components (PC1 and PC2), as indicated by their eigenvalues which are higher than 1. The components accounted for over 86% of multi-trait variation between the concretes (Table 2). The first principal component was positively correlated with tensile strength (0.928), silica content (0.894) and compressive strength (0.878). The following characteristics were the most strongly associated with the second principal component: compressive strength in a corrosive environment (-0.712) and Al_2O_3 content. Multi-trait relationships indicate that the concretes which contained more silica had a higher compressive strength, tensile strength as well as compressive strength in a corrosive environment. The association of silica content with compressive strength and tensile strength was quite strong as indicated by a small inclination angle between the variables. Such an effect may result from chemical reactions between SiO_2 and concrete components. Silica reactions between aggregate and concrete improve the properties of the aggregate-set cement contact point, which positively influences the final strength parameters of the composites. Concretes which contained more Al_2O_3 had lower compressive strength in a corrosive environment as demonstrated by the reciprocal location of the vectors (Fig. 4).

Table 2. Eigenvalues, share of principal components in the overall variation and correlation coefficients between the components and concrete parameters

Specification	Principal components	
	PC1	PC2
Tensile strength	0.928	0.103
Compressive strength	0.878	-0.054
Compressive strength in a corrosive environment	0.646	-0.712
Al_2O_3 content	0.524	0.811
SiO_2 content	0.894	-0.015
Eigenvalue	3.12	1.17
Cumulated variance (%)	62.54	86.13

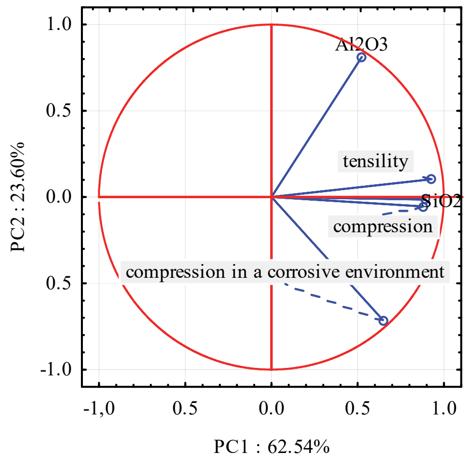

Fig. 4. Graph of factor coordinates for the components PC1 and PC2

The location of concrete types in the system of the first two principal components is presented in Fig. 5. The distance between the objects (concretes) approximately reflects the multi-trait similarity between them in terms of the five analysed characteristics. It can be inferred from the graph that there was a poor multi-trait similarity between the concretes, the most similar being the concretes produced using basalt grit and tile ceramics. The concretes were characterised by average values of traits associated with the first principal component (silica content as well as compressive strength and tensile strength) as the values for this component fluctuated around zero. Concrete made with red ceramics had high negative values of the first principal component so its silica content, compressive strength and tensile strength were low. Concrete whose component were sanitary ceramic aggregates contained more silica and its compressive strength and tensile strength were higher compared with concrete based on aggregates of basalt grit and tile ceramics as well as conventional concrete. The relationships were confirmed by cluster analysis which yielded three groups of concretes classified based on all the analysed characteristics (Fig. 6). The first group was made up of concretes made with tile ceramics, basalt grit and conventional aggregates. The second group included concrete made with sanitary ceramics only, and the third group consisted of concrete containing red ceramic aggregate. The agglomeration course indicated that, in terms of all the analysed characteristics, concrete including tile ceramic aggregate and basalt grit aggregate had the most similar properties as they formed a cluster at the first step. At the second step, concrete produced from conventional aggregates joined the first cluster. At the third and fourth step, group two and three were formed as a result of agglomeration (table 3.)

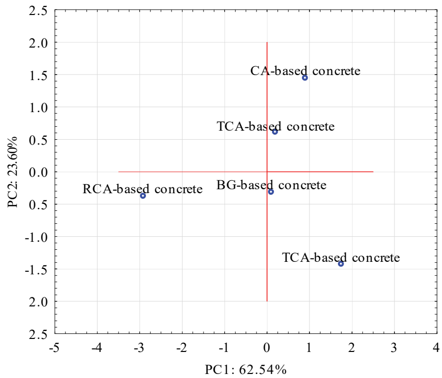

Fig. 5. Location of concrete types in the system of the first two components

Table 3. Agglomeration schedule (clustering) of concretes

Step	Concrete type				
1	TCA-based	BG-based			
2	TCA-based	GBA-based	CA-based		
3	SCA-based	TCA-based	GBA-based	CA-based	
4	RCA-based	SCA-based	TCA-based	GBA-ba	CA-based

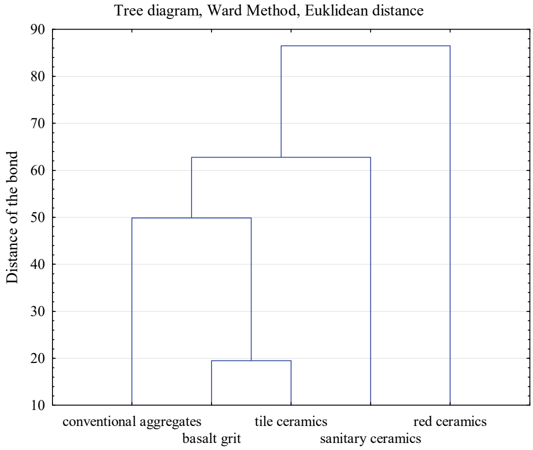

Fig. 6. Dendrogram of division of concretes

4. Summary

Having joined the European Union, Poland has committed herself to comply with European directives concerning a systematic increase in the amount of recycled waste. The present-day state of technology makes it possible to process various forms of unwanted matter into recycled raw materials. However, there are many substances whose storage, although non-aggressive towards the environment, increases the quantity of produced waste. Such substances include ceramics which cannot be bio-reprocessed and, due to growing demand for ceramic products, the amount of this type of waste is on the increase. As a result, attempts are made to search for rational ways of their use. Utilisation of building waste includes production of concrete made with aggregates from these materials. The present research, involving an application of statistical methods, demonstrated that aggregates of building waste materials of sanitary ceramics are suitable for use as aggregate for concrete production, the concrete having superior strength parameters compared with concrete produced using conventional aggregate. The poorest concrete quality parameters were obtained when conventional aggregate was replaced with red ceramic aggregate. Parameters of concretes produced using tile ceramics and sanitary ceramics demonstrated that the aggregates can be a substitute of gravel aggregate. Utilisation of recycled aggregate for concrete production may contribute to reduction in the amount of stored waste materials and reduction in demand for natural aggregate.

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Abstract

The work presents statistical analysis and comparison of quality parameters of concretes produced using conventional and recycled aggregates. The analysis is the continuation of the authors' previous research. The following properties of aggregates were tested: bulk density, specific density, water absorbability, crushing rate, and concrete properties such as compressive strength and tensile strength as well as compressive strength in a corrosive environment. There were determined statistical differences between the characteristics for all the aggregate and concrete types. The analysis demonstrated that concrete containing red ceramics had significantly the lowest values of compressive strength and tensile strength. Use of sanitary and tile ceramics significantly improved concrete properties. Cluster analysis revealed that concretes containing conventional aggregates (gravel and basalt grit) and tile ceramics were the most similar in terms of all the characteristics (compressive strength, tensile strength, compressive strength in a corrosive environment and Al_2O_3 and SiO_2 contents).

Key words:
sanitary ceramics, quality parameters, recycled substance, principal component analysis, cluster analysis

Wykorzystanie metod statystycznych do porównania właściwości betonów wytworzonych z odpadów budowlanych

Streszczenie

W pracy przedstawiano statystyczną analizę i porównanie parametrów jakościowych betonów wytworzonych z udziałem kruszyw tradycyjnych i recyklingowych. Analiza ta jest kontynuacją wcześniejszych badań własnych. Analizie statystycznej zostały poddane cechy kruszyw (gęstość objętościową, gęstość właściwa, nasiąkliwość i współczynnik rozkruszenia) oraz cechy betonów (odporność na ściskanie i rozciąganie oraz ściskanie w środowisku korozyjnym). Określono statystyczne różnice pomiędzy cechami dla wszystkich rodzajów kruszyw i betonów. Analiza wykazała, że beton do produkcji którego użyto ceramiki czerwonej odznaczał się istotnie niższymi wartościami odporności na ściskanie i rozciąganie. Zastosowanie ceramiki sanitarnej i glazurniczej w istotny sposób polepszyło właściwości betonów z tych kruszyw. Na podstawie analizy skupień ustalono, że pod względem wszystkich cech (wytrzymałości na ściskanie, rozciąganie, ściskanie w środowisku korozyjnym, zawartości Al_2O_3 i SiO_2) najbardziej podobne okazały się betony oparte na kruszywach tradycyjnych (żwirowym i bazaltowym) i ceramice glazurniczej

Słowa kluczowe:
ceramika sanitarna, parametry jakościowe, substancja recyklingowa,
analiza składowych głównych, analiza skupień

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Circulation Conditions Determining High PM_{10} Concentrations in the Sącz Basin (Poland)

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1. Introduction

Increasing amounts of hazardous pollutants are present in the air. This is due to the progressive growth of industry, including the automotive industry, and to burning of solid fuels for heating purposes in individual households. Particularly harmful are fine suspended particles, and among these PM_{10}, with a diameter below 10 μm. Particles of such small size easily penetrate the upper respiratory tract and lungs, causing dyspnoea and cough and exacerbating allergic symptoms. However, health effects can be much more serious if toxic substances are absorbed on the surface of the particles (Degórska, 2016; American Meteorological Society, 2014; Pascal et al. 2013; Jacobson, 2002).

Most scientific studies dealing with air pollution focus on identifying emission sources and the volume of emissions in urban and industrial agglomerations (Pasela et al. 2017; Whiteman et al., 2014; Russo et al. 2014; Trivedi et al. 2014; Wang et al. 2014). The authors of some studies have attempted to determine the effect of meteorological conditions on the level of pollution concentrations (Kalbarczyk et al. 2018; Czarnecka & Niedzgorska-Lencewicz 2017; Palarz 2014; Bokwa 2012; Majewski et al. 2018; Majewski & Przewoźniczuk 2009b; Walczewski 2009; Malek et al. 2006; Kukkonen et al. 2005).

Malek et al. (2006) described the meteorological determinants of one of the largest smog episodes in the United States. The authors noted that a high concentration of $PM_{2.5}$ (fine particulates with a diameter below 2.5 μm) in a relatively small metropolis with about 100,000 inhabitants was caused by adverse meteorological conditions impeding the dispersion of air pollutants and by the unfavourable location of the town in concave terrain.

The problem of air pollution in upland and mountainous areas of southern Poland and determination of the influence of meteorological and circulation conditions on PM$_{10}$ concentrations has been the subject of numerous scientific works (Tomaszewska 2010; Bokwa 2012, Palarz 2014). Walczewski (2009) and Hajto & Rozwoda (2010), based on the example of cities located in basins, have shown that certain characteristic types of synoptic conditions, especially those accompanied by temperature inversions, may adversely affect the sanitary state of the air. Palarz (2014) and Palarz & Celiński-Mysław (2017) have demonstrated that the location of a city in concave terrain is particularly conducive to stagnation of cold air and the formation of cold pools, as well as the appearance of inversion layers that interfere with mixing of the air. They observed the highest concentrations of pollutants during night-time periods accompanied by thermal inversions associated with specific circulation types.

In many cities in Poland, PM$_{10}$ concentrations very often exceed the limit values (Adamek & Ziernicka 2017, Pasela et al. 2017, Majewski & Przewoźniczuk 2009a). This also applies to Nowy Sącz, which is located on the flat bottom of the Sącz Basin. According to the WHO report, Nowy Sącz ranked 14th in 2016 and 10th in 2017 among the most polluted cities in the European Union (WHO report 2017).

A review of existing works shows that in addition to monitoring of air pollution and inventory of sources of emissions of harmful substances to the atmosphere, it is very important to recognize the weather conditions that are conducive to the concentration of air pollutants in a given location. This knowledge is particularly important in predicting the occurrence of high concentrations. This prompted the authors of the present study to analyse the dependence of the level of particulate matter in the air of the Sącz Basin on circulation conditions. The main objective of the research was to examine the influence of the type of atmospheric circulation on the PM$_{10}$ concentrations in particular seasons of the year.

2. Study area, materials and methods

The Sącz Basin is located in the south-eastern part of the Lesser Poland Voivodeship and constitutes a large concave landform with a bottom situated at an altitude of 280-300 m above sea level (Kondracki, 2002). The area of the basin is about 300 km^2, of which its flat bottom occupies about 80 km^2. The bottom of the basin was formed by the rivers Dunajec, Poprad and Kamienica Nawojowska, which belong to the Upper Vistula River Basin. The Sącz Basin is surrounded by the elevations of the Rożnów Foothills to the north, the Low Beskids to the east, Beskid Sądecki to the south, and the Island Beskids to the west. The surrounding areas rise to a height of several hundred metres above the bottom of the basin. Nowy Sącz is located in the centre of the flat bottom of the valley. It is the third most populous city in the Lesser Poland Voivodeship and has the fifth largest area (Fig. 1).

The study used average daily PM_{10} concentrations measured from December 2006 to November 2016 at the air monitoring reference station in Nowy Sącz, belonging to the Regional Inspectorate for Environmental Protection in Krakow. The monitoring station is located on Nadbrzeżna Street on the flat bottom of the Sącz Basin at 305 m above sea level, with geographic coordinates 20°42'52"E 49°37'09"N. The station is surrounded by dispersed buildings, and the results of measurements performed at the station represent the background of air pollution in the built-up area of the Sącz Basin.

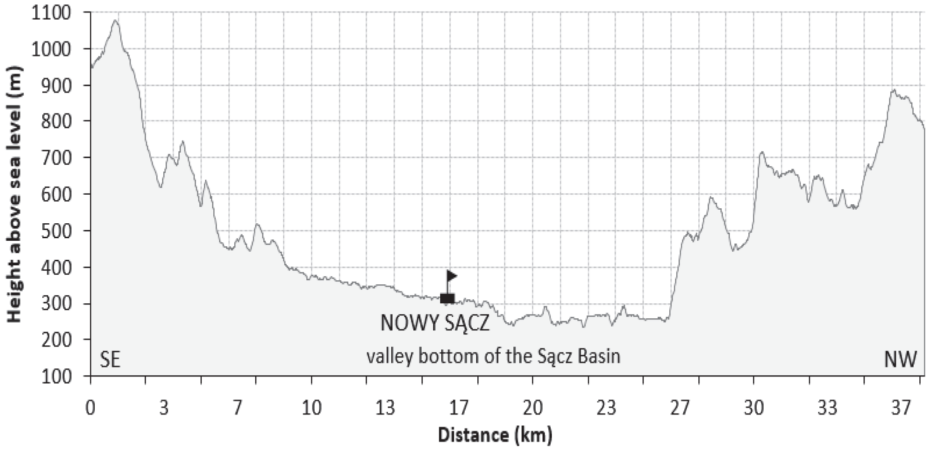


Fig. 1. Location of the air monitoring station in the SE-NW profile of the Sącz Basin

A calendar of atmospheric circulation types for southern Poland, developed by Niedźwiedź (2017), was also used in the research. It distinguishes 21 types of atmospheric circulation depending on the pressure system and the direction of incoming of air masses (Table 1).

PM_{10} concentration limits were adopted in accordance with the Regulation of the Minister of the Environment of 24 August 2012 on the levels of certain substances in the air (Journal of Laws (Dz.U.) 2012, item 1031).

Table 1. Circulation types for southern Poland (Niedźwiedź 2017)

Type	Anticyclonic conditions (a)	Type	Cyclonic conditions (c)
Na	North	*Nc*	North
NEa	North-east	*NEc*	North-east
Ea	East	*Ec*	East
SEa	South-east	*SEc*	South-east
Sa	South	*Sc*	South
SWa	South-west	*SWc*	South-west
Wa	West	*Wc*	West
NWa	North-west	*NWc*	North-west
Ca	Central anticyclonic	*Cc*	Central cyclonic
Ka	Anticyclonic wedge or ridge of high pressure	*Bc*	Trough of low pressure
*X**	Unclassified conditions	*X**	Unclassified conditions

* Note – type X is unclassified, so it was included in both anticyclonic and cyclonic conditions

Table 2. Acceptable PM_{10} concentrations according to the Regulation of the Minister of the Environment of 24 August 2012 on the levels of certain substances in the air Dz.U.(2012)[1] and the WHO (2005)[2]

Averaging period of measurement results	Acceptable concentration ($\mu g \cdot m^{-3}$)[1,2]	Acceptable frequency of exceedances[1]	Information level ($\mu g \cdot m^{-3}$)[1]	Alarm level ($\mu g \cdot m^{-3}$)[1]
24 hours	50	35 times/year	200	300

Note: [2] The WHO standard does not specify the acceptable frequency of exceedances of the acceptable level, information level or alarm level

The collected data on average daily PM_{10} concentrations were used to calculate seasonal mean values for spring, summer, autumn and winter for the period from December 2006 to November 2016. Based on the limit value for 24-hour average PM_{10} concentration ($50\ \mu g \cdot m^{-3}$), the frequency of its exceedances (%) was calculated in the analysed time intervals, as well as the frequency of exceedances of the information level ($200\ \mu g \cdot m^{-3}$) and alarm level ($300\ \mu g \cdot m^{-3}$) (Table 2).

In the last stage of the research, for each of the 21 atmospheric circulation types, the mean, maximum and minimum PM_{10} concentrations were calculated for the analysed time intervals, and then the mean values were plotted against the frequency of these types in each season.

3. Results

In the decade from 2006 to 2016, air pollution in Nowy Sącz exceeded acceptable levels of pollutant concentrations (Journal of Laws of 2012, item 1031, WHO 2006) on 34% of days of the year. The average daily PM_{10} concentration was 85 $\mu g \cdot m^{-3}$ for winter, 45 $\mu g \cdot m^{-3}$ for spring, 25 $\mu g \cdot m^{-3}$ for summer, and 49 $\mu g \cdot m^{-3}$ for autumn. The highest PM_{10} concentrations were recorded in the winter of 2010/2011 (Fig. 2). Pronounced seasonal variation in concentrations was observed over the course of the year. The particulate concentration increased in the colder half of the year and decreased in the warmer half.

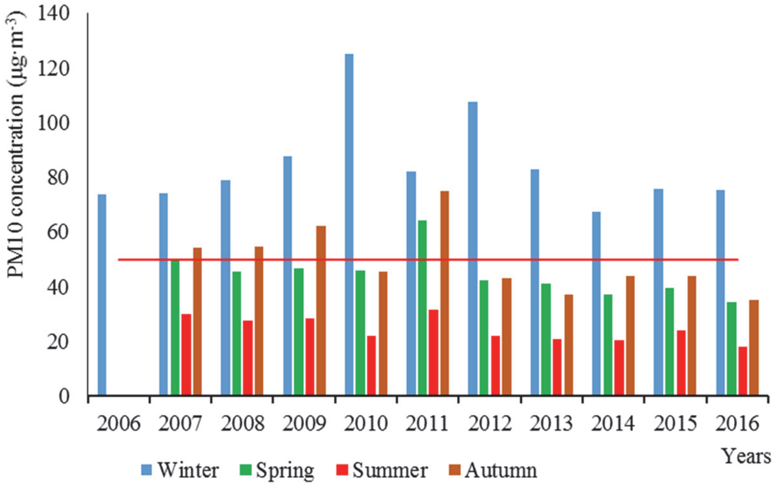


Fig. 2. Mean daily PM_{10} concentrations ($\mu g \cdot m^{-3}$) in seasons of successive years of the research period (horizontal line indicates the acceptable daily concentration)

The most days when standards were exceeded were recorded in the coldest months of the year (Tables 3 and 4). The frequency (%) of exceedances of the PM_{10} limit values was 69% for winter, 36% for the autumn, 30% for spring, and only 2% for summer (Table 3).

Exceedances of the information level and the alarm level occurred almost exclusively in the winter months, i.e. in December, January and February (Tab. 4). The most exceedances the limit values were found in 2011-162 days (47%), while the acceptable annual number is 35 days (9.6%). The acceptable, information and alarm levels were most frequently exceeded in 2009, 2010 and 2012, and in February 2012 the information level was exceeded on as many as 30% of days.

Table 3. Frequency of days (%) in which the acceptable concentration of PM_{10} was exceeded in Nowy Sącz (2006-2016)

Frequency	Winter			Spring			Summer			Autumn		
	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
Mean	69.5	66.7	69.4	58.1	30.4	1.4	0.7	0.7	3.9	13.3	41.9	53.3
Max	93.5	90.3	85.7	87.1	56.7	6.5	6.7	6.5	22.6	43.3	74.2	90.0
Min	51.6	41.9	35.7	38.7	10.0	0.0	0.0	0.0	0.0	0.0	12.9	30.0
Mean for season	68.5			30.0			1.8			36.2		
Mean for year	33.9											

Atmospheric circulation is one of the basic processes shaping weather conditions. As this is a highly variable process in time, there is a need for research aimed at determining how variation in the degree of air pollution depends on the prevailing type of synoptic conditions. In the Sącz Basin, weather conditions are highly variable, which is linked to the movement of pressure systems, as well as the very frequent and active incoming air masses from various directions. In the analysed multi-annual period from 2006 to 2016, anticyclonic types were predominant, occurring on 53% of days in the year. Among these, the most frequent were high-pressure stagnation systems (anticyclonic wedge *Ka*), with a frequency from 11% in autumn to 13% in summer. Low-pressure conditions appeared on 46% of days of the year, and the most common type of circulation was the low-pressure trough *Bc* – 12%. Advections from the west (*Wc* and *Wa*) and from the south-west (*SWc* and *SWa*) and north-west (*NWc* and *NWa*) sectors, which are most typical of the climate of southern Poland, were somewhat less common.

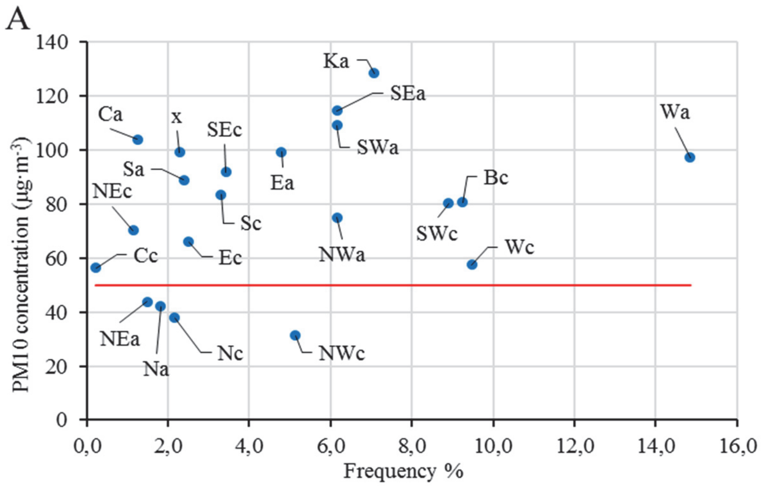
Table 4. Frequency of days (%) in which the acceptable (A), information (B) and alarm (C) levels of PM_{10} concentration was exceeded in Nowy Sącz (2006-2016)

Month	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016
January	-	19-0-0	58-0-0	76-7-14	75-7-14	63-7-0	45-13-0	61-10-0	70-0-0	52-0-0	81-3-0
February	-	66-0-0	55-7-0	82-7-0	82-7-0	86-0-0	53-30-0	62-0-0	64-0-0	83-0-0	34-0-0
March	-	53-0-3	45-0-0	64-0-0	64-0-0	83-3-0	57-0-0	57-0-0	43-0-0	72-0-0	40-0-0
April	-	33-0-0	40-0-0	20-0-0	20-0-0	55-0-0	10-0-0	23-0-0	17-0-0	10-0-0	10-0-0
May	-	0-0-0	0-0-0	0-0-0	0-0-0	6- 0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0
Jun	-	0-0-0	0-0-0	0-0-0	0-0-0	7-0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0
July	-	6-0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0
August	-	6-0-0	0-0-0	0-0-0	0-0-0	23-0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0
September	-	14-0-0	20-0-0	4-0-0	4-0-0	43-0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0
October	-	58-0-0	74-0-0	67-0-0	67-0-0	58-0-0	36-0-0	33-0-0	23-0-0	29-0-0	0-0-0
November	-	43-3-0	47-3-0	34-0-0	34-0-0	87-3-0	60-0-0	31-0-0	40-0-0	53-0- 0	40-0-0
December	70-0-0	61-6-6	48-6-0-	70-10-0	70-0-0	52-3-0	87-6-0	61-0-0	68-0-0	90-0-0	-
Mean for year	-	30-1-1	32-1-0-	35-2-1	35-2-1	47-1-0	29-4-0	27-1-0	27-0-0	33-0-0	-

Legend: *(A-B-C): A – acceptable level, B –information level, C – alarm level
Objaśnienia:* (A-B-C): A – poziom dopuszczalny, B – poziom informowania, C – poziom alarmowy

Table 5. Extreme values of PM_{10} concentrations ($\mu g \cdot m^{-3}$) for each type of atmospheric circulation (2006-2016)

Type	Spring		Summer		Autumn		Winter	
	Max	Min	Max	Min	Max	Min	Max	Min
Na	96	14	25	11	85	9	80	15
NEa	115	11	36	7	68	14	99	17
Ea	152	11	59	12	93	13	378	14
SEa	172	18	75	19	150	19	388	25
Sa	118	21	71	19	211	18	174	22
SWa	193	21	45	11	236	15	296	19
Wa	119	16	48	11	185	13	328	14
NWa	127	17	44	7	179	8	220	10
Ca	127	18	41	16	138	13	278	55
Ka	152	16	57	10	210	13	425	30
Nc	132	8	34	8	52	6	71	13
NEc	88	6	39	6	40	6	135	25
Ec	158	10	43	10	70	8	141	28
SEc	378	17	53	17	138	11	251	22
Sc	84	12	65	12	108	11	176	16
SWc	150	10	47	10	105	10	225	16
Wc	162	10	35	10	163	9	193	7
NWc	89	9	32	9	81	6	105	10
Cc	43	8	10	8	13	13	77	36
Bc	132	8	72	8	134	11	236	10
X	150	13	36	13	103	21	189	28



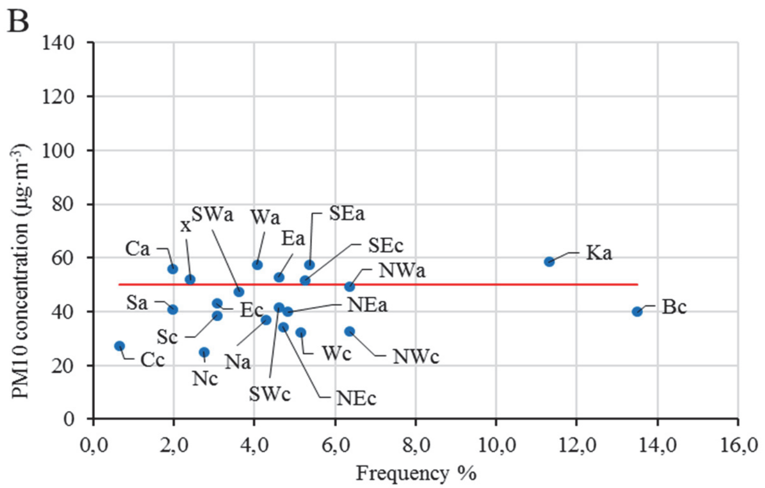


Fig. 3a. Mean concentration of PM_{10} and frequency of circulation type during: (A) winter and (B) spring, in Nowy Sącz (2006-2016) (horizontal line indicates the acceptable daily concentration)

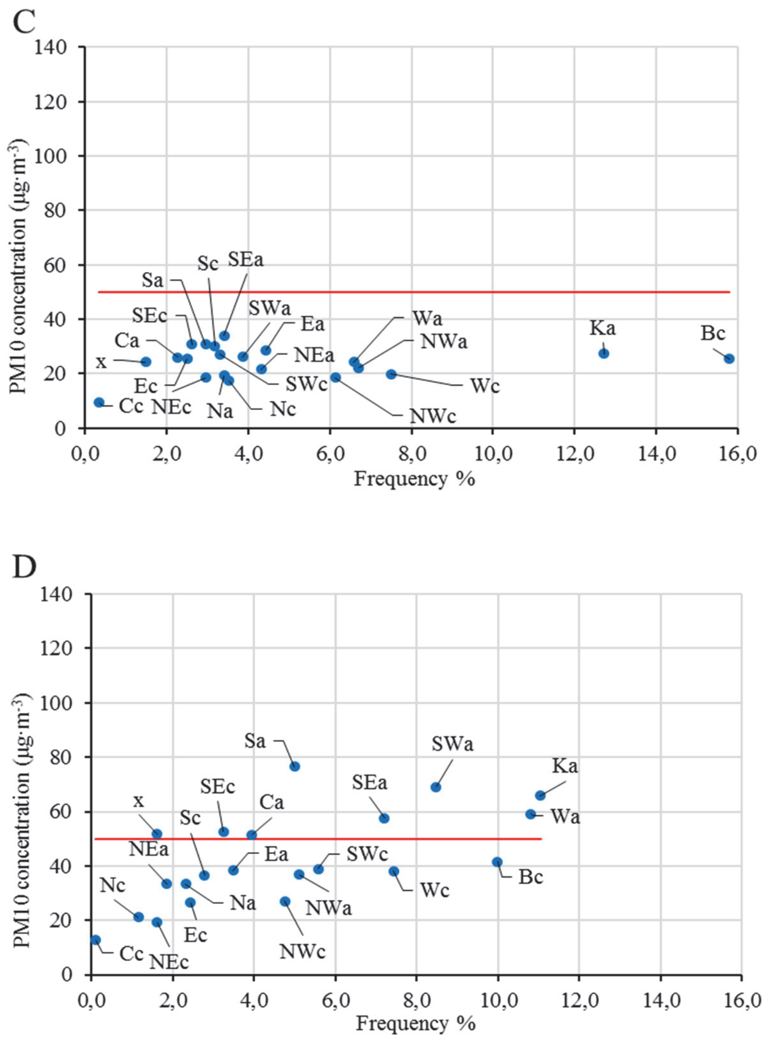


Fig. 3b. Mean concentration of PM_{10} and frequency of circulation type during: (C) summer and (D) autumn in Nowy Sącz (2006-2016) (horizontal line indicates the acceptable daily concentration)

Irrespective of the season, the highest PM_{10} concentrations were found in non-directional anticyclonic types (*Ka* and *Ca*) as well as in the case of advections of air masses from southern directions (*SEa*, *Sa* and *SWa*). The highest PM_{10} concentrations were observed in winter, on average 128 $\mu g \cdot m^{-3}$ for *Ka*, 115 $\mu g \cdot m^{-3}$ for *SEa*, and 109 $\mu g \cdot m^{-3}$ for *SWa*. In non-directional *Ka* conditions in December 2007, PM_{10} concentrations exceeded the alarm level (300 $\mu g \cdot m^{-3}$) twice, reaching a maximum value of 425 $\mu g \cdot m^{-3}$ (Tables 4 and 5).

The lowest PM_{10} concentrations throughout the year accompanied low pressure systems, especially in the case of advections of air from northern directions (*NWc*, *Nc* and *NEc*) and the non-directional type *Cc*. In cyclonic conditions, concentrations of particulate matter exceeding the limit value were noted mainly in winter, and less often in autumn and spring. High PM_{10} concentrations were associated with non-directional conditions (*Bc* and *X*) and with advections of air from southern directions (*SEc*, *Sc* and *SWc*).

The lowest PM_{10} concentrations in all types of atmospheric circulation were noted in the summer months and very rarely exceeded the limit values (Tables 3 and 5, Fig. 2, 3a and 3b).

4. Discussion

The analysis confirmed the existence of a relationship between the type of atmospheric circulation and the PM_{10} concentration in Nowy Sącz. The results coincide with those reported by numerous authors who have analysed various aspects of the influence of atmospheric circulation on the concentration of air pollution (Adamek & Ziernicka, 2018, Leśniok et al., 2010, Russo et al., 2014, Bokwa, 2012, Niedźwiedź & Olecki, 1994). In Nowy Sącz, which represents the built-up area of the Sącz Basin, the average seasonal PM_{10} concentrations were higher than in urban areas located in the lowland part of Poland (Kalbarczyk et al. 2018, Adamek & Ziernicka-Wojtaszek, 2018, Czrnecka & Nidzgorska-Lencewicz 2017). Bokwa (2012) showed that in Krakow, which has equally unfavourable ventilation conditions as Nowy Sącz, high PM_{10} concentrations were associated with incoming air masses from southern sectors in high-pressure conditions (*SEa*, *Sa* and *SWa*) and with the presence of an anticyclonic wedge (*Ka*). The author explained the reasons for the increase in the concentration of air pollution during advections from the southern sector. In directional and non-directional low-pressure conditions, warmer air flows in from lower latitudes, which promotes thermal inversion. In the valleys of the Beskid Mountains, the frequency of atmospheric calm in the winter months ranges from 18% to 21% (Wiszniewski 1971, Lorenc 2005). Miczyński (1990) emphasized that in the Sącz Basin PM_{10} concentrations exceeding 300 $\mu g \cdot m^{-3}$, i.e. the alarm level, most often occurred in conditions of atmospheric calm and at wind speeds below 2.0 $m \cdot s^{-1}$. The location of Nowy Sącz in a basin and the prevalence of days with anticyclonic weather are conducive to the formation of temperature inversion and thus greater concentrations of pollutants. Miczyński (1990) stressed that the dense build-up of Nowy Sącz and the intensity of vehicular traffic combined with the limited ventilation of the city additionally augment the concentration of particulate air pollutants. In the present study, the highest exceedances of limit values were observed in high pressure conditions, which is consistent with the observations of Miczyński (1990), Niedźwiedź & Olecki (1994), Palarz & Celiński-Mysław (2017) and other authors. Skowera & Wojkowski (2009) found that in the Upper Vistula River Basin, the most common circulation types in autumn and winter were non-directional high-pressure circulation (*Ka* and *Ca*) and advections from the east (*Ea*), south (*Sa*) and west (*Wa*). The authors observed the greatest negative air temperature deviations from the long-term average in these situations. The low temperatures resulted in higher levels of solid fuel combustion for heating purposes, mainly by individual households, which increased emissions to the atmosphere.

Circulatory conditions and the city's location at the bottom of the Sącz Basin are the main factors shaping the sanitary condition of the air in Nowy Sącz. However, the very high particulate concentrations in the Sącz Basin are due primarily to high emissions from industrial pollution and low-stack emissions. In Nowy Sącz, emissions of particulates from fuel combustion ranged from 215 Mg in 2008 to 77 Mg in 2016 (GUS, 2008-2017), which was confirmed by the high concentrations recorded at the air monitoring station.

5. Conclusions

In Nowy Sącz, located at the bottom of the Sącz Basin, the permissible 24-hour PM_{10} concentration was exceeded on average on 124 times per year in 2006-2016. The acceptable frequency of exceedances is 35 days per year (DZ.U. 2012, poz. 1031), so this limit was exceeded by over 89 days, which was significantly higher than in other parts of Poland.

The highest PM_{10} concentrations exceeding the limit value were observed in winter and autumn in anticyclonic non-directional conditions (*Ka* and *Ca*) and during advections of air masses from southern directions (*SEa*, *Sa* and *SWa*). These conditions most often determined the weather in southern Poland.

Significantly lower PM_{10} concentrations accompanied low-pressure weather. During cyclonic weather, the highest concentrations exceeding limit values were observed in autumn and winter and were linked to the appearance of non-directional conditions (*Bc* and *X*) or advections of air from southern directions (*SEc*, *Sc* and *SWc*).

The analyses indicate that recognition of circulation conditions determining levels of particulate concentrations in the air can be very useful in the predicting the occurrence of high PM_{10} concentrations in the Sącz Basin.

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Abstract

The aim of the study was to investigate the level of atmospheric particulate matter in the Sącz Basin depending on circulation conditions. The study used average daily PM_{10} concentrations measured from December 2006 to November 2016 at the air monitoring reference station in Nowy Sącz, belonging to the Regional Inspectorate for Environmental Protection in Krakow. A calendar of circulation types for southern Poland was used as well.

The collected data on average daily PM_{10} concentrations were used to calculate seasonal mean values for spring, summer, autumn and winter for the period from December 2006 to November 2016. Based on the limit value for 24-hour average PM_{10} concentration (50 $\mu g \cdot m^{-3}$), the frequency of its exceedances (%) was calculated in the analysed time intervals, as well as the frequency of exceedances of the information level (200 $\mu g \cdot m^{-3}$) and alarm level (300 $\mu g \cdot m^{-3}$). Then, particulate concentrations were analysed with respect to types of synoptic conditions. For this purpose, average PM_{10} concentrations in different types of synoptic conditions and the frequency of these types in each season were calculated.

In the decade from 2006 to 2016, the highest PM_{10} concentrations in Nowy Sącz were observed in the winter and the lowest in the summer. The average daily PM_{10} concentration was 85 $\mu g \cdot m^{-3}$ for winter, 45 $\mu g \cdot m^{-3}$ for spring, 25 $\mu g \cdot m^{-3}$ for summer, and 49 $\mu g \cdot m^{-3}$ for autumn. The most days in which the acceptable PM_{10} values were exceeded were recorded in December, January and February (66.7-69.5%). The acceptable, information and alarm levels were most frequently exceeded in 2009, 2010 and 2012, and in February 2012 the information level was exceeded on as many as 30% of days.

The research showed a relationship between the PM_{10} level and the type of accompanying atmospheric circulation. The highest exceedances of the acceptable values were nearly always observed in certain characteristic circulation conditions. Irrespective of the season, the highest PM_{10} concentrations were found in anticyclonic non-directional types (*Ka* and *Ca*) and in the case of advections of air masses from the southern sector (*SEa*, *Sa* and *SWa*). The highest PM_{10} concentrations were observed in winter, on average 128 $\mu g \cdot m^{-3}$ for *Ka*, 115 $\mu g \cdot m^{-3}$ for *SEa* and 109 $\mu g \cdot m^{-3}$ for *SWa*.

Lower concentrations accompanied low-pressure systems. In cyclonic conditions, the highest concentrations of particulate matter exceeding the acceptable level were recorded especially in autumn and winter. They were mainly associated with non-directional types (*Bc*, *Cc* and *X*).

Keywords:
PM_{10}, level of particulate matter, types of atmospheric circulation, Sącz Basin.

Cyrkulacyjne uwarunkowania występowania wysokich stężeń pyłu PM_{10} w Kotlinie Sądeckiej (Poland)

Streszczenie

Celem pracy było zbadanie poziomu stopnia zapylenia powietrza atmosferycznego w Kotlinie Sądeckiej w zależności od uwarunkowań cyrkulacyjnych. W badaniach wykorzystano średnie dobowe stężenia pyłu zawieszonego PM_{10} pomierzone w okresie od grudnia 2006 roku do listopada 2016 roku na stacji referencyjnej monitoringu powietrza w Nowym Sączu należącej do Wojewódzkiego Inspektoratu Ochrony Środowiska w Krakowie. Wykorzystano również kalendarz typów cyrkulacji dla obszaru Polski Południowej.

Zebrane dane o średnim dobowym stężeniu pyłu PM_{10} posłużyły do obliczeń wartości średnich sezonowych dla wiosny, lata, jesieni i zimy za okres od grudnia 2006 roku do listopada 2016 roku. Na podstawie dopuszczalnej wartości średniego dobowego (24-godzinnego) stężenia pyłu PM_{10} (50 $\mu g \cdot m^{-3}$) obliczono w analizowanych przedziałach czasowych częstość jego przekroczeń (%), a także częstość przekroczeń poziomu informowania (200 $\mu g \cdot m^{-3}$) i poziomu alarmowego (300 $\mu g \cdot m^{-3}$).

Następnie stężenia pyłu przeanalizowano na tle sytuacji synoptycznych. W tym celu obliczono średnie wartości stężeń pyłu PM_{10} w poszczególnych typach sytuacji synoptycznych oraz częstości występowania tych typów w analizowanych sezonach kalendarzowych.

W badanym dziesięcioleciu 2006-2016 najwyższe wartości stężeń pyłu PM_{10} obserwowano w Nowym Sączu w sezonie zimowym, a najniższe latem. Średnie dobowe stężenie pyłu PM_{10} wyniosło dla sezonu zimowego 85 $\mu g \cdot m^{-3}$, wiosennego 45 $\mu g \cdot m^{-3}$, letniego 25 $\mu g \cdot m^{-3}$, a jesiennego 49 $\mu g \cdot m^{-3}$. Najwięcej dni, w których wystąpiło przekroczenie wartości dopuszczalnych pyłu PM_{10} zanotowano w grudniu, styczniu i lutym (66,7-69,5%). Przekroczenia poziomów dopuszczalnych, informowania i alarmowych najczęściej obserwowano w latach 2009, 2010 i 2012, a w lutym 2012 roku aż w 30% dni przekroczone były poziomy informowania.

Przeprowadzone badania wykazały zależność pomiędzy stopniem zapylenia pyłem PM_{10} a występującym typem cyrkulacji atmosferycznej. Najwyższe przekroczenia wartości dopuszczalnych prawie zawsze były obserwowane tylko w pewnych charakterystycznych warunkach cyrkulacyjnych. Niezależnie od pory roku, najwyższe poziomy stężeń pyłu PM_{10} stwierdzono w sytuacjach antycyklonalnych bezadwekcyjnych (*Ka* i *Ca*) oraz przy adwekcjach mas powietrza z sektora południowego (*SEa, Sa* i *SWa*). W sezonach zimowych obserwowano najwyższe wartości stężeń PM_{10}, średnio 128 $\mu g \cdot m^{-3}$ dla *Ka*, 115 $\mu g \cdot m^{-3}$ dla *SEa* i 109 $\mu g \cdot m^{-3}$ dla *SWa*.

Niższe stężenia towarzyszyły pogodzie niżowej. Podczas pogody cyklonalnej najwyższe zarejestrowane stężenia pyłu przekraczające dopuszczalny poziom, występowały szczególnie jesienią i zimą. Były one związane przede wszystkim z sytuacjami bezadwekcyjnymi (*Bc, Cc,* i *X*).

Słowa kluczowe:
PM_{10}, stopień zapylenia, typy cyrkulacji atmosferycznej, Kotlina Sądecka

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The Influence of the Soil Type on the Permeability of Petroleum Derivatives

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1. Introduction

Petroleum substances are chemical substances obtained under the oil rectification, which results in fractions of different molecular sizes (Nazir 2011, Piecuch et al. 2015). The fractions emitted from crude oil are gasoline, aviation fuels, diesel oils, lubricating oils, lubricants, asphalt, waxes and bitumens (Iloeje & Aniago 2016, Skwarczynski & Skwarczynska-Kalamon 2016). Petroleum substances are non-polar, lithophilic and slightly soluble in water (Gitipour et al. 2016, Piecuch & Dabrowski 2014). They have strong toxic and carcinogenic properties, they are dangerous for human health and life and easily penetrate into the environment (Piecuch & Piecuch 2013, Głobińska et al. 2017).

The sources of incidents involving petroleum substances and the oil itself are industrial processes, including failures of processing and extraction installations, storage and transport such as rail, road (tank disasters), pipeline and water transport (Alimohammadi-Jelodar & Karimpour-Fard 2018). The most serious effects occur in events related to pipeline transport due to its location and the most common reason of leakage of petroleum-derived substances from pipelines, is the theft of transported fuels, in particular gasoline. During the drilling of pipelines through thieves, there is an uncontrolled leakage of a substance that directly enters the ground and the aquatic environment (Streche et al. 2018, Piechota-Polanczyk et al. 2013). Additionally, crude products in Poland account for 91% of substances transported by land (Piechota-Polanczyk et al. 2018, Kowalska et al. 2018).

The dominant soils in Poland are brown and ground soils. The map of Polish soils has been divided into zone, non-zone, inter-zone and non-zonal soils (Uznije & Agunwamba 2011). The diversity of parent rocks cause the occurrence of not one, but several types of zone soils that make up the soil cover of Poland. They occupy 75% of the country's territory, and their representatives are brown soils, which constitute 50% of the country's surface, podzolic soil that constitutes about 26% of the area, rusty soils occupying 14% of the area, podzolic soils occupying about 10%. A representative of non-zone soils is a black earth, occupying about 1% of the total area of the country. Intra-zone soils occupy less than 25% of the country's surface, lining the bottoms of river valleys (Piechota-Polanczyk & Gorąca 2012). Their representatives are river rivers covering 5% of Poland, hydrogenic soils constituting 7.8% of the country's territory, peat soils occupying 6.5% of the country, black earth constituting about 1% of the country's surface and rendzinas occupying about 0.9% of the area. Non-zoned soils are works that do not have a well-developed soil profile (Piechota & Goraca 2011).

The water permeability of soils is defined as the amount of water soaked by a given cross-section of soil, at a given time, per unit of hydraulic slope. The measure of permeability is the permeability coefficient, which depends on the properties of the test medium. In laboratory tests, the liquid used during tests, the research method adopted and the calculation algorithm play a significant role in the filtration coefficient (Streche 2018). There are many methods for testing soil permeability: "Paramex" method – modeled on observations of water table fluctuations in hydrogenic holes caused by earthquakes ("ibid" 129); The "Slug test" method is based on the measurement of the speed of water state changes in the piezometer due to its inflow from the aquifer. Another method of water permeability is the Kamieński's pipe method, which allows a simple and quick determination of the approximate value of the soil filtration coefficient. It consists in measuring the speed of lowering the water table flowing through the studied soil at variable pressure of the water column.

The purpose of the work was to determine the influence of soil structure on the permeability of petroleum derivatives. The measurements were carried out on black earth and wetland soil using three petroleum substances, gasoline (95 octanes), diesel, used oil, and water as a reference liquid.

2. Materials and methods

2.1. Samples collection

The study on permeability of soils was carried out using Ostromęcki's method which allows to precisely determine the coefficient of soil permeability. The soil samples (wetland soil and black earth) were collected form lubuskie voivodship and placed in sealed containers.

Thanks to modifications, measurements can be made both in the field and in the laboratory using Ziemnicki's apparatus. Soil samples were taken up to Kopecky's cylinders with a capacity of 250 cm^3. The composition of Ziemnicki's apparatus includes: a liquid tank soaked through the soil, a dense grid under and over the soil sample. Each time 150 cm^3 of soil was analyzed. Next, to the weighted soil, 50 ml of tested liquid was added on the soil surface. The height "h", time of disappearance of the liquid mirror, total time of condensation and the amount of condensed substance were measured. The measurements continued with additional two volumes of liquid until the total of 150 ml was added. Measured parameters included permeability, permeability coefficient and capillary capacity. Permeability was calculated using the following equation (1):

$$P = V / (S \cdot t) \tag{1}$$

where:
P – soil unit permeability, [cm/s],
V – volume of liquid absorbed or soaked by S, [cm^3],
S – infiltration area, [cm^2],
t – total infiltration time, [s].

Permeability coefficient was calculated from the equation (2):

$$K_t = V / (S \cdot t \cdot i) \tag{2}$$

where:
K_t – coefficient of permeability,
S – infiltration area, [cm^2],
t – total infiltration time, [s],
i – drop in hydraulic pressure, i = h/l, [-],
h – the height of the liquid column in the cylinder,
counted from the bottom of the soil, [cm],
l – thickness of the soil layer, [cm].

Capillary capacity was calculated using equation (3):

$$P_k = (M_c - M_{c1}) / M_g \tag{3}$$

where:
P_k – capillary capacity of the tested soil, [g/g],
M_c – ass of liquid poured, [g],
M_{c1} – mass of liquid soaked, [g],
M_g – soil mass, [g].

All measurements were done in triplicates.

In the research gasoline 95 octanes, diesel and used oil were applied. The term “used oil” was used for the oil that was replaced from a car engine after one year of usage.

2.2. Statistical analysis

Data are presented as mean±standard error (SEM). Comparison between groups was performed using two-way ANOVA after verification of normality with Statistica 12.0 software. Data were considered statistically different when $p < 0.05$.

3. Results and discussion

The first analyzed parameter presented of Fig. 1 showed permeability of wetland soil and black earth for four liquids: water (as reference), gasoline, diesel and used oil. Permeability of water decreased with addition of subsequent volumes of liquid (Fig. 1A). Meanwhile, permeability of gasoline, diesel and used oil increased significantly with each added volume (Fig. 1A, $p < 0.001$). Interestingly, permeability of used oil was over 20-times lower comparing to gasoline and petrol tested in the same conditions (Fig. 1A, $p < 0.001$).
The results for the second tested soil, black earth, indicated that permeability for gasoline increased over 5-times with the second addition of 50 ml of gasoline ($p < 0.001$, Fig. 1B). Similarly, permeability for diesel and used oil showed similar pattern causing 3-time rise for gasoline ($p < 0.001$) and 4-time increase for water ($p < 0.001$, Fig. 1B).

Second analyzed parameter was permeability coefficient depicted on Fig. 2. Similarly, to results on Fig. 1 we observed a significant decrease of permeability coefficient for water in both wetland soil (Fig. 2A) and black earth (Fig. 2B) as well as an increase for gasoline ($p < 0.001$), diesel ($p < 0.001$) and used oil ($p < 0.001$) (Fig. 2).

Capillary capacity presented on Fig. 3 indicated that at the beginning gasoline and diesel capillary capacity was significantly lower compared to water ($p < 0.001$) for wetland soil (Fig. 3A) but not for black earth where gasoline capillary capacity was even higher compared to water ($p < 0.01$; Fig. 3B). Addition of subsequent volumes of liquid significantly decreased capillary capacity for all tested liquids in both soils type (Fig. 3). Additionally, capillary capacity for wetland soil was as low as zero when the third volume of diesel and used oil was added (Fig. 3A).

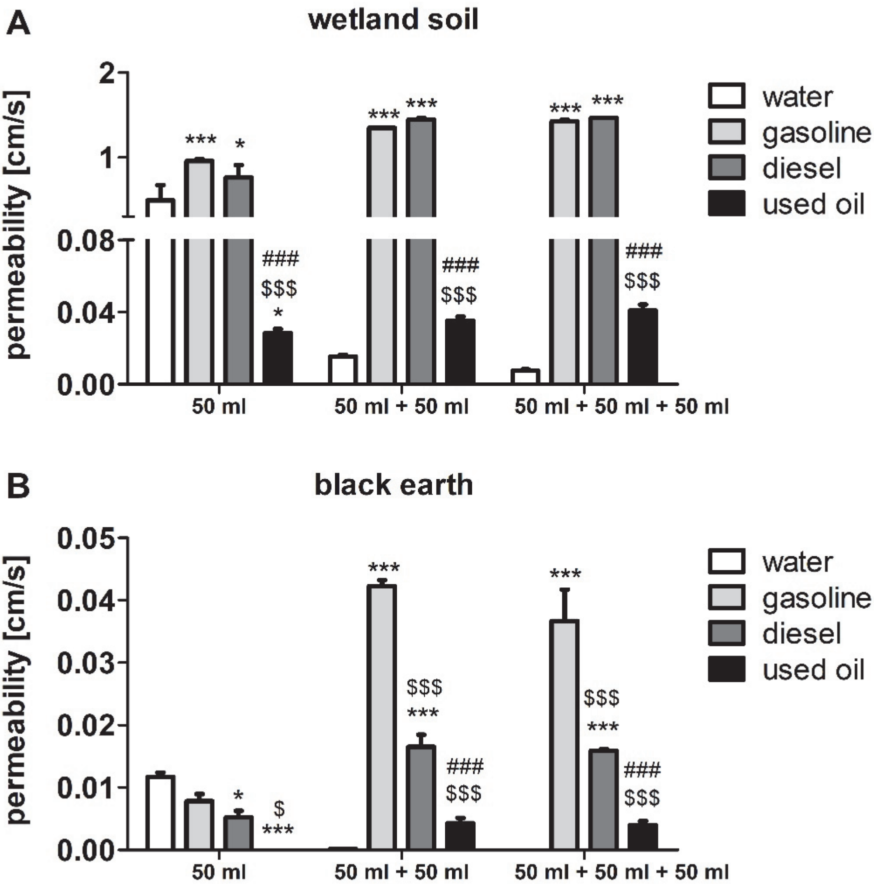

Fig. 1. Permeability of wetland soil (A) and black earth (B) for water, gasoline, diesel and used oil in the volume of 50 ml added subsequently to the total of three repetitions. Data are presented as mean±SEM. *p < 0.05; **p < 0.01, ***p < 0.001 vs water, ###p < 0.001 vs diesel; $p < 0.05; $$p < 0.01; $$$p < 0.001 vs gasoline

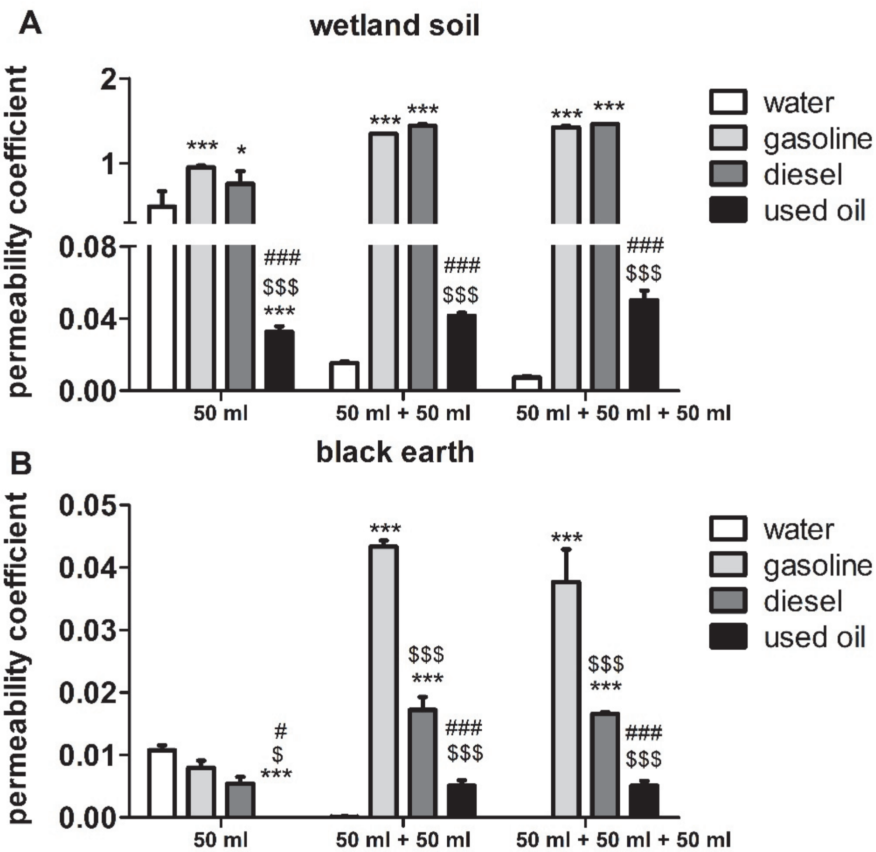

Fig. 2. Permeability coefficient of wetland soil (A) and black earth (B) for water, gasoline, diesel and used oil in the volume of 50 ml added subsequently to the total of three repetitions. Data are presented as mean±SEM. ***$p < 0.001$ vs water, #$p < 0.05$, ###$p < 0.001$ vs diesel; $$$$p < 0.001$ vs gasoline

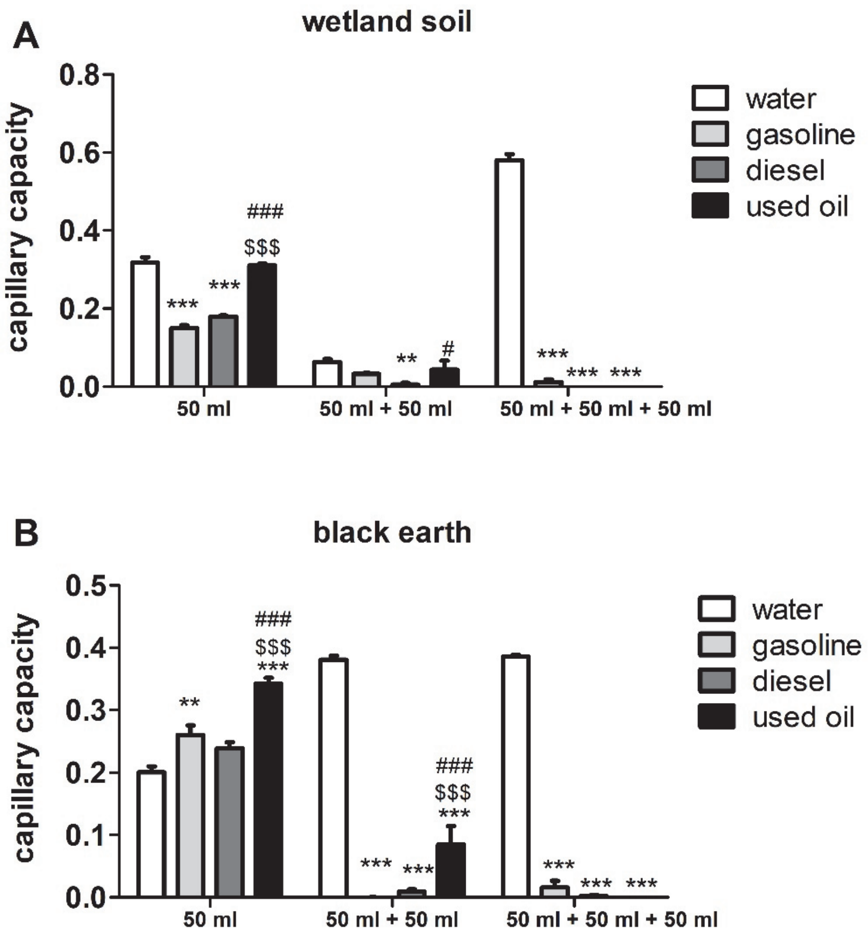

Fig. 3. Capillary capacity of wetland soil (A) and black earth (B) for water, gasoline, diesel and used oil in the volume of 50 ml added subsequently to the total of three repetitions. Data are presented as mean±SEM. $^{**}p < 0.01$, $^{***}p < 0.001$ vs water, $^{\#\#\#}p < 0.001$ vs diesel; $^{\$\$\$}p < 0.001$ vs gasoline

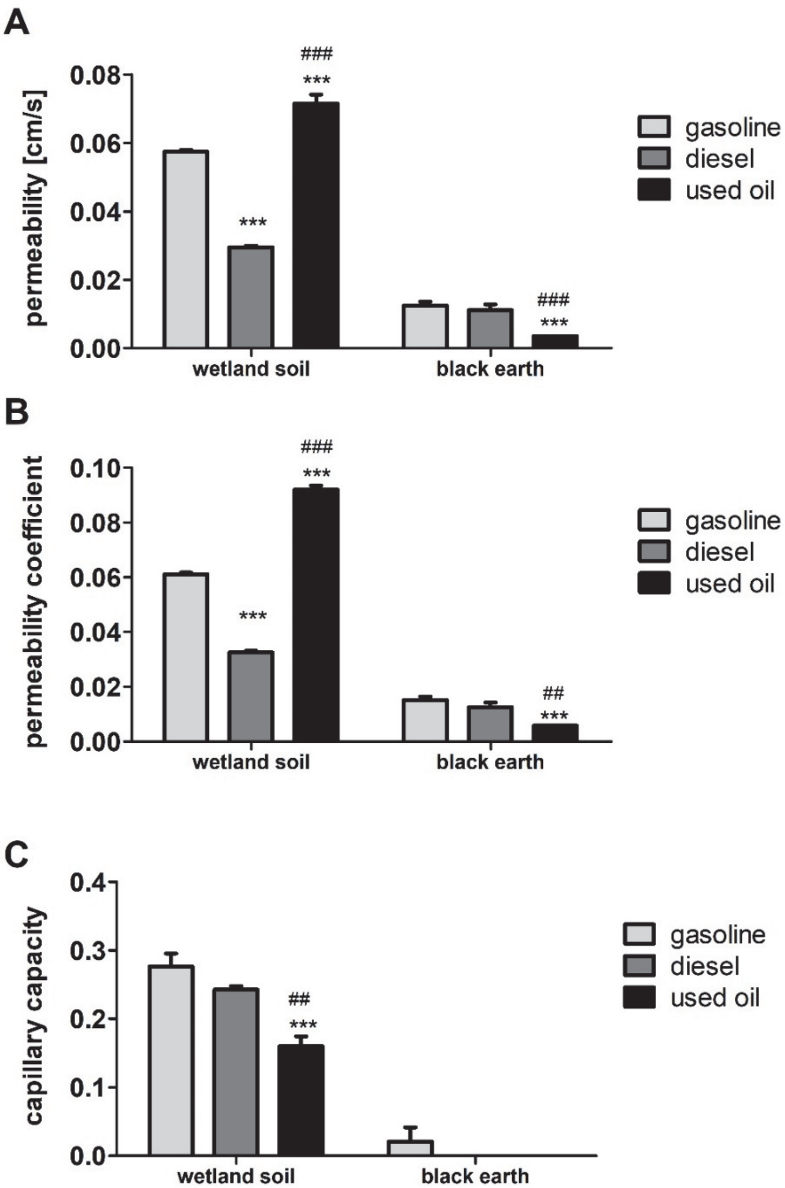

Fig. 4. The influence of experimental rain conditions on soil permeability (A), permeability coefficient (B) and capillary capacity (C) for gasoline, diesel and used oil. Data are presented as mean±SEM. ***$p < 0.001$ vs gasoline, ##$p < 0.01$, ###$p < 0.001$ vs diesel

Finally, comparison of wetland soil and black earth soils presented in Fig. 4 indicated that permeability, permeability coefficient and capillary capacity was 2-5-times higher for wetland soil compared to black earth for all tested liquids. The highest value of permeability and permeability coefficient was observed for used oil for wetland soil (Fig. 4a-B) but not for black earth where this fluid had the lowest values of analyzing parameters comparing to gasoline and diesel ($p < 0.001$, Fig. 4). Diesel and gasoline had similar permeability, permeability coefficient and capillary capacity on black earth but not on wetland soil where diesel had lower permeability compared to gasoline ($p > 0.05$, Fig. 4).

These results are in line with, Li et al. who presented that soil permeability can be changed when the soil is contaminated by oil pollutants, which can influence the transport of water or solute in the soil-water system (Li et al. 2009). In they paper Li et al. showed that soil polluted with crude oil had decreased permeability coefficient to the greater extent than diesel oil. Similar results were presented by Lopez et al. (2019).

4. Conclusions

This study aimed to determine the influence of soil structure on the permeability, permeability coefficient and capillary capacity wetland soil and black earth for gasoline, diesel and used oil using water as a reference liquid. The results indicated that permeability of gasoline, diesel and used oil increased significantly with each added volume while permeability of used oil was over 20-times lower comparing to gasoline and petrol tested in the same conditions. Meanwhile for black earth permeability of all tested fluids increased compared to water. Similar results was observed for permeability coefficient. Furthermore, capillary coefficient for wetland soil was lower for all tested liquids compared to water and it decreased with each added volume. On the contrary capillary coefficient for black earth was higher compared to water after adding of first volume of liquids but it decreased when additional volumes were added. Therefore, the results indicated that permeability of wetland soil is higher compared to black earth in case of gasoline and diesel but not used oil. Interestingly, permeability of black earth for diesel was markedly lower compared to wetland soil.

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Abstract

Petroleum substances are non-polar, lithophilic and very slightly soluble in water. They have strong toxic and carcinogenic properties, they are dangerous for human health and life; they easily get into the environment. The sources of incidents involving petroleum substances and the oil itself are industrial processes, including failures of processing and extraction installations, storage and transport, which includes rail, road (tank disasters), pipeline and water transport. Often there is an uncontrolled leakage of a substance that directly enters the ground and the aquatic environment. The dominant soils in Poland are brown and ground soils. The water permeability of soils is defined as the amount of water soaked by a given cross-section of soil, at a given time, per unit of hydraulic slope. The measure of permeability is the permeability coefficient, which depends on the properties of the test medium.

This study aimed to determine the influence of soil structure on the permeability, permeability coefficient and capillary capacity wetland soil and black earth for gasoline, diesel and used oil using water as a reference liquid.

The study on permeability of soils was carried out using Ostromęcki's method and Ziemnicki's apparatus. The soil samples (wetland soil and black earth) were collected form lubuskie voivodship. Each time 150cm^3 of soil was analyzed. Next, 50 ml of tested liquid was added on the soil surface and soaking time was recorded. The action was repeated 3 times to the total of 150 ml of tested fluid. Measured parameters included permeability, permeability coefficient and capillary capacity.

Permeability of gasoline, diesel and used oil increased significantly with each added volume ($p < 0.001$). While permeability of used oil was over 20-times lower comparing to gasoline and petrol tested in the same conditions ($p < 0.001$). The results for black earth, indicated that permeability for gasoline increased over 5-times with the second addition of 50 ml of gasoline ($p < 0.001$) and permeability for diesel and used oil lead to 3-time rise for gasoline ($p < 0.001$) and 4-time increase for water ($p < 0.001$). Analysis of capillary capacity showed that at the beginning gasoline and diesel capillary capacity was significantly lower compared to water ($p < 0.001$) for wetland soil but not for black earth where gasoline capillary capacity was even higher compared to water ($p < 0.01$). Addition of subsequent volumes of liquid significantly decreased capillary capacity for all tested liquids in both soils type. Furthermore, comparison of wetland soil and black earth soils indicated that permeability, permeability coefficient and capillary capacity was 2-5-times higher for wetland soil compared to black earth for all tested liquids.

The results indicated that permeability of wetland soil is higher compared to black earth in case of gasoline and diesel but not used oil. Interestingly, permeability of black earth for diesel was markedly lower compared to wetland soil.

Keywords:
permeability, permeability coefficient, capillary capacity, permeability of petroleum, permeability of soils

Przepuszczalność różnych typów ziemi w kontakcie z wybranymi substancjami ropopochodnymi, spotykanymi w akcjach ratowniczych Państwowej Straży Pożarnej

Streszczenie

Substancje ropopochodne są niepolarne, litofilne i bardzo słabo rozpuszczalne w wodzie. Mają silne właściwości toksyczne i rakotwórcze, są niebezpieczne dla ludzkiego zdrowia i życia; łatwo dostają się do środowiska. Źródłem wypadków z udziałem substancji ropopochodnych i samej ropy naftowej są procesy przemysłowe, w tym awarie instalacji przetwórczych i wydobywczych, magazynowania i transportu, które obejmują transport kolejowy, drogowy (katastrofy czołgowe), transport rurociągowy i wodny.

Często dochodzi do niekontrolowanego wycieku substancji bezpośrednio do ziemi i środowiska wodnego.

Dominującymi glebami w Polsce są gleby brunatne i gruntowe. Przepuszczalność wodną gleb definiuje się, jako ilość wody przesiąkniętej przez dany przekrój gleby, w określonym czasie, na jednostkę spadku hydraulicznego Miarą przepuszczalności jest współczynnik przepuszczalności, który zależy od właściwości badanego ośrodka.

Celem tego badania było określenie wpływu struktury gleby na przepuszczalność, współczynnik przepuszczalności i pojemność kapilarną gleby bagiennej i czarnoziemu dla benzyny, oleju napędowego i przepracowanego oleju przy użyciu wody jako cieczy referencyjnej.

Badanie przepuszczalności gleb przeprowadzono metodą Ostromęckiego i aparatem Ziemnickiego. Próbki gleby (bagiennej I czarnoziemu) pobrano z województwa lubuskiego. Za każdym razem analizowano 150 cm^3 gleby. Następnie dodano 50 ml badanej cieczy na powierzchnię gleby i zarejestrowano czas namaczania. Czynność powtórzono 3 razy do całkowitej objętości badanego płynu wynoszącej 150 ml. Zmierzone parametry obejmowały: przepuszczalność, współczynnik przepuszczalności i pojemność kapilarną. Przepuszczalność benzyny, oleju napędowego i zużytego oleju znacznie wzrosła z każdą dodaną objętością ($p < 0{,}001$). Przepuszczalność zużytego oleju była ponad 20-krotnie niższa w porównaniu z benzyną i benzyną badaną w tych samych warunkach ($p < 0{,}001$). Wyniki dla czarnoziemu wskazują, że przepuszczalność benzyny wzrosła ponad 5-krotnie przy drugim dodaniu 50 ml benzyny ($p < 0{,}001$), a przepuszczalność dla oleju napędowego i zużytego oleju wykazała 3-krotny wzrost dla benzyny ($p < 0{,}001$) i 4-krotny wzrost dla wody ($p < 0{,}001$). Analiza pojemności kapilarnej wykazała, że na początku była ona znacznie niższa dla benzyny i oleju napędowego w porównaniu z wodą ($p < 0{,}001$) dla gleby bagiennej, ale nie dla czarnoziemu, gdzie pojemność kapilarna benzyny była nawet wyższa w porównaniu z wodą ($p < 0{,}01$). Dodanie kolejnych objętości cieczy znacząco zmniejszyło pojemność kapilarną dla wszystkich badanych cieczy w obu typach gleb. Ponadto porównanie gleby bagiennej i czarnoziemu wykazało, że przepuszczalność, współczynnik przepuszczalności i pojemność kapilarna były 2-5 razy wyższe dla gleby bagiennej w porównaniu z czarnoziemem dla wszystkich badanych cieczy.

Wyniki wskazują, że przepuszczalność gleby bagiennej jest wyższa w porównaniu z czarnoziemem w przypadku benzyny i oleju napędowego, ale nie zużytego oleju. Co ciekawe, przepuszczalność czarnoziemu dla oleju napędowego była znacznie niższa w porównaniu z glebą bagienną.

Słowa kluczowe
przesiąkliwość, współczynnik przesiąkliwości, pojemność kapilarna, przesiąkliwość ropopochodnych, przesiąkliwość gleb

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Estimation of Load Bearing Capacity of Bending Fibrocomposite Elements

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1. Introduction

Ordinary concrete is commonly used as construction material. Despite its major advantages, it has an important drawback – it is fragile and has very little tensile strength. In order to improve its qualities, various fibers are added to concrete mix. Thus, a new material called fiber-reinforced concrete is created. This material has been researched for over 30 years (Zollo 1997, Shah and Ribakov 2011, Domski 2016)and its main application areas are industrial floors, foundation slabs, road/airport pavements, tunnel linings, structures prone to seismic activity and considerable dynamic loads (de la Fuente et al. 2011, Tiberti et al. 2008, Gossla 2006, Destrée 2008, Pepin 2009, Li 2002).

By the end of the 1990s, the application of fiber-reinforced concrete was limited by the lack of standard regulations making reliable design possible. After the year 2000, the first national and international standards and guidelines concerning fiber-reinforced concrete design were introduced (DBV 2001,RILEM 2003,fib Model Code 2010, CNR-DT 204 2006, EHE-08 2008). As for flexural design, these regulations provide different models of stress distribution in tension zone.

Differences also concern the methods of defining post-cracking concrete tensile strength. This is the reason why so many researchers have focused their efforts on verifying these regulations. Blanco et al.(2013) made an attempt to verify selected standards based on the results of experimental research on reinforced concrete beams – the variables in this research being the volume content of fibers and their type. The research results demonstrated that DBV standard (2001)defined underestimated capacity in regard to both small and big strains. However, the calculations in accordance with CNR-DT 204 (2006), EHE-08 (2008), RILEM (2003) and Model Code 2010 standards represented slightly higher capacities when compared to the research findings especially in regard to small strains. Tiberti et al. (2014)conducted comprehensive research aimed at verifying Model Code 2010 regulations used to calculate crack spacing in fiber-reinforced concrete specimens. The research revealed that concrete compressive strength is a major parameter influencing crack spacing, which is not included in the standard.Kelpsa et al.(2014) verified the methods of calculating crack width in accordance withRILEM (2003). The experimental tests on concrete beams reinforced with steel bars and with the addition of steel fibers showed considerable disagreement between the calculated values and measured ones. Ning et al. (2015) conducted tests on seven steel fiber reinforced concrete beams. The ultimate moment capacities calculated in accordance with fib Model Code 2010proved to be significantly lower than the measured values of ultimate moments. Dupont (2003) proposed to modify the method of designing flexural SFRC elements in accordance with RILEM TC 162-TDFand he conducted research on full-scale reinforced concrete beams in order to verify both the original RILEM method and his own method. The research results showed good agreement of theoretical and experimental values. However, in case of high-strength fiber-reinforced concrete beams differences were considerable. The author underlined the importance of scale effect. Mertol et al. (2015)conducted vast research on full-scale fiber-reinforced concrete beams, where the main variable was conventional reinforcement ratio. The result of these analyses was to indicate stress-strain models from published literature, which best describe the load-midspan deflection relation of bending specimens. The multiplicity of research areas, standards and individual propositions regarding SFRC elements design prove that calculating values like ultimate moment capacity, crack spacing and crack width are of continued relevance in science.

One type of fiber-reinforced concrete is Steel Fiber Reinforced Waste Sand Concrete (SFRWSC), which has been developed in the Department of Concrete Structures and Concrete Technology at Koszalin University of Technology. This composite has been created primarily to manage waste fine aggregate remaining after hydroclassification process in local mines (Głodkowska and Kobaka 2009, 2012, Dvorkin et al. 2016).

To date, comprehensive research on physico-mechanical properties of this composite has been conducted (Głodkowska and Kobaka 2009, 2012, Piekarski 2011, Głodkowska and Laskowska-Bury 2015).The obtained results show that the addition of steel fibers significantly increases, among others, concrete compressive/tensile/shear strength, frost/abrasion resistance and static modulus of elasticity(Głodkowska and Laskowska-Bury 2015, Laskowska-Bury 2017). High parameters of strength in SFRWSC, particularly tensile strength and residual strengths, show that this composite can be used in the production of construction elements. Therefore, it can be expected that the addition of steel fibers to conventionally reinforced bending elements will not only increase their load bearing capacity, stiffness and ductility but will also contribute to the reduction of crack spacing and crack width (Kelpsa et al. 2014, Ning et al. 2015, Mertol et al. 2015, Meda et al. 2012).

2. Aim and significance of research

Natural aggregates are commonly used in construction industry. According to European Aggregates Association, European countries produce currently about 2.5 billion tons of aggregates per year. Due to specific geological conditions, fine and coarse aggregate deposits in Poland are qualitatively and quantitatively diverse. In the Pomerania region of Poland, aggregate deposits occur mainly as a mix of fine and coarse aggregates. It is estimated that about 90% of coarse aggregate deposits in Poland occur in the south, 6% in the middle and only 4% in the north of the country. Huge demand for coarse aggregates has contributed to the development of an extraction technology which involves washing out aggregates from deposits. This technology is called hydroclassification and its main by-product is piles of sand without coarse fractions.

Excavation sites thus created should become the object of reclamation. However, the use of waste sand as a structural materialcan provide an alternative to costly reclamation. Partially replacing ordinary concrete with SFRWSC which exhibits the same or even better properties would be an excellent solution for the regions where natural deposits of coarse aggregate are scarce e.g. Pomerania (where only 4% of total Polish coarse aggregates occur) (Głodkowska and Laskowska-Bury 2015), the Middle East and North Africa.

This article presents only a part of a vast research program exploring the possibilities of applying SFRWSC in the production of structural elements. The scope of research in this publication is limited to experimental and theoretical calculation of ultimate moment capacities for full-scale beams made from SFRWSC. In oder to determine the influence of steel fibers on the load bearing capacity of conventionally reinforced beams, the production of reference beams without fibers was foreseen in the program. The obtained results made it possible to evaluate RILEM TC-162-TDF and fib Model Code 2010 design methods.

3. Materials and test specimens

In order to produce SFRWSC, waste sand (fractions ranging from 0.125 to 4 mm) from a local mine of natural aggregates was used in the quantity of 1570 kg/m^3 . As a binder, portland cement CEM II/AV 42.5R (420 kg/m^3) was applied. Other ingredients were: silica fume (21 kg/m^3), superplasticizer BETO-

CRETE 406 FM (16.8 kg/m^3) and steel hooked-end fibers 50/0.8 mm with the aspect ratio λ=62.5. Applying superplasticizer as well as adding silica fume enabled a w/c=0.38 ratio to be obtained.

Having analysed the research results presented in the papers (Głodkowska and Laskowska-Bury 2015), it should be pointed out that increasing the amount of steel fibers in the composite above the level of 1.5% may have a negative influence on its properties. In order to obtain a material with the same physico-mechanical properties as ordinary concrete, it is important to determine an appropriate amount of fibers in the composite while maintaining an appropriate consistency of the mix. An analysis of the regression curves (Głodkowska and Laskowska-Bury 2015) helped determine the composite's maximum steel fiber content which also meets the requirements of ordinary concrete.

The functions describing splitting compressive/tensile strength failed to give a definitive answer to this question. Their values have maintained an increasing trend for the steel fiber volume percentages used in the research. Therefore, the regression functions of the properties which deteriorated with the increase of steel fibers in SFRWSC, namely abrasion resistance, static modulus of elasticity and workability, proved to be helpful in the research. A maximum steel fiber content was determined.When it was exceeded, the value of the properties decreased.According to the final findings, the most advantageous properties as well as the best economical benefits can be achieved when the maximum steel fiber content in SFRWSC is equal to 1.2%. Adding higher quantities of fibers does not result in a significant increase in both compressive and tensile strength.For the composite with steel fiber content equal to 2%, the strength increases merely by several MPa in relation to the strength of the composite with the fiber content value of 1.2%. Moreover, increasing the fiber content to 2% has a very negative effect on the consistency and workability of the mix. Therefore, the content value of 1.2% (94,5 kg/m^3) was accepted as the optimal amount of steel fibers in the composite. SFRWSC with steel fiber content equal to 1.2% has the same or even better properties than ordinary concrete does. Steel fibers were distributed randomly in the composite mix. The characteristics of steel fibers and waste sand used in the research are presented in the papers (Głodkowska and Laskowska-Bury 2015).

To calculate the ultimate moment capacities of elements made from SFRWSC, nine 150x200x3300 mm reinforced concrete beams were produced, which were next divided into three series (Table 1). The amount of conventional reinforcement in each series differed. For comparative purposes, one beam without steel fibers was produced extra for each series. In addition, all beams with steel fibers were produced in two variants – with and without stirrups. 8, 12 and 16 mm diameter ribbed steel bars provided conventional tensile reinforcement. 6 mm diameter stirrups at 125 mm spacing were applied. In the compression zone, two 8 mm diameter longitudinal reinforcement bars were used. Mechanical properties of the bars used as the longitudinal reinforcement were tested by authors according to EN ISO 6892-1 and are presented in Table 2.

For each beam, small-size elements were produced to determine the compressive strengths (in total, 30 cylinders made from a composite without steel fibers and 30 cylinders with fibers – diameter and height of specimens were equal to 150 and 300 mm respectively) as well as the residual strengths (30 prisms whose dimensions were 150x150x700mm).

Table 1. Beam characteristics

<table>
<tr><th>Beams</th><th>Dimensions
[mm]</th><th>Tensile
reinforcement</th><th>Stirrups</th><th>Volume fraction
[%]</th></tr>
<tr><td>B1</td><td rowspan="9">150x200x3300</td><td rowspan="3">2#8</td><td rowspan="2">#6 @ 125</td><td>-</td></tr>
<tr><td>BF1</td><td rowspan="2">1.20</td></tr>
<tr><td>BF1a</td><td>-</td></tr>
<tr><td>B2</td><td rowspan="3">2#12</td><td rowspan="2">#6 @ 125</td><td>-</td></tr>
<tr><td>BF2</td><td rowspan="2">1.20%</td></tr>
<tr><td>BF2a</td><td>-</td></tr>
<tr><td>B3</td><td rowspan="3">2#16</td><td rowspan="2">#6 @ 125</td><td>-</td></tr>
<tr><td>BF3</td><td rowspan="2">1.20%</td></tr>
<tr><td>BF3a</td><td>-</td></tr>
</table>

Table 2. Mechanical properties of steel bars

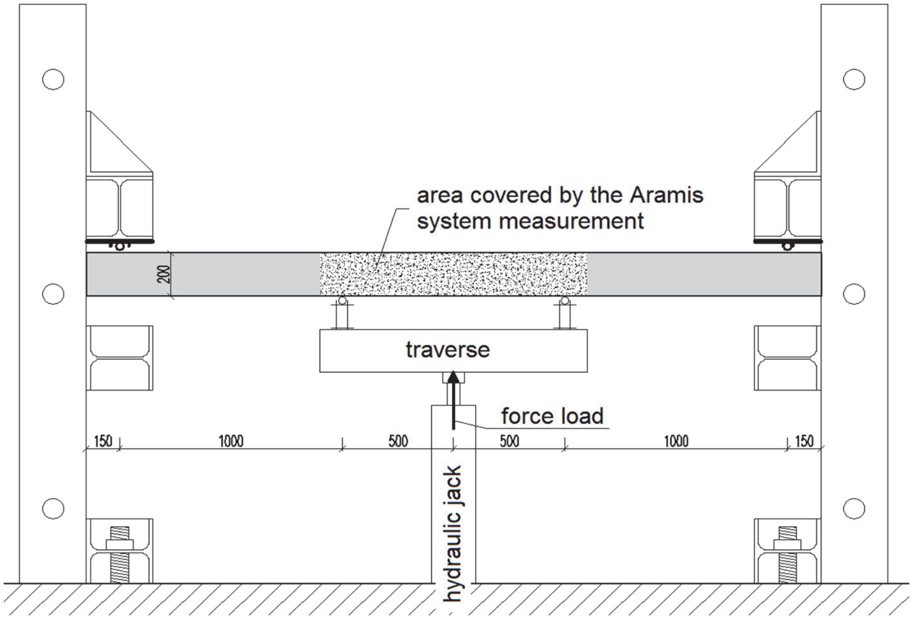
Diameter [mm]	Yielding stress [MPa]	Tensile strength [MPa]	Modulus of Elasticity [GPa]
8	559	596	197
12	597	690	208
16	535	625	207

Having been cast in moulds, all specimens were tightly wrapped in foil and stored at a temperature of 20±2°C. After 2 days, the specimens were demoulded, covered amply with water and rewrapped in foil. For the next 28 days, the specimens were cured under the same conditions. The specimens were tested 30 days after moulding since 2 more days were needed to prepare them for testing.

4. Research methodology

The beams were tested on a specially-prepared stand for inverted simply-supported beam (Fig. 1). Static load was applied with constant speed of ~0.25kN/s underneath the beam by means of a hydraulic jack.

a)



b)

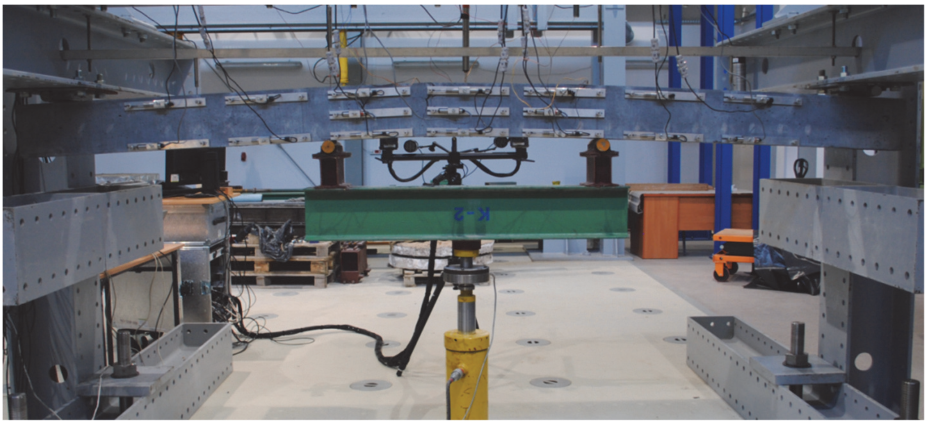


Fig. 1. Stand and static scheme of tested beams: a) schematic drawing; b) general view

When the yield stress was achieved in tensile reinforcement, the load was controlled by the beam's deflection speed, which was 0,1±0.025 mm/s.

The beams were monitored using SAD256 data acquisition system and ARAMIS 4M optical-measurement system. SAD256 was used to measure the load force "P", deflection (5 linear variable displacement transducers LVDT), strain of the beam's one lateral surface (17 LVDTs) as well as tensile reinforcement strain (6 electrical resistance strain gauges).

ARAMIS 4M optical-measurement system made it possible to track precisely the process of crack formation and crack propagation. The system also enabled the strain of the beam's second surface to be measured. The area of the tested surface was 1 m long and it covered the length of the beam between points where load was applied. All sensors of both SAD256 and ARAMIS 4M systems recorded measured displacements and load at a frequency of 1 per 2 seconds. The measurement accuracy for the two systems was $1x10^{-3}$ mm.

Residual strengths (Fig. 2) were tested on 150x150x700 mm prisms in accordance with EN 14651:2005. Load was applied at the mid-span of the beam while load, deflection and crack width were measured. Load increase values were set depending on crack mouth opening displacement (CMOD). The test was terminated when the specimen's deflection was equal to 5 mm. Ultimate deflection of the prisms was set in accordance with EN 14651:2005 in order to achieve all CMOD values and to determine residual strengths (f_{Ri}) for the corresponding value $CMOD_j$, in which j=1,2,3,4. The quantities $f_{R,1}$, $f_{R,2}$, $f_{R,3}$ i $f_{R,4}$ 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. The calculations assumed linear stress distribution in both compression and tension zones of the test prism.

An important parameter enabling a SFRC to be classified is the chart shape “load – CMOD” from the point of attaining limit of proportionality until ultimate deflection. One can distinguish two shapes of the chart: 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)*. Residual strengths determine the capacity of SFRC to transmit tensile stresses in cracked cross-section.

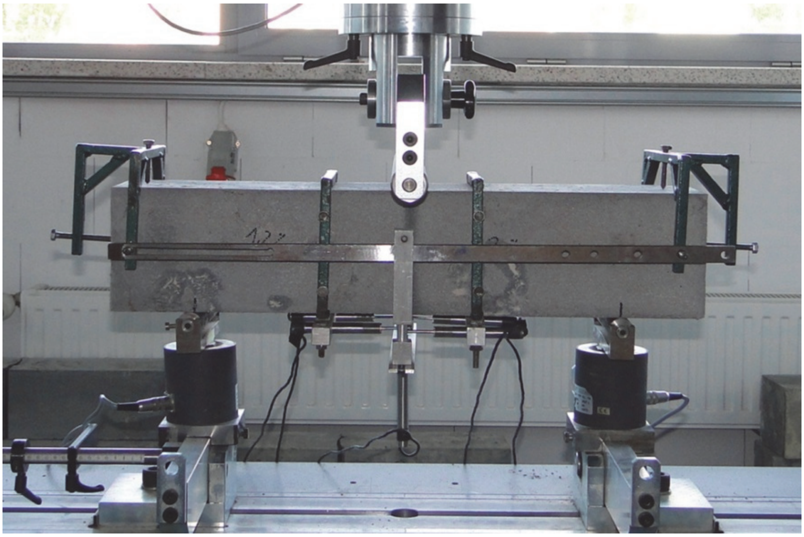


Fig. 2. Three-point bending set up according to EN 14651

The compressive strength of SFRWSC was tested on cylindrical samples in accordance with EN 12390-3:2009.

5. Experimental results

5.1. Compressive strength and residual flexural tensile strength

Research results regarding compressive strength are presented in Table 3. They reveal that the addition of steel fibers at a volume of 1.2% increases compressive strength of SFRWSC by 22% in comparison to a composite without any fibers. A similar increase in compressive strength was observed by (Głodkowska and Kobaka 2012) (Fig. 3). His research proved that the addition of a 1.2% volume fraction of steel fibers to a composite effectively increases its compressive strength. Above this level, no significant increase in compressive strength occurs. However, it must be underlined that the addition of steel fibers to concrete matrix does not always coincide with an increase in compressive strength (Rossi 1992). In light of RILEM TC-162-TDF recommendation and fib Model Code 2010 provisions, a simplified assumption can be made that steel fibers have no influence on compressive strength. This assumption, however, was not supported by the obtained research results.

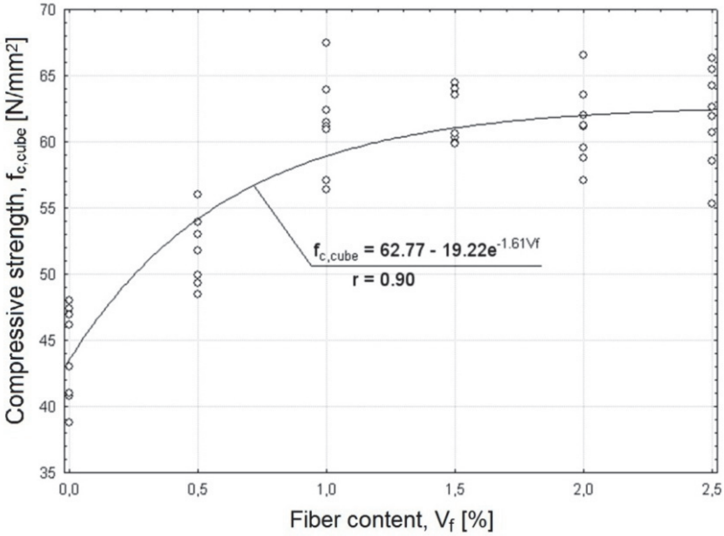


Fig. 3. Concrete compressive strength-fiber content diagram (Głodkowska and Kobaka 2012)

Table 3. Experimental values of cylinder compressive strength

Statistic parameters	Compressivestrength	
	Vf=0%	SFRWSC
Mean $\bar{x}$ [MPa]	52.6	64.4
Standard deviation, s [Mpa]	2.4	4.1
Coefficient of variation, ν [%]	5	6
Minimum value, x_{min} [Mpa]	48.7	55.3
Homogeneity index$k$ [-]	0.93	0.86
Confidenceinterval, [Mpa]	51.7-53.5	63.1-65.7
Number of results taken for analysis, n	**29***	30
* - as a result of statistical analysis, one measurement was rejected		

Research results regarding residual flexural tensile strengths (Głodkowska el al. 2015) show ductile characteristics of the tested material. For structural purposes, the material classification of fiber-reinforced concretes and high-strength concretes is based on the values typical for residual strengths. According to fib Model Code 2010 provisions, SFRWSC belongs to the class 7b. This means that the material has a high value f_{R1} (ranging from 1 to 8). The letter "b" means that the tested fiber-reinforced composite is characterised by post-crack softening, which is fixed by means of the ratio f_{R3}/f_{R1}.

5.2. Load-midspan deflection behavior

Fig. 4 illustrates the relation between load and midspan deflection of the test beams with different conventional reinforcement ratios. During the first stage of load application (to uncracked beams), the influence of steel fibers is negligible. Changes are observed when the first cracks appear. Due to SFRWSC's capacity to transmit tensile stresses in cracked cross-section, steel fiber reinforced beams have higher stiffness than beams without fibers. This means that, assuming the same load is applied, the midspan deflection of the test beams with fibers is smaller than the midspan deflection of the beams without fibers. The lower conventional reinforcement ratio, the bigger the deflection difference is. For example, in case of beams reinforced with #8 bars under a load equal to16kN, the deflection of beams BF1 and BF1a is smaller than the deflection of beam B1 by 44% and 55% respectively. In case of beams reinforced with #12 bars, the differences are smaller. Under a load equal to 35kN, the deflections of beam BF2 and beam BF2a are smaller than the deflections of beam B2 by 24% and 28%, respectively. In case of beams reinforced with #16 bars, the difference in stiffness is negligible.

As for ultimate moment capacity, the research findings are analogous. The influence of steel fibers on ultimate moment capacity is the most visible in case of beams with the lowest conventional reinforcement ratio. The maximumapplied loads to beams BF1 and BF1a (compare Table 1) were bigger than the maximum load applied to beam B1 by 40% and 44%, respectively. In case of beams reinforced with #12 bars, the ultimate moment capacities of beams BF2 and BF2a were higher than the ultimate moment capacity of beam B2 by 20% and 29% respectively. In case of fiber-reinforced beams reinforced with #16 bars, ultimate moment capacities increased by 15% and 9%, respectively when compared to beams without fibers.

By the end of the test, tensile bars rupture occurred only in beams B1, BF1 and BF1a (Fig. 4a). In case of beams reinforced with #12 bars, neither tensile bars rupture nor crushing of the compression zone was observed.Since the measuring range of the deflection sensors used in the test is limited, the research procedure was interrupted prior to the beams' failure. However, in case of beams from series 3 reinforced with #16 bars, specimens B3 and BF3a underwent failure due to crushing of the compression zone. Fig. 4c illustrates this situation in the form of load-midspan deflection curves collapse shortly after tensile reinforcement yielding.

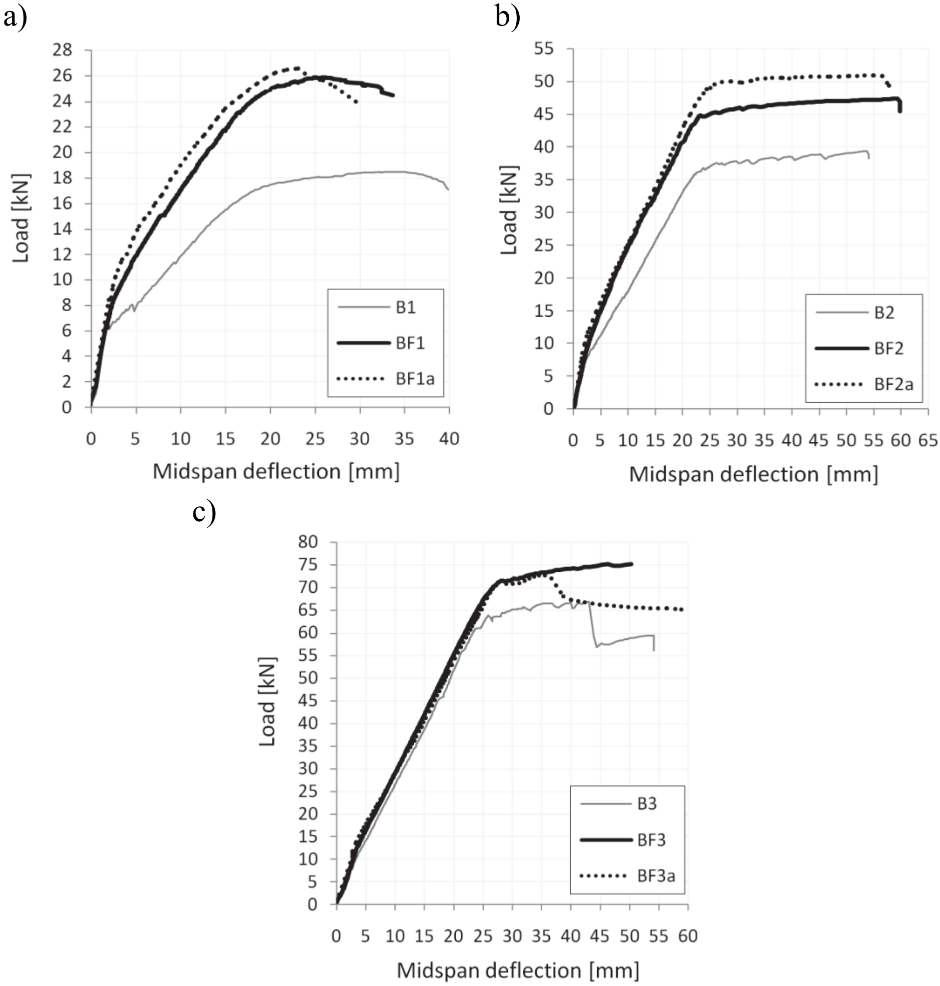


Fig. 4. Load-midspan deflection curves with different longitudinal reinforcement ratios: (a) 2#8; (b) 2#12;(c) 2#16 (Głodkowska and Ziarkiewicz 2018)

Having analysed the research results, it was stated that beams without stirrups attained larger load bearing capacity than beams with stirrups did (except for beams from series 3, Table 2, due to the crushing of the compression zone in beam BF3a). The presence of stirrups limits the beneficial distribution of fibers in the bar's direct vicinity, which may decrease the load bearing capacity of the cross-section in beams with stirrups.

5.3. Load bearing capacity

It was indispensable for further analysis to determine the maximum force (P_u) as well as the load force at which tensile reinforcement reached yield stress (P_y). Load values $P_u$and $P_y$as well as strains on lateral surfaces of the beams measured bySAD256 and ARAMIS 4M systems (ε_t – tensile edge strains; ε_c – compressive edge strains) are presented in Table 4. These values constitute the basis for theoretical analysis of ultimate moment capacity in accordance with RILEM TC-162-TDFand fib Model Code 2010.

Table 4. Load values and strains at time of tensile reinforcement yielding and ultimate bearing capacity

Speci-men	Yielding of tensile reinforcement					Ultimate bearing capacity				
	P_y	ε_t		ε_c		P_u	ε_t		ε_c	
		A4M	SAD	A4M	SAD		A4M	SAD	A4M	SAD
	kN	[‰]				kN	[‰]			
B1	**16.68**	3.08	2.81	-0.62	-0.66	**18.48**	7.53	7.75	-1.03	-1.13
BF1	**25.21**	3.78	4.12	-0.97	-0.82	**25.86**	5.49	4.97	-1.10	-0.99
BF1a	**25.51**	2.89	2.79	-0.78	-0.76	**26.61**	4.06	3.51	-0.88	-0.85
B2	**36.68**	3.57	3.13	-1.17	-1.17	**39.34**	11.64	10.17	-2.29	-2.03
BF2	**44.63**	3.48	4.29	-1.20	-1.32	**47.33**	13.01	16.76	-2.30	-2.62
BF2a	**49.03**	3.88	3.65	-1.37	-1.24	**50.93**	10.73	11.42	-2.26	-1.96
B3	**63.71**	3.67	4.13	-1.51	-1.73	**66.80**	8.11	9.61	-2.10	-2.70
BF3	**70.25**	3.28	3.41	-1.80	-1.56	**76.56**	12.01	13.59	-3.58	-2.79
BF3a	**71.25**	3.38	3.49	-1.71	-1.62	**72.68**	5.08	5.72	-1.99	-1.93

Figure 5 presents strain distribution at cross-section and longitudinal reinforcement of beams from waste sand fiber composite for yielding moment (*My*) and ultimate moment capacities (*Mu*).

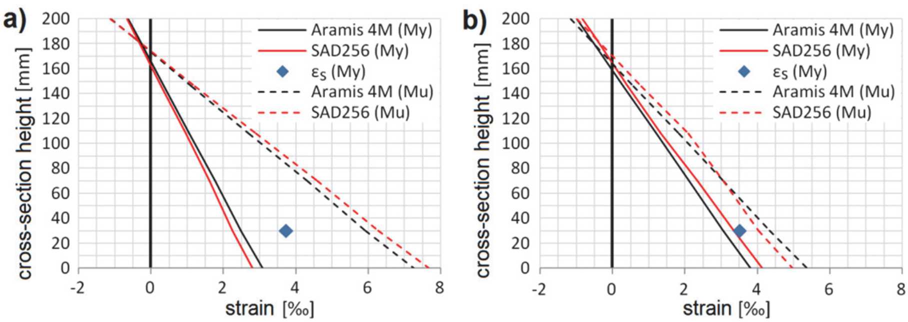


Fig. 5. Strain distribution at cross-section for yielding moment (M_y) and ultimate moment capacities (M_u) of beams:a). B1, b). BF1

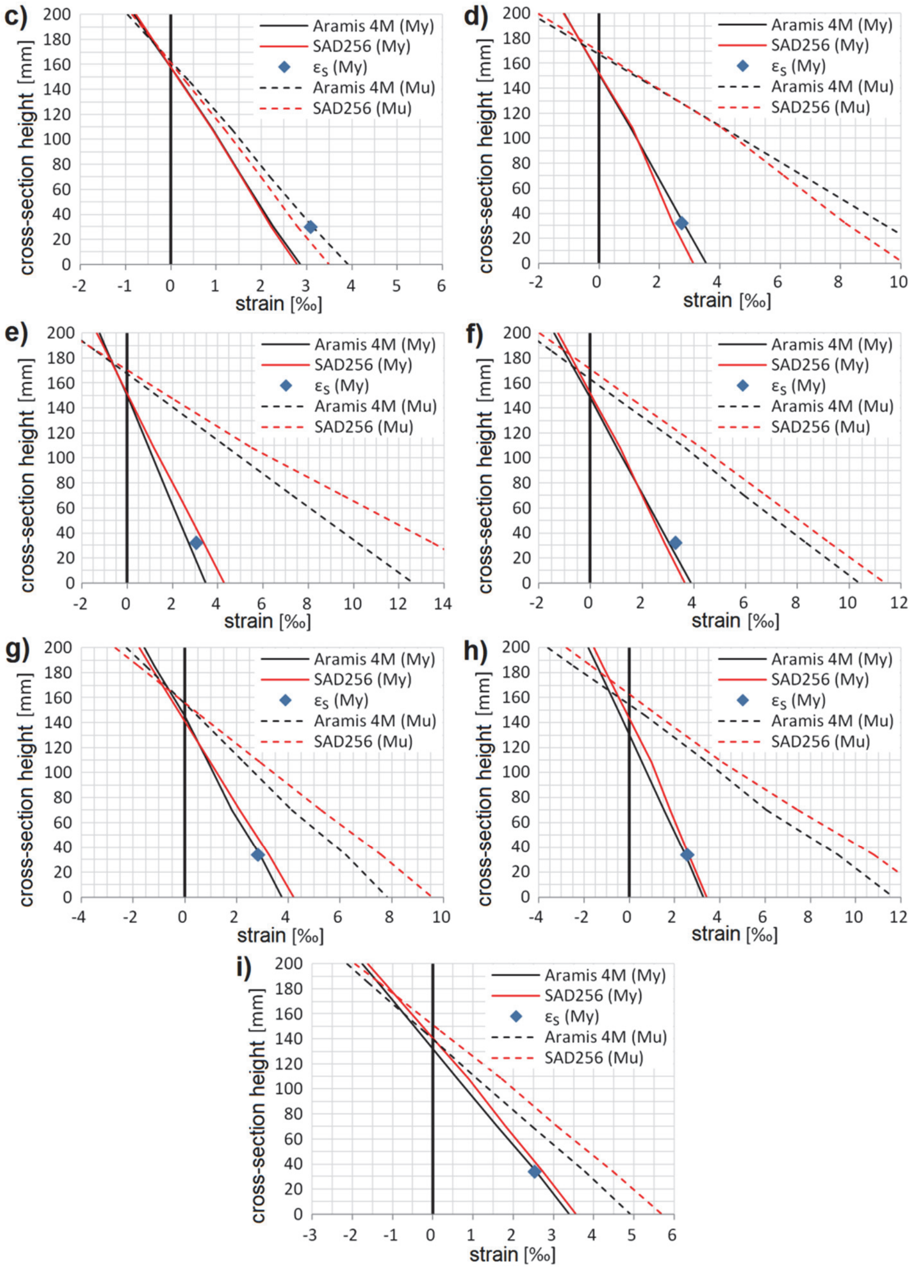


Fig. 5. Strain distribution at cross-section for yielding moment (M_y) and ultimate moment capacities (M_u) of beams: c). BF1a, d). B2, e). BF2, f). BF2a, g). B3, h). BF3, i). BF3a

Basing on presented charts (Figure 5) it is possible to determine height of compressed zone for analysed cross-section. For yielding moment *My* height of that zone is 36-43 mm for beams in series 1, 48-50 mm for beams in series 2 and 58-64 mm for beams in series 3. In beams containing fibers the compressed zone was about 8% bigger than in elements without steel fibers.

Test findings do not reveal a distinct influence of steel fibers on strain values corresponding to maximum force $P_u$and on strain values at which tensile reinforcement reached yield stress. In case of beams reinforced with #8 bars, strains corresponding to force P_u in beam B1 were significantly bigger than the strains in beams BF1 and BF1a. In case of beams from the second series, the reverse is true. In case of beams reinforced with #16 bars, strains corresponding to force P_u in beams B3 and BF3a were significantly smaller than the strains in beam BF3 due to crushing of the compression zone. It is worth mentioning that the compressive strains corresponding to the crush were smaller than 3‰.

Test results also reveal that strains on two lateral surfaces of the beams measured by two different techniques vary from each other. The ratio between SAD256 and ARAMIS 4M measurements ranged from 0.78 to 1.28 whereas the average value of this relation was 0,99. In each particular case, it was verified if the results obtained by SAD256 and ARAMIS 4M systems belong to one population. A statistical analysis showed that the results obtained by the two measurement techniques belong to one population, which means that the recorded strain differences are statistically insignificant.

6. Flexural analysis in accordance with RILEM and Model Code 2010 provisions

Residual strengths constitute the basis for designing flexural SFRC structures in accordance with RILEM TC-162-TDFrecommendation, fib Model Code 2010 and the Spanish standard EHE-08.However, these standards shape differently σ-ε relation of SFRC in tension zone of bending elements. Only international regulations, namely RILEM TC-162-TDFguidelines and fib Model Code 2010provisions, were selected for analysis.

Fig. 6 presents the composite's stress-strain relations in tensile conditions in accordance with the above-mentioned provisions. The values of tensile stresses according to RILEM TC-162-TDF depend on the composite's tensile flexural strength $f_{ctm,fl}$and residual strengthsf_{R1} and f_{R4}. Strains ε_1 are determined according to Hooke's law and are based on the composite's average static modulus of elasticity. The strains ε_2 and ε_3 are determined arbitrarily assuming that the biggest admissible strain in tension zone is 25‰. A much more complex attitude to modelling tension zone is presented in fib Model Code 2010. The values of tensile stresses depend not only on residual strengths (in this particular case f_{R1} and f_{R3})

but also on the crack width w_u. This value can be calculated from the formula (fib Model Code 2010):

$$w_u = l_{cs} \cdot \varepsilon_{Fu}$$

The ultimate strain ε_{Fu} according to fib Model Code 2010 should be assumed to be equal to 20‰ in a cross-section with variable distribution of strains. It is also crucial to know the characteristic length l_{cs}, which can be calculated from the formula:

$$l_{cs} = \min(s_{rm}; y)$$

The value s_{rm} stands for the average crack spacing and the parameter y stands for the height of tension zone. It is not easy to determine these two parameters as they are dependent on both amount and diameter of bars used in conventional reinforcement.

The characteristic length l_{cs} is essential for calculating stresses ε_{SLS} andε_{ULS}, too. It must be underlined that the maximum strains of cross section's tensile edge cannot exceed 20‰.

Additionally, fib Model Code 2010 standard allows for the simplified model to be possibly applied. This model assumes that constant tensile stresses equal to $f_{R3}/3$ exist in tension zone.

Stresses in the composite's compression zone in accordance with RILEM and MC2010 are modelled identically as in case of ordinary concrete. A parabolic graph is used for strains below 2‰. For strains ranging from 2 to 3.5‰, a linear graph with a constant value of stress equal to the composite's compressive strength is used. These rules are identical with the requirements of EN1992-1-1.

An analysis of ultimate moment capacity in accordance with RILEM TC-162-TDFand fib Model Code 2010provisions was performed based on the results of tests carried out on 6 beams made from SRWSC and on three beams without fibers. The analysis was conducted in two variants. In the first variant, the bending moment (M_y) corresponding to tensile reinforcement yielding was calculated. Average strains of cross-section (Table 4) served as an input data for calculations. In the second variant, ultimate bearing capacity (M_u) was calculated assuming the ultimate strains in compression and tension zones as defined by RILEM TC-162-TDFand fib Model Code 2010.

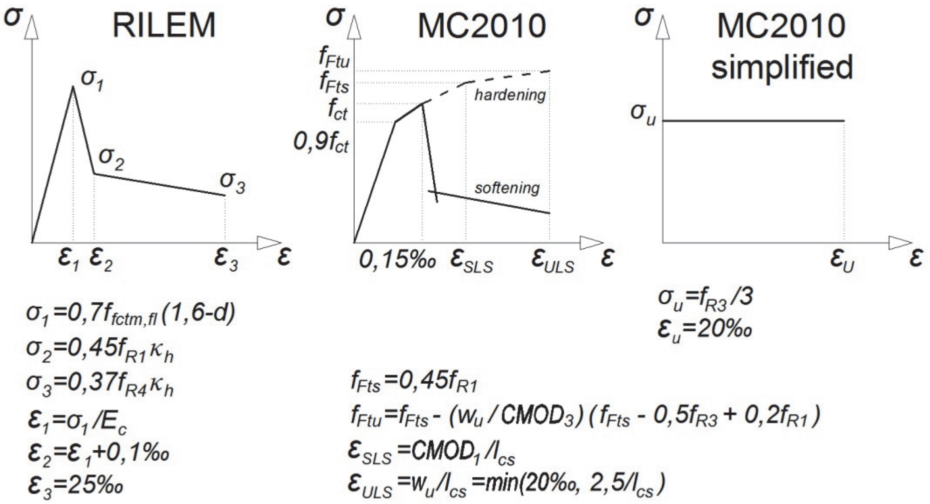


Fig. 6. Stress-strain relationship in tensile cross-section according to RILEM TC-162-TDF and fib Model Code 2010

6.1. Yielding moment M_y

The cross-section analysis at time of conventional reinforcement yielding was conducted as follows. The strains of compression and tension zones were measured by SAD256 and ARAMIS 4M and averaged. Next, tensile and compressive stresses were assigned to the strains in accordance with RILEM TC-162-TDFand fib Model Code 2010. Mean material characteristics of SFRWSC and reinforcement bars were used in the calculations. Yielding moment M_y was calculated from the equilibrium condition of moments in relation to the centroid of compressive stresses block (Table 5). Compressive reinforcement bars were taken into account in the calculations.

Moments $M_{y,pre}$ for beams without steel fibers calculated according to RILEM TC-162-TDF and fib Model Code 2010 correspond precisely to the experimental values $M_{y,exp.}$ The values of the ratio $M_{y,pre}/M_{y,exp}$ range from 0.87 to 0.99. However, the situation is different in case of beams with fibers. Moments $M_{y,pre}$ calculated according to RILEM and MC2010 are considerably bigger than the experimental values $M_{y,exp.}$ For RILEM method, the moment ratio $M_{y,pre}/M_{y,exp}$ ranges from 1.07 to 1.44 and for MC2010 method, it ranges from 1.02 to 1.36. Relative differences between the measured moments and calculated ones decrease proportionally to the increase in conventional reinforcement.

Table 5. Experimental and predicted values of Yielding Moment

Specimen	$M_{y,exp}$	$M_{y,pre}$		$M_{y,pre}/M_{y,exp}$	
		RILEM	MC2010	RILEM	MC2010
	[kNm]	[kNm]			
B1	8.70	7.57	7,61	0,87	0,87
BF1	13.00	18.74	17,67	1,44	1,36
BF1a	13.14	16.85	15,3	1,28	1,16
B2	18.70	18.44	18,48	0,99	0,99
BF2	22.70	29.6	28,29	1,30	1,25
BF2a	24.90	29.33	28	1,18	1,12
B3	32.20	31.04	31,11	0,96	0,97
BF3	35.51	37.83	36,3	1,07	1,02
BF3a	36.02	38.82	37,39	1,08	1,04
Mean [-]				1.13	1.09
Coefficient of variation, ν [%]				16	14

6.2. Ultimate Moment M_u

The ultimate moment capacity of the beams (M_u) was calculated differently than in the previous variant. An input data for the calculations was an assumption concerning maximum admissible strains both in compression and tension zones according to RILEM TC-162-TDF and fib Model Code 2010. Next, equilibrium of internal forces toward the beam's longitudinal axis was verified. In each particular case, the analysis revealed that the internal forces were not in equilibrium. The strains in either compression or tension zone were then reduced to achieve equilibrium of the internal forces. The ultimate moment capacity (M_u) was calculated from the equilibrium condition of moments in relation to the centroid of compressive stresses block (Table 6, Głodkowska and Ziarkiewicz 2018). Compressive reinforcement force was taken into account in the calculations. In the analysed variant, ultimate moment capacities were also calculated using the simplified method in accordance with fib Model Code 2010.

Calculating the ultimate moment capacity (M_u) according to RILEM TC-162-TDF and fib Model Code 2010leads to similar conclusions as calculating the yielding moment $M_y$in the previous variant. In case of beams without steel fibers, the calculated values and measured ones are in very good agreement. In case of beams with steel fibers, the calculated values of ultimate moment capacity (M_u) are considerably bigger than the experimental ones. For RILEM TC-162-

TDFmethod, the moment ratio $M_{y,pre}/M_{y,exp}$ ranges from 1.02 to 1.17 and for fib Model Code 2010 method, it ranges from 1.07 to 1.46. As opposed to the previous variant, the RILEM TC-162-TDF calculation results are closer to the experimental values than the fib Model Code 2010calculation results. The reason for this is that RILEM TC-162-TDF method omits tensile stresses transmitted by steel fibers if tensile strains are bigger than 2.5%. As could be expected, $M_u$values calculated using the simplified fib Model Code 2010 method are lower than $M_u$values calculated using the exact method. However, they are on average 9% bigger than the experimental values.

Table 6. Experimental and predicted values of Ultimate Moment

Specimen	$M_{u,exp}$	$M_{u,pre}$			$M_{u,pre}/M_{u,exp}$		
		RI-LEM	MC2010	MC2010 Simpl.	RILEM	MC2010	MC2010 simpl.
	[kNm]						
B1	9.60	9.69	9.61	9,28	1,01	1,00	0,97
BF1	13.33	15.56	19.5	16,79	1,17	1,46	1,26
BF1a	13.70				1,14	1,42	1,23
B2	20.03	20.96	21.01	21,05	1,05	1,05	1,05
BF2	24.06	29.46	31.09	28,53	1,22	1,29	1,19
BF2a	25.85				1,14	1,20	1,10
B3	33.76	31.94	31.96	32,04	0,95	0,95	0,95
BF3	38.67	40.79	41.47	39,5	1,05	1,07	1,02
BF3a	36.73				1,11	1,13	1,08
Mean [-]					1.09	1.18	1.09
Coefficient of variation, ν [%]					8	16	10

7. Conclusions

The article presents the results of experimental investigations on flexural behavior of full-scale conventionally reinforced concrete beams made from SFRWSC with the volume content of steel fibers equal to 1.2%. Based on the measured strains of test beams as well as on mechanical properties of test materials, bending moments corresponding to tensile reinforcement yielding as well as ultimate moment capacities were calculated using RILEM and Model Code 2010 methods. The calculated bending moments were then compared with the experimental moments.

Having analysed the calculation and research results, the following conclusions can be drawn:

1) Waste sand cement-based composite without the addition of fibers behaves like ordinary concrete in conventionally reinforced bending elements. For these elements, the yielding moment and ultimate moment capacity values calculated using RILEM and Model Code 2010 methods are entirely satisfactory.
2) The addition of steel fibers considerably improves the ultimate moment capacity of SFRWSC elements, which makes reduction of conventional reinforcement possible.
3) Taking into account the physico-mechanical properties of SFRWSC as well as the research results regarding ultimate moment capacities of beams made from this composite, one may safely assume that SFRWSC can be used as a structural material, which in turn creates new possibilities for waste sand management.
4) In case of elements made from SFRWSC, bending moments calculated using RILEM and Model Code 2010 methods are bigger than the experimental values. The obtained results highlight the necessity to correct these methods before using them for designing bending elements made from SFRWSC. Similar conclusions were reached by researchers specialising in SFRC.

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Abstract

Waste sands resulting from coarse aggregate extraction are becoming an increasingly pressing ecological issue in northern Poland, the Middle East or North Africa. In order to manage the waste sand, a fine-grained composite with the addition of steel fibers has been developed. As steel fibers constitute 1.2% of the composite, it has been called Steel Fiber Reinforced Waste Sand Concrete (SFRWSC). The physico-mechanical and rheological properties of the composite meet the requirements of construction materials and make it more effective than ordinary concrete. In order to prove SFRWSC's usefulness in the production of construction elements, experimental investigations on flexural behavior of full-scale conventionally reinforced concrete beams have been carried out. The test specimens were divided into three series differing as to the conventional reinforcement ratio. It has been demonstrated that SFRWSC can be readily used in the production of bending structural elements. Steel fibers increase considerably the load bearing capacity and stiffness of the specimens, which makes partial reduction of conventional reinforcement possible. Next, the calculation results in accordance with RILEM and Model Code 2010 provisions and the experimental research results have been compared. It has been proved that bending moments according to the aforementioned international regulations are overestimated in relation to the experimental values. The obtained results highlight the necessity to correct these methods before using them for designing elements made from SFRWSC and Steel Fiber Reinforced Concrete (SFRC).

Keywords:
waste sand, structural element, load bearing capacity, flexural failure, fibercomposite

Obliczanie nośności zginanych elementów fibrokompozytowych

Streszczenie

Hałdy piasku odpadowego powstałego w wyniku wydobycia kruszyw grubych stanowią coraz poważniejszy problem ekologiczny w północnej Polsce, na Bliskim Wschodzie czy tez północnej Afryce. W celu zagospodarowania tego piasku opracowano drobnokruszywowy kompozyt z dodatkiem włókien stalowych (Steel Fibre Reinforced Waste Sand Concrete – SFRWSC), których zawartość wynosi 1,2%. Opracowany kompozyt charakteryzuje się właściwościami fizyko-mechanicznymi i reologicznymi, które spełniają wymagania materiałów konstrukcyjnych i są korzystniejsze niż betonu zwykłego. Aby wykazać przydatność tego kompozytu do wytwarzania elementów konstrukcyjnych przeprowadzono badania zginanych belek żelbetowych w skali naturalnej. Badane elementy podzielono na trzy serie różniące się stopniem zbrojenia konwencjonalnego (zbrojenie z uwagi na zginanie). Wykazano, że opracowany fibrokompozyt może być z powodzeniem stosowany do wykonywania zginanych elementów konstrukcyjnych. Włókna stalowe w istotny sposób zwiększają nośność i sztywność elementów, a przez to możliwa jest częściowa redukcja zbrojenia konwencjonalnego. Wyniki badań eksperymentalnych porównano z wynikami obliczeń wg RILEM i Model Code 2010. Dowiedziono, że momenty zginające obliczone wg wspomnianych międzynarodowych przepisów są zawyżone względem wartości doświadczalnych. Uzyskane wyniki wskazują na konieczność dokonania korekty tych metod w celu ich zastosowania do wymiarowania zginanych elementów wykonanych z kompozytu SFRWSC oraz fibrobetonu (Steel Fibre Reinforced Concrete – SFRC).

Słowa kluczowe:
piasek odpadowy, element konstrukcyjny, nośność, zniszczenie, fibrokompozyt

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The Effect of Selected Parameters on the Stabilization Efficiency of the Organic Fraction of Municipal Solid Waste (OFMSW) in the Mechanical and Biological Treatment Plant (MBT)

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1. Introduction

Composting is a waste recycling method based on the biological degradation of organic matter under aerobic conditions, by many populations of microorganisms producing stabilized, deodorized and disinfected compost (Fourti 2013; Wei et al. 2017), which reduces the amount of waste neutralized and/or released into the environment (Skaggs et al. 2017).

Composting is an aerobic process, which requires oxygen for microbial biodegradation, optimal moisture, and porosity (Gea et al. 2007). In the course of a composting process, the most common procedure for aeration is through turning of the compost material. These facts make composting material readily available for microbial utilization and thus, results in gas emission (Onwosi et al. 2017). Composting requires relatively low technological advancement and a low investment cost (Gea et al. 2007), compared to other treatment technologies, i.e. anaerobic digestion. As a waste treatment method, composting can divert waste from landfill, mitigate groundwater contamination, reduce air pollution and greenhouse gas emission (Li et al. 2013; Oliveira et al. 2017). It can be applied to mixed municipal solid waste (MSW) as well as separately collected biodegradable fraction (Diaz, 2002). In the case of mixed MSW, a combination of mechanical, other physical and biological processes are required (Baptista et al. 2010). There has been increasing attention on improving the management of the organic fraction of municipal solid waste (OFMSW). Biodegradable material, especially food waste, usually accounts for over 50 wt% of the municipal/residential waste stream in less developed countries (Wei et al. 2017). In full-scale composting process is realized in the so-called mechanical – biological treatment (MBT) plant. In the case of MBT, the main aim of composting is to maximize stabilization of the organic fraction of municipal solid waste (OFMSW) before its final disposal (Colón et al. 2017).

Composting is a natural process; however, many artificial factors have been developed to improve process efficiency (Xi et al. 2005). The decomposition of the organic matter is affected by several factors that can be divided into two general groups: variables which determine the concentrations of the biodegradable compounds, affect microbial population size and its activity; and factors that directly control the reaction kinetics itself, such as: temperature, oxygen ratio, moisture content (Hamoda et al. 1998; Onwosi et al. 2017).

Temperature, oxygen and moisture content are often selected as the control variables in the composting process, jointly with another chemical, biochemical or microbiological properties (Gea et al. 2007). Regardless of whether stabilized organic residues are recovered or stored, the assessment of the effectiveness of the biological process is critical (Cesaro et al. 2016).

The resistance of the organic matter against extensive degradation or toward significant microbiological activity means compost stability. Maturity describes the ability of a product to be used effectively in agriculture and is related to the growth of plants and phytotoxicity aspects (Oviedo-Ocana et al. 2015; Cerda et al. 2017).

Since OFMSW is heterogeneous material and usually cannot be modified, management of the composting process has to be focused on environmental factors. Furthermore, OFMSW composition has been observed as an individual for different countries or even for each MBT plant. Although much research on the composting process conditions exists (Barrena Gómez et al. 2006; Waszkielis et al. 2013), only a few focused on stabilization in full scale (Gutiérrez et al., 2017; Gutiérrez et al. 2015; Sadef et al., 2015). Moreover, the available literature contains no references to similar raw-materials as used in the present research.

There are many tests of compost stability and maturity; however, there is still no universally accepted method for measuring compost stability or maturity index (Komilis et al. 2011). Stability of compost is assessed based on respirometry (a measurement of the produced carbon dioxide or oxygen consumed by microorganisms), which allows estimating the potential biological activity (Fourti 2013; Cerda et al. 2017). A high maturity index is necessary when the compost is to be used as a nutrient for soil and fertilizer (Huang et al. 2017).

In the composting process, respiratory activity has become an essential parameter in determining the stability of compost, as well as for monitoring the composting process and is considered an important factor for assessing the maturity of the material (Barrena Gómez et al., 2006). Higher rates of carbon dioxide release or oxygen consumption characterize less stable composts. Compost can be referred to as very mature, mature, and immature (Fourti 2013). A drawback of respirometric tests is the use of different temperatures and the amount of sample. It is assumed that respirometric measurements should be performed at 35-37°C.

The most recognizable respirometric indicators are effective breathing rate (DRI) and cumulative O2 consumption after four days (AT4) (Barrena Gómez et al. 2006). These indicators have been used successfully as indicators of stability in tests both on a laboratory scale and on an industrial scale (Barrena Gómez et al. 2006; Cerda et al. 2017; Colón et al. 2017). In case when the aim of composting is to produce so-called stabilized bio-waste, depending on the standards in the European Union, the AT4 value in the final product should amount from 5 (Germany), by 7 (Austria) to 10 (Poland) mg O_2 / g dry matter. If the whole process is carried out in two stages with the use of closed reactors or composted windrows aerated in halls, by the relevant regulations, the end of the first so-called hot phase requires material stabilization at the level AT4 =20 O_2/g dry matter (Sidełko et al. 2017).

The self-heating test measures the temperature rise due to the heat released from the biological and chemical activity of the compost sample. It is a simple method, and the results are easy to understand. This test cannot be directly correlated with breathing, because many chemical and biochemical reactions unrelated to breathing are also exothermic. Furthermore, other factors such as porosity or humidity also affect the heating of biomass (Barrena Gómez et al. 2006).

This study aimed to assess the effect of aeration, irrigation, turning frequency and process time on OFMSW stabilization after the intensive degradation phase of compositing in a full-scale MBT plant.

2. Materials and methods

2.1. Composting material

The material used in this study was obtained from Waste Management Company, located in Lower Silesia Region, Poland, a Mechanical Biological Treatment (MBT) plant. The mechanically pretreated wastes consist of sieving to 60 mm diameter and the magnetic separation of ferrous materials. The organic fraction of municipal solid waste (OFMSW) is characterized in Table 1.

Table 1. Characterization of the OFMSW fraction

Fraction	Content [%]	Fraction	Content [%]
Fruits	7.2	Inert waste	5.9
Vegetables	5.1	Textiles	0.6
Other biowastes	12.3	Metals	0.87
Wood	0.4	Dangerous materials	0.3
Paper	6.1	Tetrapack	4.2
Plastics	3.5	Others	7.3
Glass	10.3	0-15 mm fraction	35.93

2.2. Composting facility

The six enclosed box reactors (pile size 21.5 m x 7.5m x 2.0 m) with irrigation and positive aeration by a blower with air capacity 60.5 m^3/min were used during experiments. The scheme of the process is presented in Figure 1.

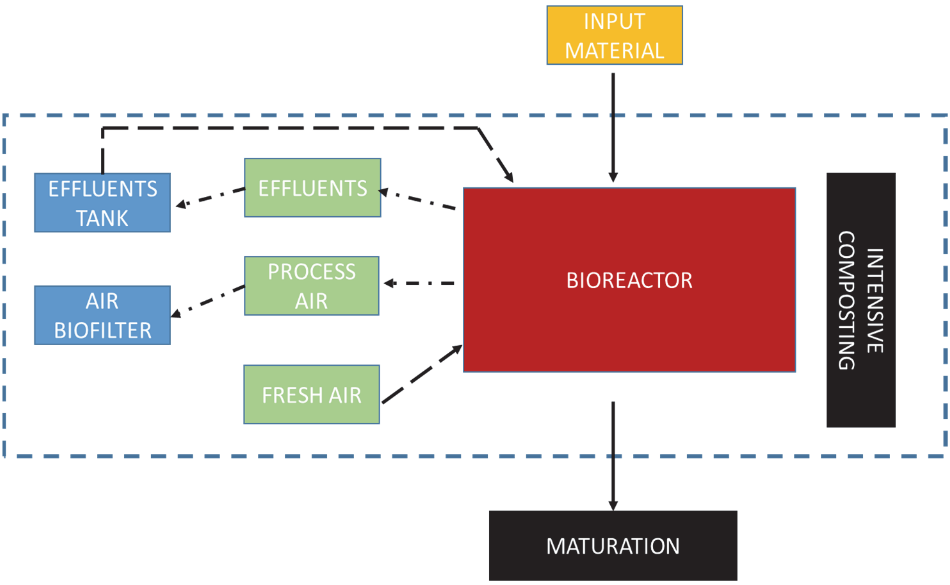

Fig. 1. The scheme of composting process facility

The temperature was measured using stainless temperature probes 2 m long. The probe had three sensors located at distances 20 cm apart, starting from the tip of the probe.

2.3. Sampling method

Ten to twelve sub-samples were taken from a pile to obtain representative samples, directly in the composting facility, and mixed in a clean pail. The weight of the sample after mixing sub-samples was approximately 10-15 kg. All analyses were done using neither frozen nor conditioned material.

2.4. Analytical methods

Stabilization of the material was determined using the self-heating test. Dewar flasks (2.0 dm^3 capacity; 100 mm internal diameter) equipped with electronic memory thermometers were used as the Dewar Kit (Brinton et al. 1995). Determination of moisture was done using a squeeze test (Anonymous 2009). If the compost was found to be too dry, water was added. If the compost was too wet, it had to be dried overnight by spreading on a flat, clean surface. After confirmation of the optimal moisture for the test, the Dewar flask was filled with compost chilled to room temperature and the thermometer probe was inserted. The internal temperature was measured at 2h intervals throughout the experiment. The moisture content was determined gravimetrically with oven drying at 105°C.

2.5. Statistical analysis

To assess how the irrigation, aeration, turning frequency and process time influence the OFMSW stabilization. The fractional factorial plan ($2^{(4-1)}$) for four factors on two levels with two replicates was generated using Design of Experiments Module of STATISTICA version 10 (StatSoft, Inc., 2011, USA) (Table 2).

Table 2. The experimental design matrix with coded values

Run	X1 aeration of the pile	X2 irrigation	X3 time of the experiment	X4 turning of compost
1	-1	-1	-1	-1
2	-1	-1	1	1
3	-1	1	-1	1
4	-1	1	1	-1
5	1	-1	-1	1
6	1	-1	1	-1
7	1	1	-1	-1
8	1	1	1	1

The fitted first-order model is:

$$Y=\beta_0+\sum\beta_i X_i, \quad (1)$$

where:
Y – the predicted response,
β_0 and β_i – constant coefficients,
X_i – the coded independent factors.

The aeration (X_1) was determined by blower working time. For minimum value after 5 minutes blowing, 10 minutes break appear. For the maximum value, the working time and pause period were changed respectively. The irrigation level (X_2) was set up for 5000 dm^3/ d as a minimum and 10000 dm^3/d as a maximum. The process was planned for 2 or 4 weeks (X_3) and in that time weekly frequency turning (X_4) was done or not.

The effect on stabilization efficiency of each variable was determined by equation (2):

$$E_{(xi)} = (\sum M_{i+} - \sum M_{i-})/N, \quad (2)$$

where:
$E_{(xi)}$ – the main effect of the tested variable on stabilization efficiency,
M_{i+} and M_{i-} – the stabilization where the variable (xi) measured was at a high and low value, respectively,
N – the number of runs (Chauhan et al. 2007).

The standard error (SE) of the stabilization effect was the square root of the variance of an effect, and the significance level (*p-value*) of each stabilization effect was determined using Student's t-test (3):

$$t_{(xi)} = E_{(xi)}/ SE, \quad (3)$$

where:
$E_{(xi)}$ – the effect of variable *xi* (Chauhan et al. 2007).

The results of the experimental design were analyzed and interpreted using STATISTICA StatSoft ver. 10. All statistical tests were evaluated at the 95% confidence level.

3. Results and discussion

The OFMSW used by Gutierrez et al. (2015) was separated manually from the voluminous matter, and particles higher than 80 mm in diameter removed. It consisted of different percentages of organic matter, glass, plastic, paper-card, and others, being the organic matter the most abundant components

(63%) (Gutiérrez et al., 2015). The material used in this study was pretreated mechanically, and the size of particles was not bigger than 60 mm (Table 1).

Figure 2 shows the reduction of self-heating possibility of OFMSW after the intensive degradation part of the composting process.

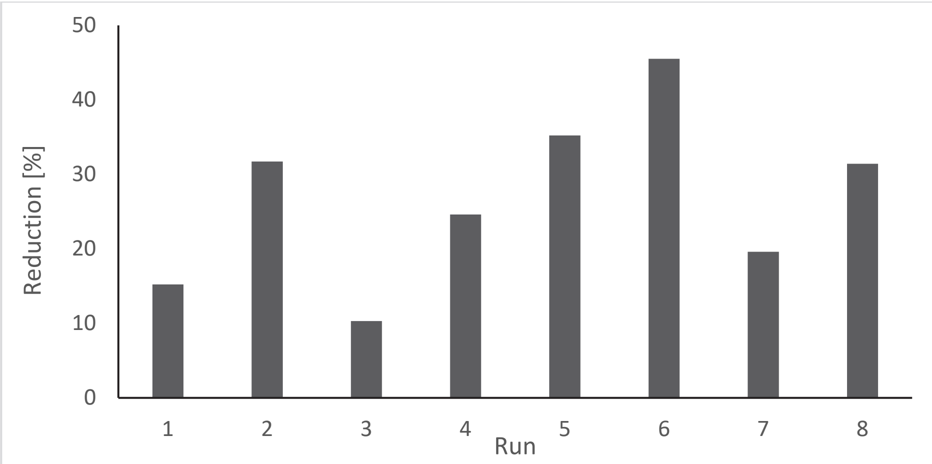

Fig. 2. Reduction in self- heating possibility after composting

The highest stabilization yield was noticed for four weeks processes. The lowest one was observed in run no 3, which characterized minimum aeration and composting time with maximal irrigation. Based on the Dewar test results statistical analysis was done, and the results are presented in Table 3.

Table 3. The statistical analysis of obtained results

Factor	Effect	t ratio	P value	Significance*
Aeration	0.0586	4.6715	0.0095	"+"
Irrigation	-0.0484	-3.8548	0.0182	"+"
Time	0.0624	4.9704	0.0076	"+"
Turning	0.0823	0.6128	0.5833	"-"

* Significant at $p \leq 0.05$, standard error = 0.0355, $R^2 = 0.94$

Among four factors, mechanical turning was found not to significantly influence the effect of stabilization. The determination coefficient (R^2) of 0.94 (which means that the model explains 94% of the total variation) suggests an adequate representation of the process model and a good correlation between the experimental and predicted values (Brinques et al. 2010; Seruga and Krzywonos 2015). Therefore, a linear equation which describes the response of material stabilization can be planned:

$$Y = 0.263 + 0.058X_1 - 0.048X_2 + 0.062X_3 \qquad (4)$$

where:
Y – predicted response,
X_1, X_2, X_3 – coded values of the factors according to Table 2.

The positive coefficients for aeration and process time indicate a linear effect increment in stabilization, while the negative values for irrigation indicate a direct effect on the decrement. For this statement confirmation, a control run was conducted.

The achieved stabilization yield was about 47.5%, where the aeration (X1) was set up as blower working cycle: 10 minutes blowing and 5 minutes break, the irrigation level (X2) was set up for 10000 dm^3/d and process was performed 4 weeks (X3).

The turning frequency has been proved to be a factor that affects the decomposition as well as compost quality (Smith and Hughes 2004; Ogunwande et al. 2008; Getahun et al. 2012; Sidełko et al. 2017). Getahun et al. (2012) conducted experiments on a specially prepared mixture of biodegradable municipal solid waste and carried out in 3 bins with different turning frequencies. They have confirmed that the decomposition rate increased with increasing turning frequency – furthermore, the shortest maturation time they have noticed for the highest turning frequency. However, at full scale, the high frequency of turnover generates costs and requires proper management (Colón et al. 2017), thus its limitation can optimize exploitation costs. Based on this study results and statistical analysis impact on material stabilization of turning frequency was not confirmed. Probably due to short process time of intensive degradation: 2-4 weeks, other process conditions and material characteristic, mainly proper porosity to ensure air flow inside the pile without loosening of material occurring during turning.

Moisture content is a critical parameter in the composting process (Petric et al. 2012). This statement was also confirmed Iqbal et al. (2015) when study optimization of process parameters for the decomposition of kitchen waste into mature, stable compost used Box-Behnken design. Oviedo-Ocana et al. (2015) have noticed a steady drop in moisture during the composting process, which was the result of the increase in temperature and the rotation of the material. Despite the production of water in the biochemical process, the net loss of water occurs during open composting.

Composting in open systems causes the release of a significant amount of odors that disrupt the well-being of residents. However, the initial composition of the composted material affects the production of volatile organic compounds and the emission of odors during the composting process (Gutiérrez et al. 2017).

As expected, a longer composting time affects the temperature decrease in the windrow and better stabilization. Results of this study have been confirmed by Siemiątkowski (2014), who determined the decomposition of the OFMSW by measuring: respiration activity – AT4 parameter (based on CO_2 production over four days), loss-on-ignition and total organic carbon content. In similar process conditions (with aeration and irrigation) material stabilization was related to process time. After five weeks of the composting value of AT4 parameter decreased to 5.29 mg O_2/g of organic matter (Siemiątkowski 2014).

The air blowing into the pile has to provide enough oxygen to enable aerobic degradation of substrates. The enforced aeration rate impacts the oxygen concentration inside a pile, cooling of the material, pathogen destruction and finally decomposition (Li et al. 2013). This factor has been confirmed in our research as significant for composting with a positive impact on decomposition. Previous studies, provided on sewage sludge confirmed that statement. In each research, the increasing of the aeration rate influences on higher stabilization and better compost quality (Hamoda et al. 1998; Dach et al. 2007; Colón et al. 2017).

As the nutrients for the microorganisms must be dissolved in water before they can be assimilated, water content is essential for the composting process (Hamoda et al. 1998). The optimum value of moisture has been found as 60 %. The content of water higher than 60% will prevent oxygen diffusion through the pile, as the voids will be filled with water and the free air space will be eliminated. In the case of low moisture, there will be no water for the dissolving of the organic matter. In both cases, organic matter degradation will decrease.

There were slight increases in the pile temperatures immediately after each turning operation in the early days of the experiment. The turning operation was responsible for the rise and fall pattern of the temperature profile and has been reported as the re-activation of the composting process (Ogunwande et al. 2008).

In this study, an increase in irrigation harms material stabilization. It confirms that after reaching optimum moisture, additional water has an adverse effect. It was found that the rate of oxygen uptake increases linearly with the increase of moisture and it reaches its maximum value at about 50-70%, after which the rate begins to decrease. Furthermore, below 20% very little biological activity occurred (Richard et al. 2002). Siemiątkowski proved that low water content with no irrigation during the process resulted in "dry stabilization". It means that after re-irrigation, all biological processes will start again (Siemiątkowski, 2014).

Using the simple method for stability test and Design of Experiments methods were able to get quite fast results without testing all possible combination of variables. It is crucial when having in mind the costs of the process. The costs for MBT plants are tough to compare because they depend on the technology used (AD or composting), treatment capacity, amount of impurities which required mechanical pre-treatment), but the most important is the characteristics of composted material (Colón et al. 2017). According to Abdoli et al. (2019) net present value in the internal rate of return for producing compost using aerated static piles was equal to 12.4%. In most cases, MTB's operating costs are the result of an agreement between the public administration and private enterprises managing MBT plants. For this reason, the costs also have other variables than strictly technological aspects (Colón et al. 2017).

4. Conclusions

As for all biological processes, the reaction rate can be influenced by various factors. In the case of composting of OFMSW in full-scale in MBT plant, which is known as being difficult to study and control, simple methods should be investigated. Dewar tests might be used as a simple method for control composting process directly in full-scale MBT plant. Determined material stabilization can be used for composting optimization, considering factors that can be modified. It has been found that aeration, irrigation and process time influenced the composting process, while mechanical turning was revealed to be insignificant. It has also been found that an increase in irrigation harms material stabilization. The OFMSW composting in full-scale focused on material stabilization with the lowest cost. That is why the results of this study might be useful for MBT plants.

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Abstract

Composting is a natural process; however, many artificial factors have been developed to improve process efficiency for the organic fraction of municipal solid waste (OFMSW) stabilization in the mechanical – biological treatment (MBT) plant. The study aimed to assess the effect of aeration (X1), irrigation (X2), process time (X3) and turning frequency (X4)on OFMSW stabilization after the intensive degradation phase of compositing in a full-scale MBT plant. The four-factorial design on two levels with two replicates was used to the optimization of compost stabilization yield. Among analyzed factors, mechanical turning was found not to significantly influence the effect of stabilization. The achieved determination coefficient (R^2) of 0.94 suggests an adequate representation of the process model and a good correlation between the experimental and predicted values. The achieved stabilization yield obtained in the control run was 47.5%, where the aeration (X1) was set up as blower working cycle: 10 minutes blowing and 5 minutes break, the irrigation level (X2) was set up for 10000 dm^3/d and process was performed 4 weeks (X3).

Keywords:
municipal solid waste, composting, mechanical-biological treatment, organic fraction, DOE

Wpływ wybranych czynników na efektywność procesu stabilizacji organicznej frakcji odpadów komunalnych (OFMSW) w zakładzie obróbki mechaniczno-biologicznej

Streszczenie

Kompostowanie to zachodzący naturalnie tlenowy proces biodegradacji wykorzystywany przemysłowo zwłaszcza do przetwarzania odpadów. Opracowano i określono wiele parametrów tego procesu w celu poprawy wydajności procesu stabilizacji frakcji organicznej odpadów komunalnych (OFMSW) w zakładzie obróbki mechaniczno-biologicznej (MBT). Niniejsza praca miała na celu ocenę wpływu napowietrzania (X1), nawadniania (X2), czasu trwania procesu (X3) i częstotliwości przewracania pryzmy (X4) na stabilizację OFMSW uzyskanej po intensywnej fazie kompostowania w zakładzie MBT. Do optymalizacji wydajności stabilizacji kompostu wykorzystano czteroczynnikowy plan eksperymentu (DOE) na dwóch poziomach z dwoma powtórzeniami. Stwierdzono, że mechaniczne przewracanie pryzmy nie ma statystycznie istotnego wpływu na efektywność stabilizacji. Osiągnięty współczynnik determinacji (R^2) wynoszący 0,94 sugeruje odpowiednią reprezentację modelu procesu i dobrą korelację między wartościami eksperymentalnymi i przewidywanymi. Uzyskana wydajność stabilizacji uzyskana w przebiegu kontrolnym wyniosła 47,5%, przy ustawieniu czasów pracy wentylatora napowietrzania jako 10 minut działania i 5 minut przerwy (X1), nawadniania na poziomie 10 000 l/dobę (X2) i eksperymencie trwający, 4 tygodnie (X3).

Słowa kluczowe:
odpady komunalne, kompostowanie, mechaniczno-biologiczne przetwarzanie,
frakcja organiczna, metoda planowania eksperymentu

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Long-term Analysis of the Operation of the Urban Heating Network Including Aspects of Environmental Protection

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1. Introduction

The primary factor determining the overall quality of pipelines is their leak-tightness. Engineers involved in the operation of heating networks believe that there is no perfectly leakproof system. Leakages are a natural phenomenon during the operation of heating networks. The technical condition of the system and its extension should be an element of care for the technical infrastructure at the local level (Lizakowski et al., 2016).

It is not possible to precisely determine the time or place of leakages' occurrence (one can only forecast them). The concept of leakages can be defined as various types of network damage that cause water leakage. It can be both the leakage in the pipeline and the leakage of the network fittings. The leakage will be both a small leak invisible on the surface of the ground, as well as a violent failure causing a massive water leak, flooding of streets, basements and underground structures. Depending on the scale of the leakage, appropriate measures and equipment necessary for its removal and trained employees should be involved (Troja et al., 2019).

All leakages, both small ones and those of a larger scale, cause significant losses for heating companies (direct and indirect). Direct losses result from the following reasons:

- the district heating water is treated water, the appropriate preparation of which costs about PLN 3-6/m^3 (Chorzelski et al., 2013),
- the cost of its pumping into the network was incurred (costs of electricity consumed by refill pumps),

- district heating water always has a temperature higher than ambient temperature, depending on the so-called heating curve,
- threats to human health and life (e.g., scalding with hot water) due to unsealing of the heating network,
- leakage causes water losses depending on the time of leakage.

Indirect losses are much more difficult to quantify and include aspects such as:

- negative perception of the company,
- lowering customer satisfaction,
- maintaining the brand's position.

To limit the losses generated by leaks and their negative impact on environmental protection, they should be detected and removed as soon as possible.

Although modern district heating networks are being constructed as networks made in pre-insulated technology together with a built-in system to detect breaks in insulation continuity and moisture (the so-called alarm system), most heating networks utilized in Poland are made according to the traditional channel technology. They are the oldest and at the same time the most prone to failure component of the heating system, which is why leak detection in these networks is so important.

Leak detection methods in district heating networks can be divided into several groups according to the scheme shown in Figure 1.

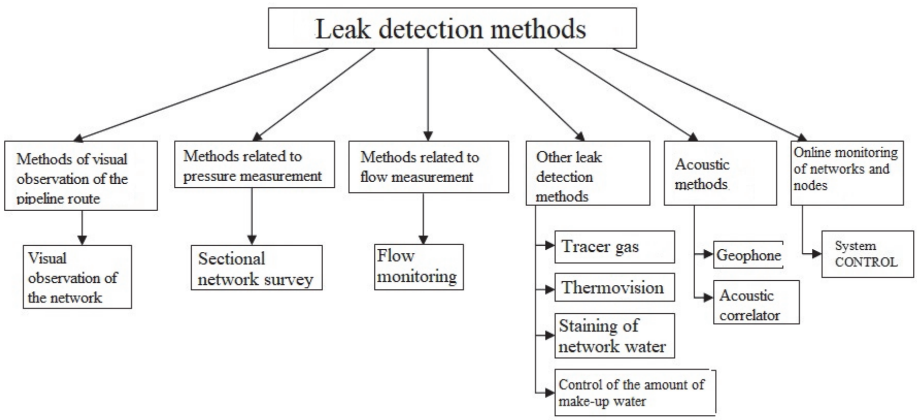

Fig. 1. Division of methods for locating leakages in heating networks

Table 1 presents the advantages and disadvantages of the methods for locating leakages in heating networks presented in Figure 1.

Table 1. The advantages and disadvantages of leak detection methods discussed in the article

Type of method	Advantages of method	Disadvantages of method
Visual observation of the network	Lack of specialized equipment, simplicity of the test, short time of the test, low cost of testing, the possibility of carrying out the test by workers during daily operations	The difficulty of unambiguously assessing the location of the leak
Sectional network survey	An uncomplicated measurement method, no specialized equipment required	Strongly depends on the leak-tightness of the network valves, the need for efficient pressure gauges, the need for access to chambers, does not specify the point of occurrence of leaks
Flow monitoring	Simplicity, fast analysis of measurements	Necessity of access to pipelines, strong impact of measurement accuracy (human factor), strong influence of sediments in pipelines, flow free of gas and steam bubbles, does not determine the place of leakage
Control of the amount of make-up water	Information for the company about the failure and the need to try to locate the leak by other methods	Small leaks are not detected, it does not determine the location of the leak
Tracer gas	Very high sensitivity, high test speed, allows one to detect the smallest leaks, allows one to test deeply located systems	The need for direct access to the pipeline or device, ambiguity, cannot be carried out during rain and wind

Table 1. cont.

Type of method	Advantages of method	Disadvantages of method
Thermovision	Comfortable measurement from the ground surface with current temperature preview, non-invasive	Strong influence of weather conditions (sunshine, wind) and time of day, quite high price of the device, sometimes ambiguity of measurement
Staining of network water	A straightforward method to use, low cost of testing	It does not specify a leak point; it is only suitable as an action to help locate leaks
Geophone	The exact method of locating the failure, the possibility of testing without access to the pipeline, one person can conduct the test	It requires much experience from the operator, a strong impact of external noise, the need to dry the heating channel when the leakage is in the water
Acoustic correlator	A very accurate method of leak detection; it does not require as much experience as geophone measurement; accuracy and speed of failure location	Necessity of access to two heating chambers, high price of the device, strong impact of the corrosion of pipelines, constant diameter of the measured section required, need to dry the heating channel when the leakage is in the water, sound disturbance caused by fixed points and pipeline supports
CONTROL comprehensive diagnostic and safety system	The exact method of leak detection. One system performs many tasks: leak location, access authorization, telemetry, high speed of operation	Necessity to train employees of companies and system dispatchers, high costs of system implementation

Source: the authors' study

When choosing the particular method, one should bear in mind that leak detection depends on many factors, such as pipeline depth, access to heat chambers and pipelines, device operators' experience, atmospheric conditions, external disturbances and economic aspects (test and diagnostic equipment prices). The considerations regarding leakage in water supply networks seem to be cognitively valuable with regard to analyzing the considered issue. Numerical leakage analysis of the water pipe was discussed by Suchorab et al. (2016).

Locating the leakage can be implemented in two ways: with the participation of trained employees and own equipment or entrusting this task to a specialist external company. Regardless of the choice of the method of implementation of the heating network diagnostics, preventive measures should be taken into account, thanks to which high direct and indirect costs generated by unsealing of the heating network, adverse effect on the environment and the health of employees can be avoided. Detection of already created and prediction of potential sites where damage to the heating network may occur is still an urgent problem that provides significant research opportunities. The direction of research on this subject should focus on system solutions based on embedded systems operating in the internal network. Such a system should also have the features of a distributed and remotely managed system.

In the article, based on long-term observations, a multi-criteria analysis of the impact of the heating network of a typical city in Poland on the natural environment and selected aspects of environmental protection was carried out.

2. Description of the analyzed heating network

The article presents an analysis of the operation and modernization of the heating network for over 10 years, i.e., from 2007 to 2016. The tested network provides heating to residential buildings and companies in the city of Kościerzyna. It is currently in 87% pre-insulated and 13% standard channel network. Over the past 10 years, the network has been successively developed to ensure its monitoring.

The control system of pre-insulated network leak-tightness is monitored in a continuous mode by analyzers located in the thermal centers around the city. The leak-tightness of the analyzed pre-insulated heating network is monitored using a pulse security system. The channel heating networks are not equipped with an alarm system informing about leaks.

Table 2 presents the development of individual sections of the heating network for over 10 years. Static measures were used to visualize the changes, i.e., mean value (M), standard error (Se), median (Me), standard deviation (Sd), skewness (Ske), minimum (Min) and maximum (Max) values.

Table 2. Development of the heating network in the years 2007-2016

Termination	M	Se	Me	Sd	Ske	Min	Max
Total length of the network [mb]	382505.78	243650.80	23689.40	808098.30	1.92	4898.41	2017013.53
Length of pre-insulated network [mb]	378491.37	243603.45	19820.90	807,941.24	1.92	1424.91	2012680.03
Cable network length [mb]	4014.41	117.98	4333.40	391.31	-0.58	3473.50	4333.60

Figure 2 presents the percentage changes of sections of the pre-insulated and channel network in particular years and their expansion in those years.

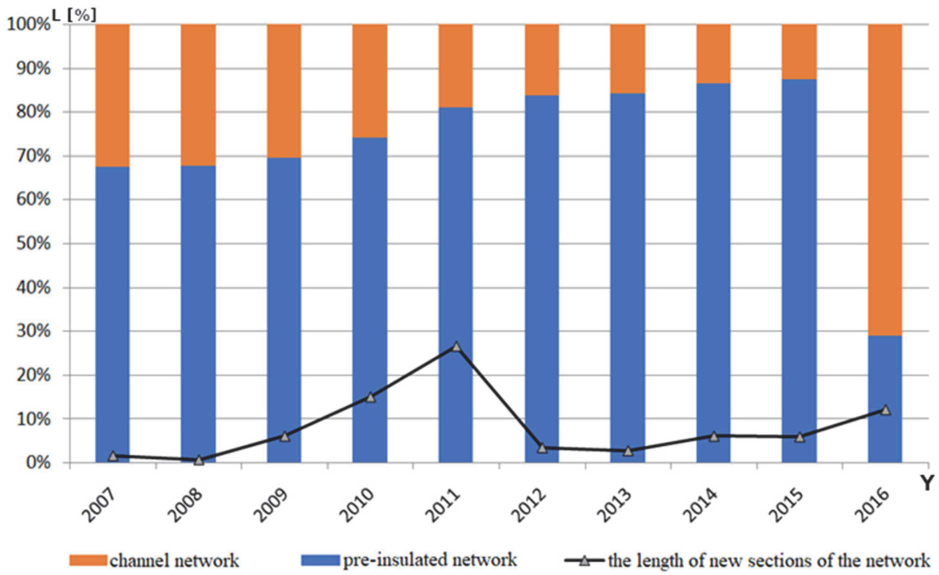

Fig. 2. Percent changes in the length of the ducted and pre-insulated network in 2007-2016

The percentage distribution of changes in the network sections presented in Figure 2 shows that in individual years the heating network was gradually developed. In particular, this development concerned the pre-insulated network, while the new sections of the heating network were most intensively built up to 2011 and in 2011, and then the extension of the network was much smaller. Since 2012, there has been a change in the concept of network development – instead of adding new sections of the network, the existing ones were modernized.

The general trend of modernization taking place over the analyzed 10-year period was that it was heading towards developing the channel network and creating a pre-insulated network.

3. Analysis of the failure and operation of the heating network

The first stage of the analysis of the operation of the heating network was to classify the failures occurring in it and the intensity of their occurrence in particular years. The identified failures were classified due to their place of occurrence, i.e., failures were identified that occurred in distribution network sections and receiving sections. However, the leakage losses were estimated based on water, which had to be replenished. Make-up water is the loss of heat carrier in heating networks (high-parameter network and external receiving installation) divided into:

- loss of the carrier during the operation of the heating network (fittings leaks, pipeline failures, planned repairs and modernization of the network),
- receiving systems (filling and refilling of water losses in the receiving installation after repairs and modernization, sale of heat carrier to recipients).

In the receiving sections, only one single cause was distinguished, which resulted in the need to refill the carrier. These were replenishments after repairs and modernizations of the receiving section, while in the examined period no heat carrier was sold to customers. However, in the distribution sections, three groups of failures were distinguished. The data presented in Table 3 shows that the failures related to the pipeline required most of the replenishment of the carrier, but they were not as intense in the analyzed years. There were years (Fig. 3), e.g., 2012, 2014 and 2015, when such failures didn't occur at all. Replenishments caused by repairs or modernizations constitute the second group of events that required large replenishments of the carrier. Over the analyzed period, they showed a constant trend of around 550 m^3.

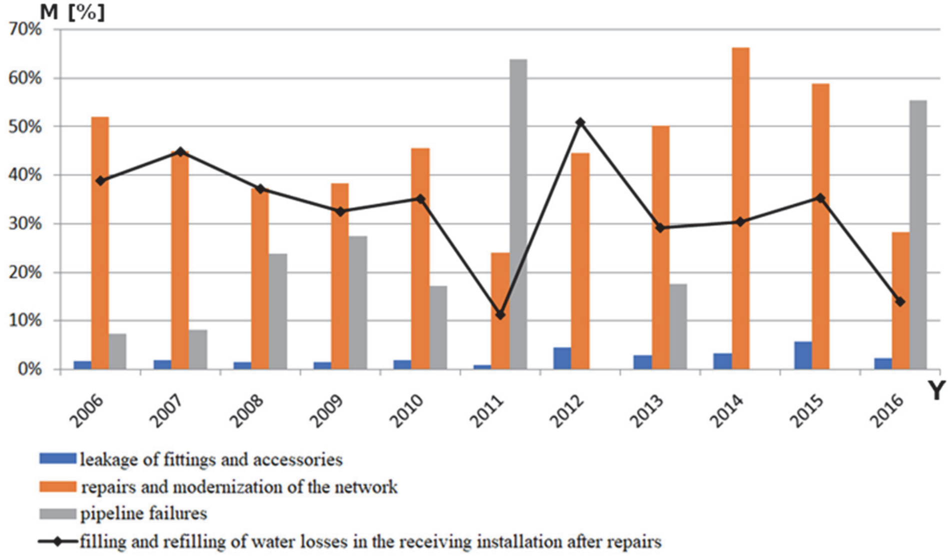

Fig. 3. Malfunctions of the heating network in 2007-2017

Network failures at a negative outside temperature are dangerous, not least because of the discomfort of heat consumers. In extreme cases, they can lead to the destruction of the internal system as a result of their most vulnerable fragments getting frozen up, e.g., in stairways, or other factors.

Table 3 presents, with the use of statistical measures, quantitative changes in network failures. The primary measure of the failure impact assessment on the network was the amount of water that had to be replenished as a result of a given type of failure.

In the history of the analyzed heating network, one major failure of the heating network and several local network failures were noted. The failure in the transmission network from February 1999 consisted of a delivery break for the entire city for 12 hours. Other failures are local, for example, in the Osiedle 1000-Lecia housing estate in February 2012, an outage took place for several buildings for 3 hours (170 inhabitants covered by a time limit), in March 2012 – outage for a few buildings for 3 hours (200 inhabitants covered by a time limit), in December 2016 – failure of the port, without interruption in the supply of heat (utility building), in January 2017 – the failure of the port, without interruption in the supply of heat (utility) January 2017 – the failure of the connection, the reduction in the supply of heat (70 residents covered by a time limit), and in December 2017 – outage for several buildings for 5 hours (500 inhabitants covered by a time limit).

Table 3. Malfunctions of the heating network in 2007-2017

Termination		M	Se	Me	Sd	Ske	Min	Max
Amount of make-up water [m^3]		1368.27	233.67	1198	774.99	2.58	707	3546
Carrier losses during the operation of the heating network	leakage of fittings and accessories	30.45	2.78	34	9.22	-0.09	20	42
	pipeline failures	407.82	204.04	208	676.74	2.48	0	2262
	repairs and modernizations	548.18	44.92	505	148.98	0.92	349	850
Carrier losses in the receiving installation	repairs and modernizations	381.82	22.38	400	74.24	-1.05	250	450

A good indicator of the quality of the network system is the information about the annual amount of water that was exchanged in the system. The examined heating system in this respect belongs to the relatively secure systems, with the norm of water changes in an annual ratio of 4 to 5.

Table 4 presents the changes in indices important for the heating network. In particular, attention was paid to the amount of make-up water, the heat amount needed to heat the carrier for the replenishing, the total cost of heat to replenish the carrier, network total disruption and the amount of water exchange in the system.

Based on the data collected in Table 4 and the distribution of selected factors presented in Figure 4, conclusions can be drawn that refer to the observations noted during the system analysis. In the case of the surveyed network, the most significant year was 2011, in which the most intense investments were implemented. Later, only the modernization of the old network and its development took place.

Table 4. Characteristics of the networking system in 2007-2017

Termination	M	Se	Me	Sd	Ske	Min	Max
Amount of make-up water [m^3]	1313.73	230.26	1186.00	763.68	2.94	707.00	3546.00
Amount of heat needed to heat the carrier for replenishment [GJ]	334.89	57.81	301.18	191.75	2.86	177.74	891.46
The cost of combined heat intended to replenish the carrier [PLN]	12279.73	2215.01	10675.82	7346.36	2.64	6481.55	33142.51
Network total disruption [m^3]	358.73	21.17	388.00	70.23	0.26	271.00	435.00
Amount of water exchange in the system	3.81	0.60	3.70	2.00	1.95	1.60	9.10

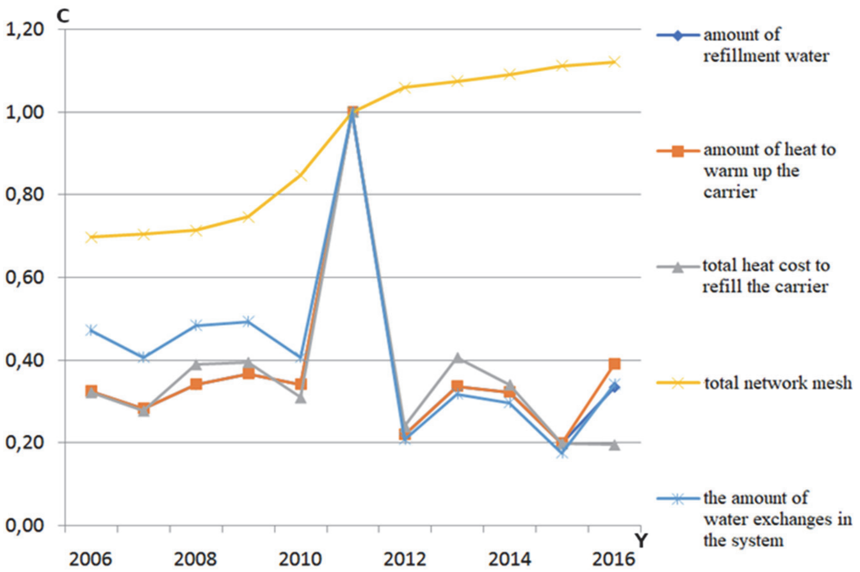

Fig. 4. Distribution of selected networking system coefficients in 2006-2016

Since 2012, the following costs have been reduced by about 10%: the total costs for replenishing the carrier, the amount of make-up water and the amount of heat to be heated. However, the other two indicators have changed a lot because the amount of water exchange has decreased by about 18%, and the total network disruption has increased by about 40%.

4. Conclusions

Detection of already created and prediction of potential sites where damage to the heating network may occur is still an urgent problem that provides significant research opportunities. The research on this subject should focus on system solutions based on embedded systems operating in the internal network.

The analysis of the actual heating network over 10 years allowed one to assess the dynamics of its development and modernization. In this respect, it was noted that the network was intensively developed until 2011 when the most significant investments took place. It can be assumed that in 2011 the development of the network became saturated, which meant that in the following years, network managers focused on the modernization of old sections through their development.

The actions taken related to the expansion and modernization of the network translated into a change in the coefficients that testify to the quality of the heating network and its impact on the natural environment. In particular, the most significant failures occurred before 2011, while later ones were quickly detected and removed.

The investment in the heating network also influenced the improvement of the quality of its operation, which is reflected in a reduction of about 10% of the costs of replenishing the carrier, the amount of make-up water and the amount of heat to be heated. Also, the other two indicators assumed for the assessment purposes have changed even more because the amount of water exchange has decreased by about 18%, and the total network disruption has increased by about 40%.

Based on a long-term analysis carried out for an urban heating network of up to 30,000 residents, it was found that investing in the modernization and pre-insulation of the network translates into a significant improvement in its functioning in a wide range. It contributes to lower costs of its operation, increased customer satisfaction, and positively affects the impact on the natural environment.

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Abstract

The article presents methods for the location of leakages in heating pipelines. The advantages and disadvantages of each of the described methods are presented. The exploitation and modernization of the actual heating network in the city of up to 30,000 inhabitants over the space of 10 years have been characterized. The examined heating network was analyzed for the degree and categories of malfunctions occurring in the examined time space in the network and impact on the natural environment was determined. The article also examines the impact of various factors, such as the amount of make-up water, the amount of heat required to heat the supplementary carrier, the total cost of heat to replenish the carrier, networks total disruption and the amount of water exchange in the system and its impact on the natural environment. At the same time, an assessment of the impact of the modernization of the heating network combined with its munition to reduce the impact of these factors on environmental protection was made.

Keywords:
heating network, network monitoring, heat network malfunctions, environmental protection, pre-insulated networks

Długoterminowa analiza eksploatacji miejskiej sieci ciepłowniczej z uwzględnieniem aspektów ochrony środowiska

Streszczenie

W artykule przedstawiono metody lokalizacji nieszczelności rurociągów ciepłowniczych. Przedstawiono wady i zalety każdej z opisanych metod. Scharakteryzowano eksploatację i modernizację rzeczywistej sieci ciepłowniczej w mieście do 30 tysięcy mieszkańców na przestrzeni 10 lat. W badanej sieci ciepłowniczej przeanalizowano stopień i kategorie awarii występujących w badanej przestrzeni czasu w sieci oraz określono ich wpływ na środowisko naturalne. W artykule zbadano również oddziaływanie rożnych czynników, takich jak: ilość wody uzupełniającej, ilość ciepła do podgrzania nośnika na uzupełnienie, koszt łączny ciepła przeznaczony do uzupełnienia nośnika, zład łączny sieci oraz ilość wymian wody w systemie i jej wpływ na środowisko naturalne. Równolegle, podjęto ocenę wpływu modernizacji sieci ciepłowniczej, połączonej z jej uzbrojeniem, na zmniejszenie oddziaływania wymienionych czynników na ochronę środowiska.

Słowa kluczowe:
sieć ciepłownicza, monitoring sieci, awarie sieci ciepłowniczych, ochrona środowiska, sieci preizolowane

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Influence of Restored External Spoil Tip of a Lignite Mine on the Discharge in a Cross-Border Watercourse (PL−CZ)

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1. Introduction

In recent decades, the need for research on the impact of lignite mine spoil tips on hydrographic conditions and the magnitude of flows in watercourses has been frequently reported both in Poland and abroad; however, no adequate methodology has been developed for such research so far. Moreover, there is no up-to-date information on the hydrological and hydraulic inventory of watercourses in the vicinity of reclaimed sites and water structures on these watercourses (Stachowski et al. 2013, Szafrański et al. 2011). The case also becomes very important when such studies concern catchment areas located in cross-border zones (Czamara et al. 2009, Wiatkowski et al. 2015).

Opencast lignite mining is always associated with the disturbance of the landscape and groundwater conditions. It results from deep transformations of the natural environment, carried out by opencast mining (Kasztelewicz et al. 2007a, Kocher et al. 2009, Kołodziejczyk et al. 2007, Rehor & Ondrácek 2008). Both the soil cover and geological structure, as well as landform features and the structure of soil use (Bender 1995, Szafrański et al. 2011) are subject to considerable changes, which are followed by a change in water conditions and a visible impact on soil degradation, devastation and infertility (Dimitrijević et al. 2014). Excavation pits and soil tips are formed and the area is drained (Szafrański et al. 2011). Operation in opencast mines requires rational and environmentally friendly engineering solutions (Oparin et al. 2012; Kasztelewicz et al. 2007b) because only properly performed reclamation gives an opportunity to minimise the negative effects of mining interference in the natural environment and to return to conditions similar to those prevailing before exploitation (Galiniak et al. 2015), including water conditions and the hydrographic network.

The Report on the Lower Silesia Province Environment Condition (WPOŚWD 2008) shows that the Lower Silesia region is ranked second in Poland in terms of the area of degraded and devastated land. The reasons for such a situation should be seen primarily in the intensive development of industry, including operations related to mining and energy sectors. One of the areas degraded on a large scale in the past by removing overburden and forming a spoil tip is "Turów" Lignite Mine in Bogatynia. Negative impact in this region is manifested by land transformation, destruction of the natural morphology of the area and disturbance of the water regime (WPOŚWD 2008, Opracowanie 2005). The cross-border character of the watercourses flowing through the spoil tip, including the Bezimienny Stream (Czech: Minkovický Potok), is of the interest to the R Group, which deals, among others things, with the issues of the impact of the external spoil tip on the surface waters on the Czech side. This is performed within the framework of the agreement between the Government of the Republic of Poland and the Government of the Czech Republic on the water management of border waters.

This paper presents an assessment of the impact of the reclaimed external spoil tip of the "Turów" Lignite Mine on the volume of flows in the cross-border watercourse of the Bezimienny Streem – Minkovický Potok, on the Polish-Czech border. Furthermore, the paper presents the methodology of hydrological and hydraulic calculations for the needs of such an assessment and indicates possible needs for flood protection of the areas located below the spoil tip on the Czech side.

2. Material and method

2.1. The water catchment area of the Bezimienny Stream

In the hydrographic division of the external spoil tip of the "Turów" Lignite Mine, the catchment area of the Bezimienny Stream (Czech: Minkovický Potok) belongs to the "eastern mountain slope region." Surface waters from its area reach the Lusatian Neisse via the river Witka (Czech: Smědá) at the 167+300 km of its course. The spoil tip in the Bezimienny Stream catchment was commenced in 1980 and completed in 1991. The surface drainage in this area is based on drainage ditches, embankments and sedimentation tanks, which are made as the works on the formation of particular levels of the spoil tip body progress. The construction of these facilities resulted in a significant increase in the retention capacity of the catchment area (Wojarnik & Iwaniak 2009).

The Bezimienny Stream (Czech: Minkovický Potok) is a left-bank tributary of the river Witka (Czech: Smědá), to which it flows at the 19+250 km of its course on the territory of the Czech Republic, in Minkovice. Until 1980, in the area of Wigancice Żytawskie, the Bezimienny Stream served as a reservoir for water from drainage ditches and drainage systems. The catchment area of the analysed profile of Tank No. 4, determined on the map in the scale 1:25000, is 1.08 km^2 (Fig. 1).

The southern part of the catchment area has large declines of up to 20%. The declines in the central and northern parts are between 2 and 5%. The ordinate of the area in the calculative profile H_o is 253.5 m a.s.l. The ordinate of the area on the water divide H_{max} is 378.4 m a.s.l. The average decline in the catchment area is 12.02%. The actual average decline in the catchment area is much lower, with more than two thirds of the catchment area falling by 2-5%. A large decline – about 20% – occurs only in the area of Świniec Mountain, on a small area. The length of the Bezimienny Stream valley is approx. 1.0 km. The Bezimienny Stream Valley was divided by two partitions, forming dry retention reservoirs.

The land use pattern in the catchment area of the Bezimienny Stream is as follows: arable land (0.76 km^2, i.e. 70%), grassland (0.22 km^2, i.e. 20%), forests (0.10 km^2, i.e. 10%).

On the 1:5 000 scale situation and altitude map (Fig. 2), the borders of partial catchment areas in the profiles of individual sedimentation tanks were determined, marking them with an index corresponding to the numbering of particular tanks. The catchment areas were determined together with their characteristics, including the area of slopes, shelves and tops of the spoil tip, the average decline of the catchment area and the degree of afforestation. The total area of the catchment area in the profile of Tank No. 4 is 1.45 km^2, of which 0.82 km^2 is the spoil tip (Wojarnik & Iwaniak 2009).

2.2. Climate characteristics

The precipitation characteristics for the area of the eastern slope of the external spoil tip, including the catchment areas of the Okleśna and Bezimienny Streams, were prepared based on the study (Prace 2008). For hydro-meteorological calculations, the values of precipitation recorded with the rain gauge and pluviograph, situated at an altitude of 320 m a.s.l on the eastern slope of the spoil tip, were assumed. The measurements of precipitation were carried out during the summer half-year (i.e. from May to October). The amounts of precipitation recorded at rainfall stations of the Institute of Meteorology and Water Management (IMiGW) in the close vicinity, i.e. in Wyszków [330 m a.s.l.] and Bogatynia [295 m a.s.l.], were used as a reference material.

Fig. 1. Catchment of the Bezimienny Stream – original condition

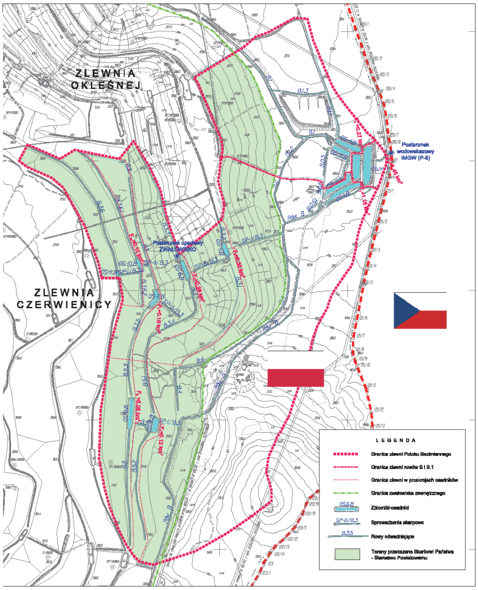

Fig. 2. Catchment of the Bezimienny Stream – current condition

Based on the lists of daily precipitation sums presented in the work (Measurement and Research Report 2002-2008), a breakdown of monthly and annual precipitation sums covering the years 2002-2008 was made in comparison with the average monthly and annual precipitation for the years 1971-2000. The work also presents the average monthly air temperatures for the Działoszyn station.

2.3. Hydrology – maximum likelihood flows

The calculations of maximum flows with a specified likelihood of occurrence due to the lack of measurements of water levels were performed with empirical formulae. As experience in engineering practice shows, the maximum annual flows with a certain likelihood of exceeding are the basic hydrological characteristics. For catchment areas where long-term observation lines exist, these flows are determined using generally accepted methods based on the analysis of likelihood curves of maximum flows. The situation is different in the case of catchment areas where long-term observations of water levels and flow measurements are not carried out. In such a case, indirect methods are used, characterised by a much higher degree of uncertainty. These are hydraulic analogy and empirical methods (Banasik et al. 2012, Wałęga & Młyński 2015).

In this paper, the Wołoszyn's method was adopted due to the fact that it is the most suitable for the Lower Silesia region (Wołoszyn 1967). It takes into account the intensity of rain that causes maximum flows. This method uses the analysis of the elements of the catchment area and assumes that the relations established for Wrocław are important for regional localities. The Wołoszyn's method consists in transposing the rain intensity from the station in Wroclaw to regional stations. Rainfall intensity is presented as a function of its duration and the likelihood of exceeding it with the storminess index, defined as the product of the many-year average of precipitation and the air temperature for the months from May to September. This relation applies to catchment area of the up to 100 km^2 (Wołoszyn 1967, Czamara & Krężel 1983). In the Wołoszyn's method, applied in this paper to calculate the flows of large waters, a significant role of the forest influence on the magnitude of runoff (surface runoff velocity) is emphasised. Specialists pay great attention to the fact that the forest is able to take over and store considerable amounts of water for some time, delaying the flow of water, reducing the culmination of large waters and limiting the frequency of floods (Miler 2015, Mioduszewski 2016, Stasik et. al 2011).

The map in the scale of 1:25 000 was used to determine the catchment area in the calculation profile of water discharge from the Tank No. 4.

2.4. Reduction in swelling flows in sedimentation tanks

In order to determine the retention capacity of the Bezimienny Stream catchment, in the profiles of sedimentation tanks, calculations of the reduction of large water flows ($Q_{1\%}$ and $Q_{10\%}$) were carried out based on the mapped swell hydrograph, assuming that the falling time of the wave t_o is equal to 2 times the concentration time t_k ($t_o = 2t_k$) (Metodyka 2009). The usable capacity of the sedimentation tanks was used to calculate the reduced flow $Q_{1\%reduced}$ and $Q1_{0\%reduced}$, which were then increased by the flows authoritative for the sedimentation tanks located below, assuming that the waves peaks overlap (unfavourable option).

2.5. Maximum likelihood flows in the stream gauge profile

On the Bezimienny Stream, below Tank No. 4, the Wigancice Żytawskie (P–8) water gauge station is located, belonging to the Institute of Meteorology and Water Management in Wrocław, where water levels and flows have been observed since 1995.

On the basis of data obtained from the "Turów" Lignite Mine (Measurement and Research Report 2002-2008), measurement sequences were compiled from the maximum annual flows of WQ [m^3·s^{-1}]. The above data were used to calculate the likelihood flows, using statistical methods. Calculations were made with the Kaczmarek's method and additionally with the maximum likelihood method (Metodyka 2009).

2.6. The capacity of the Bezimienny Stream river bed and the structure located in the Czech Republic territory

As the Bezimienny Brook (Minkovický Potok) in the Czech Republic serves as a reservoir of drainage and rainwater, the capacity of the Stream's river bed was calculated. The flow $Q_{max} = 1.19\ m^3 \cdot s^{-1}$ (corresponding to the flow of p = 20%), calculated for the 1.45 km^2 catchment area, was used as the basis for the dimensioning of the Streams' river bed. In addition, an analysis of the impact of existing communication structures on the flow conditions of large waters was carried out. This is extremely important as the condition for proper functioning of irrigation and drainage systems is to maintain the network of ditches with structures in technical efficiency (Mioduszewski 2016, Wiatkowski & Gruss 2017).

3. Test results

3.1. Precipitation

Average monthly and annual total precipitation for Bogatynia, Wyszków and Zwałowisko stations are listed in Table 1. Average annual rainfall of 1971-2000 ranges from 704 mm in Bogatynia to 720 mm in Wyszków. Between 2002 and 2008, the average monthly precipitation totals in the period from May to September at the stations in Bogatynia and Zwałowisko are similar. Compared to Bogatynia, lower precipitation at the Zwałowisko station was recorded only in June (8 mm) and in July (14 mm), whereas in August, it was 14 mm higher.

The maximum recorded daily precipitation of 144 mm was recorded at the Zwałowisko rainfall station on 10 August 2007. The highest intensity of rainfall occurred between 3 p.m. and 4 p.m. when about 100 mm of rain fell on the spoil tip. Much lower amounts of precipitation were recorded in Bogatynia (69.5 mm) and in Wyszków (45.8 mm), which proves that that exceptionally heavy precipitation had a very local character (Wojarnik & Iwaniak 2009).

3.2. Air temperatures

Average monthly air temperatures for the Działoszyn station, quoted in this work (Wojarnik & Iwaniak 2009), are summarised in Table 2.

Table 1. Monthly and annual mean total precipitation for the stations in Bogatynia, Wyszków and Zwałowisko

Period	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Year
Climate station Bogatynia [295 m a.s.l]													
2002-2008	53.1	34	36.9	37.3	58	53.5	101	112.6	52.8	53.6	57.1	41.3	689.4
1971-2000	38	32	42	44	68	94	96	90	59	48	47	46	704
Precipitation station Zwałowisko [320 m a.s.l.]													
2002-2008	-	-	-	-	62.3	61.9	87.2	126.5	49.9	56.1	-	-	-
Precipitation station Wyszków [330 m a.s.l.]													
1973-2000	45	37	47	49	69	84	93	84	59	46	52	55	720

Table 2. Mean monthly air temperature in °C for Działoszyn station

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Year
-2.8	-2.9	2.3	6.9	11.6	14.4	16.8	16.6	13.1	8.2	2.4	-0.1	7.2

3.3. Maximum likelihood flows

The following data were used for calculations:

- Water catchment area F = 1.08 km^2,
- Longest runoff course L = 1.92 km,
- h_{max} = 300.00 m a.s.l.,
- h_{min} = 253.50 m a.s.l.,
- Mean decline of the catchment area $I_{average}$ = 4.47%,
- Afforestation of the catchment area Z = 10%,
- Runoff velocity v = 1.61 $m \cdot s^{-1}$ (as read for mean decline and afforestation).

The list of maximum likelihood flows in the calculative profile is presented in Table 3.

Table 3. Summary of maximum likelihood flows calculated by the Wołoszyn's method

p [%]	1	2	5	10	20	50	100
Reduction coefficient	1	0.70	0.47	0.33	0.23	0.15	0.10
$q_{p\%}$ [$m^3 \cdot s^{-1} \cdot km^{-2}$]	7.86	5.50	3.69	2.59	1.81	1.18	0.79
$Q_{p\%}$ [$m^3 \cdot s^{-1}$]	8.49	5.94	3.99	2.80	1.95	1.27	0.85

3.4. Drainage system in the external spoil tip

The spoil tip in Bezimienny Stream catchment area started in 1980 and was completed in 1991. As the spoil tipping progressed, reclamation operations were carried out, including the formation of slopes and spoil tipping shelves as well as the afforestation of slopes. In the catchment area of the Bezimienny Stream, all the reclaimed land on the external spoil tip of the area 0.82 km^2 is owned by the State Treasury under the control of the County Office in Zgorzelec. Parallel to the reclamation works, a number of surface drainage solutions were constructed, such as drainage ditches, slope flows, and sedimentation tanks. The total length of the drainage ditches located on the shelves of the spoil tip is approx. 5.7 km, and on the foreland of the spoil tip – approx. 3.2 km. In order to secure the purity of the Bezimienny Stream waters and increase the flood retention in Wigancice, Tank No. 4 was constructed on the foreland of the spoil tip, which consists of the following:

- OS–1.B and OS–2.B sedimentation tanks in the mouth section of ditch B;
- OS–3.B and OS–4.B sedimentation tanks in the mouth section of ditch B.1;
- Two-chamber retention reservoir (4.1 and 4.2).

In the current operating manual of Tank No. 4, two variants of operation of the sedimentation tanks and the reservoir were adopted:

- Variant I assumes simultaneous operation of the sedimentation tanks OS–2.B and OS–3.B and chamber 4.2 of the reservoir;
- Variant II, on the other hand, envisages simultaneous operation of the OS–1.B and OS–4.B sedimentation tanks and chamber 4.1 of the reservoir.

List of sedimentation tanks with their characteristics is given in the Table 4 below.

Table 4. Summary of sedimentation tanks in the catchment area of the Bezimienny Stream

Sedimentation tank name	Dimensions of the bottom [m]		MaxPP [m a.s.l.]	Maximum sedimendation level [m a.s.l.]	Volume in m^3		
	Length	Width			V_{max}	V_{os}	$V_{uż}$
OS-11.B	17	5.0	354.60	353.76	350	190	-
OS-10.B	34	6.0	339.50	337.95	660	160	500
OS-9.B	108	10.0	341.00	339.44	2880	510	2370
OS-8.B	50	15.0	330.40	329.60	1790	940	850
OS-7.B	66	10.0	337.40	336.50	1910	960	950
OS-6.B	72	11.0	323.10	321.90	2360	910	1450
OS-5.B	43	13.0	300.00	298.60	2060	790	1270
OS-4.B	-	-	-	-	2510	680	850
OS-3.B	-	-	-	-	3740	1650	1830
OS-2.B	-	-	-	-	3740	850	2890
OS-1.B	-	-	-	-	4300	660	3640
Reservoir 4.2	-	-	-	-	5130	1160	3970
Reservoir 4.1	-	-	-	-	9200	2200	7000
Total:					40630	11660	27570

3.5. Maximum likelihood flows in the profiles of sedimentation tanks

Due to a too short a period of hydrological observations (14 years) made by the Institute of Meteorology and Water Management at the Wigancice Żytawskie (P–8) water gauge station, the calculation of the flows of large waters with a certain probability of occurrence was performed with the use of the Wołoszyn's method. Drainage coefficient α was adopted depending on the percentage share of the slope area in the calculative catchment area, as shown in Table 5.

Table 5. Summary runoff coefficient values on the "Turów" Lignite Mine external Soil tip

No.	Share of slopes in the total area	Drainage coefficient α
1	0-10	0.30
2	10-20	0.35
3	20-30	0.40
4	30-40	0.45
5	40-50	0.50
6	50-60	0.55
7	60-70	0.60
8	70-80	0.65
9	80-90	0.70

The process and calculation results are presented on the example of Tank No. 4 and the results are presented in Tables 6-8.

<u>Calculation data:</u>

- Water catchment area of the Fzl = 1.45 km^2
- Longest runoff course L = 2.260 km
- h_{max} = 372.,20 m a.s.l.
- h_{min} = 253.50 m a.s.l.
- Mean decline of the catchment area $I_{average}$ = 9.86%
- Afforestation of the catchment area Z = 70%. For the mean decline and afforestation the run-off velocity v = 1.08 $m \cdot s^{-1}$ as was read.

The list of maximum likelihood flows in the calculative profile is presented in Table 6.

Table 6. Summary of maximum likelihood discharge calculated using the Wołoszyn's method in the profile of Tank 4

p [%]	1	2	5	10	20	50	100
Reduction coefficient	1	0.81	0.6	0.45	0.33	0.21	0.14
$q_{p\%}$ [$m^3 \cdot s^{-1} \cdot km^{-2}$]	8.29	6.71	4.97	3.73	2.74	1.74	1.16
$Q_{p\%}$ [m^3/s]	12.02	9.74	7.21	5.41	3.97	2.52	1.68

3.6. Reduction in swelling flows in sedimentation tanks

Sedimentation tank OS–11.B (Fig. 2), due to its small retention capacity, was excluded from the calculations of flood wave reduction, assuming that it has only a sedimentation function.

Table 7 shows the reduced flows of $Q_{1\%reduced}$ and $Q_{10\%reduced}$ in the profiles of sedimentation tanks.

Table 7. Summary of results of calculations of flows $Q_{10\%}$ and $Q_{1\%}$ in profiles of sedimentation tanks/reservoirs

Sedimentation tank's name	$Q_{1\%}$ [$m^3 \cdot s^{-1}$]	$Q_{1\%reduced}$ [$m^3 \cdot s^{-1}$]	$Q_{10\%}$ [$m^3 \cdot s^{-1}$]	$Q_{10\%reduced}$ [$m^3 \cdot s^{-1}$]	Comments
OS–10.B	1.52	0.85	0.68	0.23	
OS–7.B	1.52	0.68	0.53	0.04	
OS–6.B	2.20	1.09	0.72	0.09	
OS–5.B	2.77	1.65	0.83	0.22	
OS–9.B	1.25	0.00	0.56	0.00	
OS–8.B	0.61	0.03	0.28	0.00	
OS–2.B	7.87	5.29	3,01	1.42	Variant I
OS–1.B		4.98		1.22	Variant II
OS–4.B	3.20	1.83	1.44	0.52	Variant II
OS–3.B		1.18		0.09	Variant I
Reservoir 4.2	6.47	3.61	1.51	0.13	Variant I
Reservoir 4.1	7.34	2.92	1.86	0.00	Variant II

Table 8. Summary of discharge calculations $Q_{10\%}$ and $Q_{1\%}$ in the profiles of sedimentation tanks/reservoirs

Sedimentation tank's name	Designation of the catchment area	Area of the catchment area [km^2]	Average decline in catchment areas [%]	Afforestation [%]	Drainage speed [m·s^{-1}]	Final time [h]	Drainage coefficient [-]	Authoritative flows calculated by the Woloszyn's [m^3·s^{-1}·km^{-2}] [m^3·s^{-1}]			
								q10%	Q10%	q1%	Q1%
OS10.B	F_{10}	0.10	10.28	90	0.73	0.31	0.65	6.82	0.68	15.16	1.52
OS-7.B	F_7–F_{10}	0.06	6.94	90	0.64	0.29	0.45	5.06	0.30	11.24	0.67
	F_7	0.16	8.80	90	0.69	0.39	0.60	5.28	0.85	11.74	1.88
OS-6.B	F_6–F_7	0.10	6.04	90	0.57	0.28	0.60	6.82	0.68	15.15	1.52
	F_6	0.26	10.06	90	0.72	0.48	0.60	4.38	1.14	9.74	2.53
OS-5.B	F_5–F_6	0.09	10.57	90	0.74	0.25	0.65	8.19	0.74	18.21	1.64
	F_5	0.35	12.20	90	0.78	0.52	0.60	4.13	1.45	9.18	3.21
OS-9.B	F_9	0.08	4.95	90	0.48	0.27	0.60	7.03	0.56	15.62	1.25
OS-8.B	F_8–F_9	0.04	6.25	90	0.58	0.25	0.55	6.90	0.28	15.34	0.61
	F8	0.12	6.35	90	0.59	0.28	0.55	6.25	0.75	13.90	1.67
OS-2.B OS-1.B	F_1-F_8-F_5	0.69	15.04	80	1.10	0.53	0.60	4.04	2.79	8.97	6.19
	F_1	1.16	11.02	80	0.92	0.63	0.60	3.49	4.04	7.75	8.99
OS-4.B OS-3.B	F_3	0.27	7.56	80	0.90	0.27	0.45	5.33	1.44	11.83	3.20
Reservoir No. 4	F_{res4}	1.45	10.37	70	1.08	0.58	0.60	3.73	5.41	8.29	12.02

Table 7 shows that in tanks and reservoirs located in the catchment area of the Bezimienny Streem, a reduction in the flow $Q_{1\%} = 12.02\ m^3 \cdot s^{-1}$ (Tab. 7) will be noted, depending on the variant of operation of Tank No. 4, to:

- $Q_{1\% reduced} = 3.61\ m^3 \cdot s^{-1}$ – for variant I
- $Q_{1\% reduced} = 2.92\ m^3 \cdot s^{-1}$ – for variant II

and flow $Q_{10\%} = 5.41\ m^3 \cdot s^{-1}$ (Tab. 8) to:

- $Q_{10\%\ reduced} = 0.13\ m^3 \cdot s^{-1}$ – for variant I
- $Q_{10\%\ reduced} = 0.00\ m^3 \cdot s^{-1}$ – for variant II

As a result of changes in the management of the catchment area, including forest reclamation, and after taking into account the retention of sedimentation tanks located on the shelves of the spoil tips in the catchment area of the Bezimienny Stream, the calculated values of flows of large waters significantly decreased. The results obtained confirm the information presented in the literature (Miler 2015, Mioduszewski 2016, Stasik et al. 2011).

3.7. Maximum likelihood flows in the gauge profile

Table 9 presents measurement sequences from the maximum annual flows of WQ $[m^3 \cdot s^{-1}]$.

Table 9. Summary of maximum annual flows WQ $[m^3 \cdot s^{-1}]$ from the gauging station P–8 water recorded in 1995-2008

Summer Half-year						
1995	1996	1997	1998	1999	2000	2001
3.00	0.16	0.17	0.11	0.11	0.15	0.34
2002	2003	2004	2005	2006	2007*	2008
0.49	0.12	0.18	0.25	0.61	3.95*	0.51
Winter Half-year						
1995	1996	1997	1998	1999	2000	2001
0.23	0.09	0.03	0.02	0.13	0.11	0.20
2002	2003	2004	2005	2006	2007	2008
0.49	0.25	0.11	0.35	0.33	0.22	0.18

*Due to the incidental, exceptionally catastrophic rainfall caused by an atmospheric storm, 2007 was not taken into account in the calculation for the summer half-year.

The above data were used to calculate the likelihood flows, using statistical methods. Calculations were made with the currently used Kaczmarek's method (Czamara & Krężel 1983) and with the maximum likelihood method. Due to the short period of hydrological observations (14 years), the results obtained are treated as comparative. As the results obtained using the Wołoszyn's method are based on maximum likelihood flows, calculated on the basis of precipitation take place from May to September, the following calculations were made separately for summer and winter half-year periods.

3.7.1. Maximum annual rain flows

The results of calculations for the summer half-year (rainy) are presented in Tables 10-11 and on the likelihood scale (Kaczmarek's method).

Table 10. Maximum likelihood rain flows calculated by the Kaczmarek's method in the water profile Żytawskie Wigancice on the Bezimienny Stream

p%	50%	10%	5%	3%	1%	0.3%	0.1%
$Q_{max\ p\%}$	0.3	1.0	1.3	1.6	2.1	2.7	3.2
$Q_{max} + \delta$ (Q)	0.4	1.4	1.9	2.3	3.1	4.1	5.0

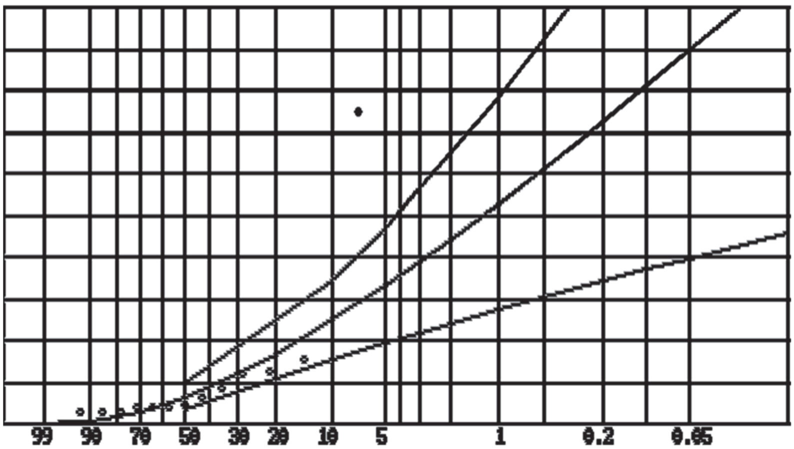

Fig. 3. Graph of likelihood curve in the water profile Żytawskie Wigancice on the Bezimienny Stream – Kaczmarek's method, summer half-year

Table 11. Maximum likelihood rain flows calculated by the maximum likelihood method in the water profile Żytawskie Wigancice on the Bezimienny Stream

p%	50%	10%	5%	2%	1%	0.2%	0.1%
$Q_{max\ p\%}$	0.2	1.1	1.6	2.4	3.0	4.4	5.0

3.7.2. Maximum annual melt flows

The results of calculations for the winter half-year (snowmelt) are presented in Tables 12-13 and on the likelihood scale (Kaczmarek's method).

Tabela 12. Maximum likelihood melt flows, calculated with the Kaczmarek method in the water Profile Żytawskie Wigancice on the Bezimienny Stream

p%	50%	10%	5%	3%	1%	0.3%	0.1%
$Q_{max\ p\%}$	0.1	0.5	0.7	0.8	1.1	1.4	1.7
$Q_{max} + \delta$ (Q)	0.2	0.7	1.0	1.2	1.6	2.1	2.6

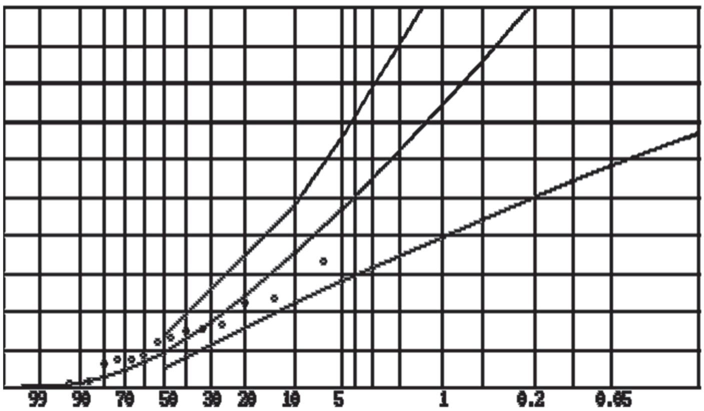

Fig. 4. Graph of likelihood curve in the water profile Wigancice Żytawskie on the Bezimienny Stream – Kaczmarek's method, winter half-year

Table 13. Maximum likelihood melt flows, calculated with the maximum likelihood method in water profile Żytawskie Wigancice on the Bezimienny Stream

p%	50%	10%	5%	2%	1%	0.2%	0.1%
$Q_{max\ p\%}$	0.1	0.4	0.6	0.8	0.9	1.2	1.4

The maximum likelihood flows in the gauge profile (Tank No. 4), calculated using the Kaczmarek's method and the maximum likelihood method, confirm the convergence of two applied calculation methods: empirical and statistical.

3.8. Flow capacity of the Bezimienny Stream river bed and the structure located in the Czech Republic territory

Minkovický Potok was regulated in 1994 at the length of 1.1 km, i.e. from the Frydlant-Višňová road bridge (km 0+000) to the state border (Studium hydrologiczne 1995). The hydraulic calculations made in the Study (Wojarnik & Iwaniak 2009) confirm that the river bed in the upper section will accommodate the regulatory flow assumed in the project. At flows greater than 1.7 $m^3 \cdot s^{-1}$, the adjacent area will be flooded.

Mainly, the conditions of the large waters flow in the estuary section are influenced by the existing communication structures, i.e.:

- The railway culvert located about 15 m from the left bank of the river Witka; dimensions: width b = 1.0 m, height h = 3.5 m,
- The road culvert situated 12 m above the railway culvert, dimensions; width b = 1.1 m, height h = 1.8 m.

According to the hydraulic calculations included in the study (Studium hydrologiczne 1995), the flow capacity of the road culvert is 2.8 $m^3 \cdot s^{-1}$ and is closely related to the water levels in the Witka river.

4. Conclusions

The catchment area of the Bezimienny Stream in the calculative profile before the transformation, i.e. before the start of overburden dumping on the external spoil tip, amounted to 1.08 km^2. The calculated flows of large waters with a certain probability of occurrence, for the original surface of the catchment area and the way in which the catchment was used at that time, are as follows:

- $Q_{10\%} = 2.80\ m^3 \cdot s^{-1}$, $q_{10\%} = 2.59\ m^3 \cdot s^{-1} \cdot km^{-2}$,
- $Q_{1\%} = 8.49\ m^3 \cdot s^{-1}$, $q_{1\%} = 7.86\ m^3 \cdot s^{-1} \cdot km^{-2}$.

Currently, after the transformation of the Bezimienny Stream catchment area, i.e. after the formation of the spoil tip, the execution of reclamation works and surface drainage facilities (ditches, embankments/slopes, and sedimentation tanks), the catchment area in the profile of Tank No. 4 amounts to 1.45 km^2, which is an increase of 33% in relation to the original area. Out of this area, the spoil tips cover 0.82 km^2, while the remaining 0.63 km^2 is the natural catchment area of the Bezimienny Stream.

The flows of large waters with a certain likelihood of occurrence, calculated for the current catchment area, without taking into account artificially created retention in sedimentation tanks, are as follows:

- $Q_{10\%} = 5.41\ m^3 \cdot s^{-1}$, $q_{10\%} = 3.73\ m^3 \cdot s^{-1} \cdot km^{-2}$,
- $Q_{1\%} = 12.02\ m^3 \cdot s^{-1}$, $q_{1\%} = 8.29\ m^3 \cdot s^{-1} \cdot km^{-2}$.

The results of the large water flow calculations show that the unit runoffs increased as a result of the catchment area transformation, for the probability of p = 10% by 1.14 $m^3/s/km^2$, i.e. by 44%, and for p = 1% by 0.43 $m^3/s/km^2$, i.e. by 5.4%.

As a result of the retention established in the sedimentation tanks, the floodwater flows are reduced. The calculated values of reduced flows of $Q_{10\%reduced}$ and $Q_{1\%reduced}$, using their total retention capacity, are as follows:

– for variant I (retention capacity approx. 16.000 m^3):

- $Q_{10\%reduced} = 0.13\ m^3 \cdot s^{-1}$
- $Q_{1\%reduced} = 3.61\ m^3 \cdot s^{-1}$

– for variant II (retention capacity approx. 19.000 m^3):

- $Q_{10\%reduced} = 0.00\ m^3 \cdot s^{-1}$
- $Q_{1\%reduced} = 2.92\ m^3 \cdot s^{-1}$

Calculations of the flow capacity of the Bezimienny Stream and water structures show that in Minkovice, in the Czech Republic, the minimum flow capacity of the river bed and water structures is approx. 1.7 $m^3 \cdot s^{-1}$. Higher flows will result in water from the river bed and flooding of adjacent areas.

The main cause of the flood risk in Minkovice are the existing transport structures (railway and road culverts), whose capacity does not ensure the drainage of large waters, and therefore they should be rebuilt.

In order to further improve the level of flood protection of areas located below Tank No. 4, it is advisable to rebuild the drain devices in order to ensure the possibility of regulating the outflow from the sedimentation tanks, as well as to increase the capacity of the inlet buildings to the settlers together with the adjacent sections of the supply ditches.

On the basis of calculations and analyses, it was stated that the construction of the external spoil tip together with the reclamation and the system of hydro-technical devices did not adversely affect the hydrological regime in the Bezimienny Stream catchment area.

The retention capacity established in the sedimentation tanks located in the Bezimienny Stream catchment area, with proper water management, improves flood protection of the areas located below Tank No. 4.

The presented methodology has been developed for the exploitation of the external spoil tip in Turów (south-western Poland, at the border with the Czech Republic). The main assumptions and principles of the work implementation are universal and can be used in other facilities of this type.

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Abstract

This article presents a novel method for the assessment of the influence of a restored external spoil tip in "Turów" Lignite Mine (Poland) on the discharge in the cross border watercourse called in Poland Bezimienny Potok and in the Czech Republic – Minovický Potok. Moreover, possible flood protection needs of the areas below the spoil tip in the Czech Republic (below the Tank No. 4) are indicated. In the investigated area, after the spoil tip had been formed, restoration work was carried out, i.e. a forest was planted on it. This restoration work, combined with the surface drainage structures, helped to reduce the rate of surface runoff. This, in turn, reduced the flood risk, since the high water culmination and the frequency of flood events were reduced. The hydrological and hydraulic calculations of the watercourse channel and hydro-technical structures' flow capacity indicate that the creation of the external spoil tip followed by the restoration work and the system of hydro-technical devices do not adversely affect the hydrological regime in the Bezimienny Potok catchment area, near the village of Minkovice in the Czech Republic. The forests planted as part of the restoration work play a significant role in reducing the high water culmination and the frequency of flood events. These forests cover the entire surface of the spoil tip and slow down the runoff of water. Moreover, it was confirmed that alternative solutions based on reservoirs – waste ponds located in the Bezimienny Potok catchment area – will improve the flood protection of the areas located in the Czech Republic (thanks to their storage capacity and provided that appropriate water management is ensured). The main stages of the method used for the assessment of the influence of the external spoil tip of "Turów" Lignite Mine on the discharge in the investigated cross-border watercourse are explained by means of the calculation of maximum discharge with a given probability of exceedance by the Wołoszyn's method used in Poland in the Lower Silesia region. This method accounts for the intensity of rainfall. Moreover, in order to determine the retention capacity of the investigated watercourse catchment area, the reduction of high water discharge ($Q_{1\%}$ and $Q_{10\%}$) was calculated in the profiles of the sedimentation tanks, based on the reproduced hydrograph of the flood wave and with the assumption that the time required for the flood wave to go down t_o equals twice the time of concentration t_k ($t_o = 2t_k$). The sedimentation tanks' useful capacities were used to calculate the reduced discharge $Q_{1\%reduced}$ and $Q_{10\%reduced}$. These values were added to the design flows for the sedimentation tanks located below, with the assumption that the swell waves coincide (the most unfavourable case). The calculation of probable discharges was carried out using the Kaczmarek's method (adopted in Poland) and using the maximum likelihood method.

The methodology presented has been developed for the purpose of operation of the lignite waste external spoil tip in Turów (South-West of Poland, on the border with the Czech Republic). The main assumptions and implementation rules are universal and may be used for other sites of this kind.

Keywords:
open-cast mining, borrow pit and spoil tip management, river network,
hydrological and hydraulic calculations, Wołoszyn's method, Kaczmarek's method,
cross-border catchment

Wpływ zrekultowywanego zwałowiska zewnętrznego kopalni węgla brunatnego na wielkości przepływów w cieku transgranicznym (PL−CZ)

Streszczenie

W pracy zaprezentowano nowatorską metodę oceny wpływu zrekultywowanego zwałowiska zewnętrznego, znajdującego się w Kopalni Węgla Brunatnego „Turów" (Polska) na wielkości przepływów w cieku transgranicznym o nazwie Potok Bezimienny – Minovickỳ Potok (Republika Czeska). Ponadto wskazano na ewentualne potrzeby w zakresie ochrony przeciwpowodziowej terenów położonych poniżej zwałowiska na terenie

Republiki Czeskiej (poniżej Zbiornika nr 4). Na omawianym obszarze po zakończeniu formowania zwałowiska prowadzono zabiegi rekultywacyjne, które polegały na zalesianiu. Przeprowadzone prace rekultywacyjne i wykonane urządzenia odwodnienia powierzchniowego przyczyniły się do zmniejszenia natężenia spływu powierzchniowego. To spowodowało zmniejszenie zagrożenia powodziowego poprzez zmniejszenie kulminacji wielkich wód i ograniczenie częstotliwości wezbrań. Wykonane w pracy obliczenia hydrologiczne i hydrauliczne przepustowości koryta cieku i budowli wodnych wskazują na to, że budowa zwałowiska zewnętrznego wraz z wykonaną rekultywacją i systemem urządzeń hydrotechnicznych nie wpływa ujemnie na reżim hydrologiczny w zlewni Potoku Bezimiennego w obrębie miejscowości Minkovice w Republice Czeskiej. Dużą rolę w zmniejszeniu kulminacji wielkich wód i ograniczeniu częstotliwości wezbrań pełnią powstałe w wyniku rekultywacji obszary leśne, obejmujące całą powierzchnię zwałowiska, które opóźniają spływ wody. Wyniki badań potwierdziły, że alternatywne rozwiązania wykorzystujące zastosowanie zbiorników wodnych – osadników zlokalizowanych w zlewni Potoku Bezimiennego, poprzez utworzoną pojemność retencyjną i przy właściwie prowadzonej gospodarce wodnej, wpłyną na poprawę ochrony przed powodzią terenów położonych w Republice Czeskiej. Główne etapy stosowanej metody oceny wpływu zwałowiska zewnętrznego kopalni węgla brunatnego „Turów" na wielkości przepływów w cieku transgranicznym wyjaśnione zostały za pomocą obliczeń przepływów maksymalnych o określonym prawdopodobieństwie przewyższenia metodą Wołoszyna stosowaną w Polsce w regionie Dolnego Śląska, uwzględniającą natężenie deszczu. Ponadto w celu określenia zdolności retencyjnej zlewni rozpatrywanego cieku, w przekrojach zbiorników-osadników przeprowadzono obliczenia redukcji przepływów wielkich wód ($Q_{1\%}$ i $Q_{10\%}$), opartej na odwzorowanym hydrogramie fali wezbraniowej, przy założeniu, że czas opadania fali t_o jest równy 2-krotności czasu koncentracji t_k ($t_o = 2t_k$). Pojemności użytkowe zbiorników-osadników posłużyły do obliczenia zredukowanego przepływu $Q_{1\%zred}$ i $Q_{10\%zred}$, o które następnie zostały powiększone przepływy miarodajne dla osadników położonych poniżej, przy założeniu, że szczyty fal nakładają się na siebie (wariant niekorzystny). Wykonane w pracy obliczenia przepływów prawdopodobnych wykonano obowiązującą w Polsce metodą Kaczmarka oraz dodatkowo metodą największej wiarygodności.

Przedstawiona metodyka została opracowana na potrzeby eksploatacji zwałowiska zewnętrznego kopalni Turów (południowo-zachodnia Polska, przy granicy z Czechami). Główne założenia i zasady realizacji prac mają charakter uniwersalny i mogą być wykorzystywane na innych tego typu obiektach.

Słowa kluczowe:
górnictwo odkrywkowe, zagospodarowanie wyrobiska i zwałowiska, sieć rzeczna, obliczenia hydrologiczne i hydrauliczne, metoda Wołoszyna, metoda Kaczmarka, zlewnia transgraniczna

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Public Expenditure on Environmental Protection in the European Union Countries

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1. Introduction

Care for the natural environment should be the domain of every human being and business entity. However, enterprises appreciate the maximization of profits, and paying the attention to the environment is on the second place. The role of the state and international organizations is to regulate environmental protection by creating appropriate regulations. Legal acts force people and enterprises to act as little as possible to harm the environment. Individual countries are also actively involved in securing the environment, allocating funds for this purpose in their budget. The scale of expenses depends on the possibilities and needs. Public expenditure should stimulate beneficial changes in environmental protection in many aspects (Portney 1990, Rokicki et al. 2018). The article presents the directions and strength of changes that are taking place in this area in EU countries.

In accordance with the Classification of Environmental Protection Activities and Expenditure (2000) nine fields of environmental protection can be distinguished. Expenses are generated in each of them. The list of fields is as follows:

- Protection of ambient air and climate,
- Wastewater management,
- Waste management,
- Protection and remediation of soil, groundwater and surface water,

- Noise and vibration abatement (excluding workplace protection),
- Protection of biodiversity and landscapes,
- Protection against radiation (excluding external safety),
- Research and development,
- Other environmental protection activities.

The fields also include categories and subcategories.

2. Literature review

The increased importance of environmental protection in people's awareness has also led to the need to count cash flows in this area. For the first time, economists became interested in the environment in the 1970s (Ruff 1970, Baumol & Oates 1971, Mills 1978, Baram 1979, Loehman et al. 1979). In the following years, the idea of economic accounts, valuation of expenditures and costs related to environmental protection were developed (Ellis & Fisher 1986, Hazilla & Kopp 1990, Zhu & ReVelle 1990). An important issue was the inclusion of the environment in national accounts. It was found that the interaction between the economy and the environment is so important that a tool should be created that would show this interaction. Thus, environmental economic accounts were created, which are satellite accounts in relation to national accounts. In the European Union, these issues have been regulated by relevant regulations (Regulation (EU) No. 691/2011, Regulation (EU) No. 538/2014).

It is necessary to distinguish the concepts of environmental protection costs and expenses for this purpose. The term costs is often used at the enterprise level and the term expenses at the macroeconomic level. Expenses refer to the actual cash input, while the cost is not necessarily related to the input (Environmental... 2005). Environmental costs arise as a result of statutory or voluntary actions aimed at preventing, limiting, and neutralizing waste, as well as taking into account the adverse effects of the lack of environmental actions to protect the environment. They include economic and social costs of environmental protection, often difficult to evaluate (Dimitroff-Regatschnig et al., 2002). Expenditure on environmental protection, on the other hand, means economic resources devoted to environmental protection by resident units. Environmental protection covers all types of activities and actions which main purpose is to reduce and eliminate pollution and other forms of environmental degradation, as well as to prevent these phenomena. These activities and actions cover all funds spent to restore a degraded environment (Regulation (EU) No. 538/2014). Referring to this definition, public expenses on environmental protection are the domain of state authorities at various levels.

In the 1980s, the importance of expeditures on environmental protection was low. Governments focused rather on creating conditions for the development of the economy, including industry. Environmental protection was in opposition to these goals (Gillroy & Shapiro 1986). However, environmental protection quickly became a global problem (Barrett 1990). Regulations favoring the preservation of the environment and preventing its degradation were introduced (Hahn & Stavins 1992). Gradually, environmental protection grew in importance, which was also reflected in the increase in spending for this purpose (Dunlap & Scarce 1991). The problem was still the low economic effectiveness of environmental protection expenditures and the devaluation of social benefits (Pearce 1998). Nowadays, care for environmental protection has become a standard. Enterprises apply pro-active environmental management under the influence of government, investors and consumers. As the research results show, such activity ultimately favors the increase of productivity and competitiveness of enterprises (Berry & Rondinelli 1998). In developed countries, the economic impact of economic growth on emissions is significantly different. Diversified income generates a gap between the ability and willingness of a given country to pay for environmental protection (Magnani 2000, Rokicki 2016). A methodology for counting expenses for environmental protection was also developed. By this means, it is possible to compare such expenses in various countries and enterprises. Such accounts do not include external costs (environmental and social) (Jasch 2003, Soukopová & Struk 2011). The analysis of environmental protection expenditures is of strategic importance and allows the assessment of existing environmental policies. A low level of expenditure does not always mean that the country does not effectively protect its environment. Expenditure is often associated with reduction of adverse effects on nature, reduction of pollutant emissions or application of more effective protection measures (Broniewicz 2004, Georgescu & Cabeca 2010, Rokicki 2017).

3. Aim, materials and methods

The main goal of the paper is to show the level of public spending on environmental protection in the European Union countries. The specific objectives are: to present the variation in expenses on environmental protection in the EU countries, to determine their significance in the total expenditure of countries, to show the dynamics of changes in expenditure on environmental protection, to identify factors correlated with the level of environmental protection expenses. The paper presents a hypothesis that the level of public expenses on environmental protection in the EU countries was correlated with the economic situation. All European Union member states were selected for research stated by day December 31, 2017 (28 countries). The research period concerned the years 2004-2017. The sources of materials were EUROSTAT data and the literature of the subject. For analysis and presentation of materials, the following methods were used: descriptive, tabular, graphical, fixed-rate dynamics indicators, Gini concentration coefficient, concentration analysis using the Lorenz curve, density diagram (nuclear estimator), Pearson's linear correlation coefficients.

The dynamics indicators with a fixed base are determined as follows (Starzyńska 2002):

$$i = \frac{y_n}{y_0} \text{ or } i = \frac{y_n}{y_0} \cdot 100\% \tag{1}$$

where :
y_n – the level of the phenomenon in a certain period,
y_0 – the level of the phenomenon during the reference period.

The Gini coefficient is a measure of concentration (unevenness) of distribution of a random variable. If the observations y_i are sorted in ascending order, the coefficient can be presented by the formula (Dixon et al. 1987, Damgaard & Weiner 2000):

$$G(y) = \frac{\sum_{i=1}^{n} (2i - n - 1) * y_i}{n^2 * \bar{y}} \tag{2}$$

where:
n – number of observations
y_i – value of the "i-th" observation,
$\bar{y}$ – the average value of all observations, i.e. $\bar{y} = \frac{1}{n}\sum_{i=1}^{n} y_i$

The Lorenz curve determines the degree of concentration of a one-dimensional distribution of a random variable (Dagum 1980). With sorted observations y_i., which are non-negative values $0 \le y_1 \le y_2 \le ... \le y_n$, $\sum_{i=1}^{n} y_i > 0$, the Lorenz curve is a polyline which apexes (x_h, z_h), for h = 0,1,…, n, have the following coordinates:

$$x_0 = z_0 = 0, \qquad x_h = \frac{h}{n}, \qquad z_h = \frac{\sum_{i=1}^{h} y_i}{\sum_{i=1}^{n} y_i} \tag{3}$$

The Gini coefficient determines the area between the Lorenz curve and the diagonal of a unit square multiplied by 2.

In the case of a nuclear density estimator, the nucleus is such a function K : R -> [0,∞] that (Kulczycki 2005):

1) $\int_{-\infty}^{\infty} K(x)dx = 1$

2) K(0) >= K(X) for each R

3) K – symmetrical to zero.

A nuclear estimator is a function $\hat{f}_n(x) = \frac{1}{nh}\sum_{i=1}^{n} K(\frac{X - X_i}{h})$, (4) where h is a constant called a bandwidth for h>0.

The Doornik-Hansen test was used to determine compliance with the normal distribution (1994):

$$DH = z_1^2 + z_2^2 \tag{5}$$

where:
z_1 – transformed skewness,
z_2 – transformed oddity.

Pearson's linear correlation coefficient is a measure of the strength of a straight line relationship between two measurable features. It is expressed by means of the following formula (Jajuga & Walesiak 2004):

$$r_{XY} = \frac{C(X,Y)}{\sqrt{S_X{}^2 \cdot S_Y{}^2}} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \cdot \sum_{i=1}^{n}(y_i - \bar{y})^2}} = \frac{C(X,Y)}{S_X \cdot S_Y} \tag{6}$$

where:
C(X,Y) – covariance between the X and Y features,
$S_X{}^2$ – X feature variance,
$S_Y{}^2$ – Y feature variance,
S_X – X feature's standard deviation,
S_Y – Y feature's standard deviation.

The linear correlation coefficient can be treated as normalized covariance. Correlation always takes values in the range (-1, 1).

4. Research results

Public expenses on environmental protection in the EU in 2005-2017 increased by 16% (Table 1). At that time, individual countries were developing economically, so an increase in this type of spending was beneficial for the environment. In the analyzed period, in most countries there was an increase in public spending on environmental protection, the largest in Romania (by 279%) and Croatia (by 158%). A decrease in this type of expenditure was recorded only in a few countries, i.e. United Kingdom and Ireland (40% each), Slovenia (18%), Finland (12%) and Denmark (10%). Among the countries with the largest public expenditure for environmental protection, only in United Kingdom there was a decrease. This may be due to changes in the government's policy in this country or the allocation of budgetary resources to other competing goals. The group of countries with the largest public expenses for environmental protection included mainly countries from Western Europe.

Table 1. Total public expenditures on environmental protection in EU countries in 2005-2017 (EUROSTAT)

Countries	Public expenditures for environmental protection in EU countries (years)					Dynamics of changes 2017/2005
	2005	2008	2011	2014	2017	
France	15326	17796	20406	21995	21699	141.58
Germany	12612	13098	15796	17689	20672	163.91
United Kingdom	27669	17022	16756	18363	16738	60.50
Italy	11933	13235	14455	15302	15603	130.76
Netherlands	8477	9948	10105	9357	10148	119.71
Spain	8374	10884	10174	9096	10071	120.27
Belgium	2422	2857	4463	4033	4014	165.77
Greece	1177	2199	1749	2629	2860	242.99
Poland	1598	2402	2620	2542	1814	113.48
Czechia	1186	1465	2104	1629	1542	130.02
Sweden	1185	1176	1319	1338	1479	124.78
Austria	1311	1350	1505	1514	1363	103.96
Denmark	1327	1100	951	1234	1192	89.84
Portugal	958	1144	1209	987	1100	114.79
Romania	256	702	1241	1197	968	378.94
Ireland	1603	2137	1243	987	950	59.28
Hungary	540	694	723	1229	680	125.93
Slovakia	332	521	548	641	610	183.95
Luxembourg	345	433	470	452	549	159.48
Finland	517	594	480	521	453	87.62

Table 1. cont.

Countries	Public expenditures for environmental protection in EU countries (years)					Dynamics of changes 2017/2005
	2005	2008	2011	2014	2017	
Bulgaria	168	252	284	295	351	208.49
Croatia	120	173	153	162	310	257.90
Slovenia	236	294	294	370	194	82.36
Estonia	103	173	-47	130	177	171.48
Lithuania	123	275	232	206	175	142.51
Latvia	94	202	138	161	152	160.49
Malta	74	94	88	126	105	142.12
Cyprus	43	52	61	46	50	116.28
EU 28	100107	102271	109518	114229	116019	115.89

Public expenses on environmental protection in 2005-2017 accounted for about 1.6-1.7% of all public expenses in the entire EU. There were differences in individual countries. The lowest shares of this type of expenses were in Romania in 2005 and in Finland in 2011-2017 (around 0.4% in the structure of public expenses in these countries). The greatest importance of this type of expenses was in the budget of Malta in 2010 (4.7%). In general, in Western European countries, especially the most economically developed, the share of public expenses on environmental protection in total government expenditure was at a level close to the EU average. Greater funds from national budgets are allocated for defense, public order and safety, economic affairs.

An interesting indicator is also the share of public expenses on environmental protection in GDP. In the analyzed years, it amounted to 0.7-0.9% in the EU. The lowest share was recorded in Finland in 2011-2012 and in 2015-2017 (0.2% of GDP), and the highest in Malta in 2010 and 2015 (1.9%). The regularities were similar to the share of public expenses on environmental protection in total public spending.

Unevenness in the distribution of public expenses on environmental protection was also examined. To determine the degree of concentration of energy consumption in the European Union countries, the Gini coefficient was applied. The data concerned the beginning of the research period, namely the year 2005 and the final stage, i.e. 2017, and the number of observations was 28. The Gini coefficient for public expenditure on environmental protection in 2005 calculated from the sample was 0.73 and the estimated coefficient for the population 0.76. This means a very high concentration of public expenses on environmental protection in several EU countries. In the case of repeating the research for 2017, the results were slightly lower (coefficient from the sample = 0.70, and estimated for the population = 0.73). Therefore, no significant changes occurred in the expenditure of this type distribution. In addition, public spending on environmental protection in 2017 is presented on the Lorenz concentration curve (Figure 1). Although there were changes in the value of total public expenditure for environmental protection, there were virtually no changes in the structure. The countries with the largest expenditure on environmental protection still had a dominant position. On the basis of the conducted research, it can be stated that public expenditure on environmental protection in the EU was characterized by high stability.

The largest amount of public funds for environmental protection was allocated in France, Germany, Great Britain and Italy, i.e. the largest EU economies. In the structure of public spending on environmental protection, the smallest countries were of lower importance. This is also confirmed by the density diagram (Figure 2). In 21 countries, which accounted for 75% of all countries, a maximum of EUR 3.6 billion was spent in 2017 (in total in this group of countries only EUR 17 billion was spent, which accounted for only 15% of total public expenses on environmental protection in the EU). The consumption of renewable energy was not in accordance with the normal distribution.

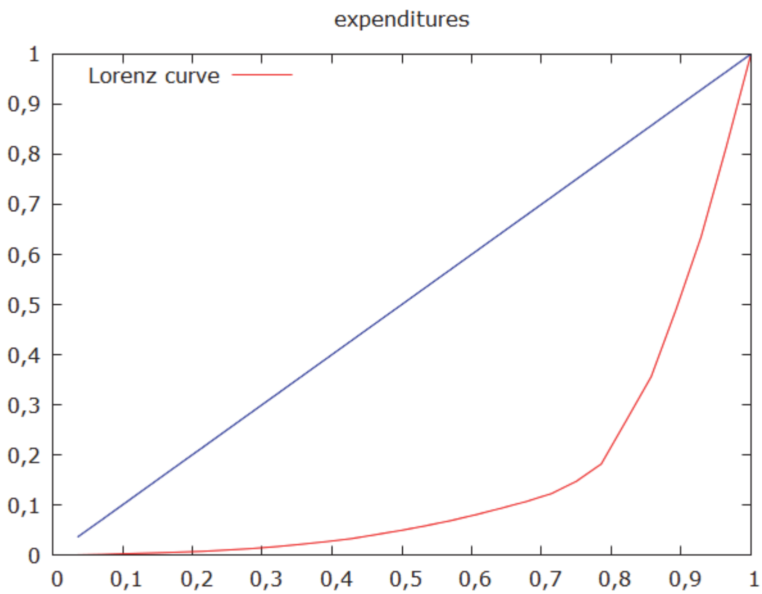

Fig. 1. Lorenz concentration curve for the public expenditures on environmental protection in EU countries in 2017

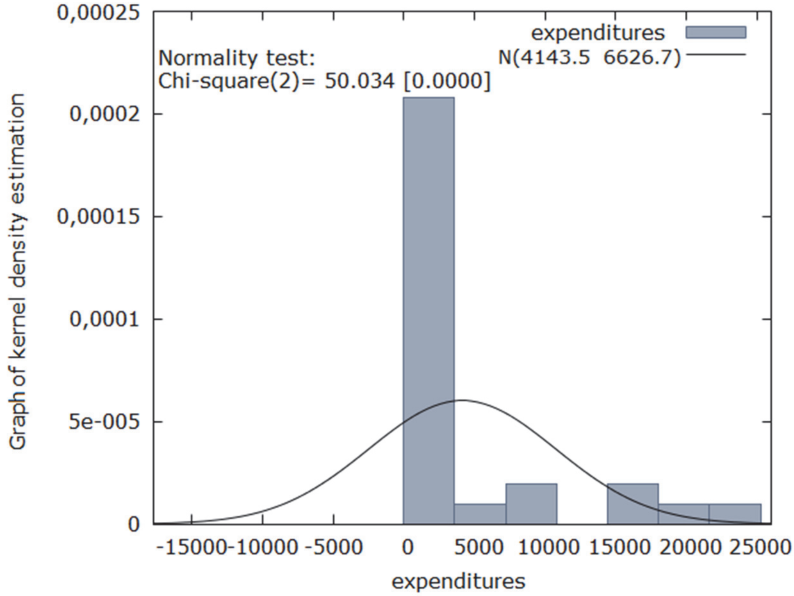

Fig. 2. Graph of kernel density estimation for public expenditure on environmental protection in EU countries in 2017

In order to find a connection between the value of public expenses on environmental protection in European Union countries and economic parameters that could be related, Pearson's linear correlation coefficients were calculated (Table 2). The p = 0.05 was assumed as the limit value of significance level. Significant results were marked with a gray background in the table. Correlation coefficients were calculated for EU countries in 2005-2017 and divided into periods of economic stabilization in 2005-2008, economic crisis in 2009-2010, crisis recovery and economic growth in 2011-2017. The paper tried to check the correlation, which does not indicate that a given factor affects another, only that there is a strong or weak relationship between them.

There were very strong positive associations of public expenses on environmental protection with the value of GDP and the value of exports and imports. This indicates a very large interdependence of the economic situation with the amount of funds allocated for environmental protection. Such regularities appeared irrespective of the period of research. During the economic crisis (2009-2010) they were stronger than during the stabilization period. It has already been shown that public expenditure on environmental protection was quite stable in relation to GDP.

Table 2. Pearson's linear correlation coefficients between public expenditures on environmental protection and selected economy parameters

Tested parameters	Pearson's linear correlation coefficients for years			
	2005-2008	2009-2010	2011-2017	2005-2017
Correlation coefficients between public expenditures on environmental protection and:				
GDP value in mln Euro	0.934	0.961	0.958	0.952
p value	0.001	0.001	0.001	0.001
GDP per capita in Euro	0.259	0.220	0.184	0.211
p value	0.006	0.103	0.010	0.001
Households consumption per capita in Euro	0.453	0.406	0.403	0.418
p value	0.001	0.002	0.001	0.001
Export value in mln Euro	0.831	0.873	0.869	0.855
p value	0.001	0.001	0.001	0.001
Import value in mln Euro	0.891	0.916	0.908	0.901
p value	0.001	0.001	0.001	0.001

The relation of expenditures on environmental protection and the level of household consumption per capita was also significant. The relationship was positive with medium strength. In the case of GDP per capita there were very weak dependencies. During the economic crisis, they proved irrelevant. The amount of public expenditure on environmental protection was interdependent from the economic situation of the country and the possibility of generating funds for various purposes important to society. The level of income per person was not an important factor in this case.

5. Conclusions

Today, public spending on environmental protection is a must. States must set the course of action and support pro-environmental solutions. The conducted research allowed to draw the following conclusions.

1 Public expenditure on environmental protection in EU countries has been systematically growing. There was a very high concentration of this type of expenditure in several EU countries. The situation was stable, because in the years 2005-2017 the concentration of expenses on environmental protection did not change significantly. The first four countries were the largest economically, namely France, Germany, Great Britain and Italy.

2 The significance of environmental protection expenditures in national budgets was low (more funds were allocated for other public purposes). However, there were differences between individual countries. In this case, the level of economic development was not decisive. Similar dependencies were in the

case of public expenditure on environmental protection in GDP. In general, the situation in this respect was quite stable.

3 A significant relationship was found between the economic situation of the country and the value of public expenditure on environmental protection. The hypothesis of the paper was confirmed. Average positive relationships were found in the case of household consumption per capita, and very weak with GDP per capita. Parameters in calculation per capita were not suitable for determining interdependencies.

4 The presented research allow to state that the level of public expenditure on environmental protection depends on the economic situation of the country. Bigger economies can afford greater support for pro-environmental ventures. The wealth of the society was not a decisive factor in the amount of support. In many countries, spending on environmental protection is an element of policy. Rulers are more likely to use public funds for purposes that give more visible effects and are economically effective. The issue of public spending is very important in the context of environmental protection.

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Abstract

The main objective of the paper was to show the level of public spending on environmental protection in the European Union countries. All European Union member states were selected for research purposefully. The research period concerned the years 2005-2017. The sources of materials were EUROSTAT data, literature of the subject. For the analysis and presentation of materials, descriptive, tabular and graphical methods, constant basis dynamics indicators, Gini concentration coefficient, concentration analysis using the Lorenz curve, density diagram (nuclear estimator), Pearson's linear correlation coefficients were used. Public spending on environmental protection is gradually becoming more and more accepted by the government, as evidenced by their systematic growth. There was a very high concentration of this type of expenditure in several EU countries. The first four countries were the largest economically, namely France, Germany, Great Britain and Italy. The importance of spending on environmental protection in national budgets was low, however, there were differences between countries. In this case, the level of economic development was not decisive. A significant relationship was found between the economic situation of the country and the value of public expenditure on environmental protection. On the other hand, parameters per person were not suitable for determining interdependencies. The wealth of the society was not a decisive factor in the amount of support. In many countries, spending on environmental protection is an element of policy. Rulers are more likely to use public funds for purposes that give more visible effects and are economically effective.

Keywords:
expenditure on environmental protection, EU, economic situation, environmental policy

Wydatki publiczne na ochronę środowiska w krajach Unii Europejskiej

Streszczenie

Celem głównym pracy było ukazanie poziomu wydatków publicznych na ochronę środowiska w krajach Unii Europejskiej. W sposób celowy wybrano do badań wszystkie kraje członkowskie Unii Europejskiej. Okres badań dotyczył lat 2005-2017. Źródłami materiałów były dane EUROSTAT, literatura przedmiotu. Do analizy i prezentacji materiałów zastosowano metody opisową, tabelaryczną, graficzną, wskaźniki dynamiki o podstawie stałej, współczynnik koncentracji Giniego, analiza koncentracji za pomocą krzywej Lorenza, wykres gęstości (estymator jądrowy), współczynniki korelacji liniowej Pearsona. Wydatki publiczne na ochronę środowiska stopniowo są coraz bardziej akceptowane przez rządzących, o czym świadczy ich systematyczny wzrost. Występowała bardzo duża koncentracja tego typu wydatków w kilku państwach UE. W pierwszej czwórce krajów były największe gospodarczo kraje, a więc Francja, Niemcy, Wielka Brytania i Włochy. Znaczenie wydatków na ochronę środowiska w budżetach krajowych było małe, występowały jednak różnice między poszczególnymi krajami. W tym przypadku poziom rozwoju gospodarczego nie był decydujący. Stwierdzono istotny związek między sytuacją gospodarczą kraju a wartością wydatków publicznych na ochronę środowiska. Z kolei parametry w przeliczeniu na osobę nie były odpowiednie do określenia współzależności. Zamożność społeczeństwa nie była czynnikiem decydującym o wysokości wsparcia. W wielu państwa wydatki na ochronę środowiska są elementem polityki. Rządzący chętniej przeznaczają środki publiczne na cele, które dają bardziej widoczne efekty i są efektywne ekonomicznie.

Słowa kluczowe:
wydatki na ochronę środowiska, UE, sytuacja gospodarcza,
polityka ochrony środowiska

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Comparison and Assessment of Emission Factors for Toxic Exhaust Components During Combustion of Biomass Fuels

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1. Introduction

One of the basic factors determining the state of the environment, and thus significantly affecting the quality of life, is air cleanliness. Among the anthropogenic sources of pollutant emissions the most significant are fuel combustion processes, in which power industry plays the main role, including small power industry. The types of pollutants introduced into the air during combustion of fuels depend mainly on the type of fuel burned. The dominating role in the energy sector is played by conventional fuels: hard and brown coal, natural gas and crude oil. These fuels contribute to significant environmental pollution and the increase of greenhouse effect.

The European Union pays special attention to the broadly understood protection of the environment, as a result of which member states focus on ecological education, promotion of new energy sources, reclamation of post-mining areas, nature protection and rational waste management (Grudziński & Stala-Szlugaj, 2016). The desired sources of energy in the energy and ecological policy of Poland and the European Union are the renewable ones, in particular biomass, understood as any organic substance of plant or animal origin, as well as all the derived substances obtained from the transformation of such raw materials (Borycka, 2009).

Biomass is a renewable energy source, the use of which has recently grown worldwide. It is mainly used for heating households, as an alternative to fossil fuels (Lasek et al., 2018; Pastorello et al., 2011). However, the combustion of biomass, like fossil fuels, releases pollutants into the air, such as: carbon monoxide, nitrogen oxides, sulfur oxides, as well as organic and inorganic particulates (Gonçalves et al., 2012). They have a significant impact on the climate (Chen &

Bond, 2010), air quality (Zielinska & Samburova, 2011) and human health (Lewtas, 2007, Lighty et al., 2000).

The use of small boilers and furnaces (<50 kW) as a source of heat in households (home heating, CWU preparation) is widespread throughout the world (Lasek et al., 2018). Automatic pellet boilers powered by various types of biomass fuels are used for this purpose more and more commonly (Dołżyńska & Obidziński, 2017; Stolarski et al., 2015). The use of pellets allows automation and easier control of the combustion process.

The assessment of environmental benefits resulting from biomass combustion is a complex issue. It is the most reliable when there is a possibility of empirical emissions evaluation using various fuels in energy installations. If no specific emissions data are available, they should be estimated using appropriate factors (Borycka, 2008, Kowalczyk-Juśko, 2010, Maj 2017). Some studies have shown that emissions from various types of pellet burning systems can vary considerably, depending on many factors, e.g. the type and quality of equipment, technical conditions of its operation, fuel properties (Boman et al., 2011; Evtyugina et al., 2014).

There is still considerable uncertainty in the assessment of the impact of pollutant emissions during the combustion of biomass on air quality on a local and global scale (Pastorello et al., 2011). This is caused not only by the lack of data on the amount of biomass burned but also by the lack of emission factors that would characterize real combustion. In this context, it is extremely important to expand knowledge on environmental aspects resulting from the use of energy biomass. Biomass is a very diverse fuel in terms of physical-chemical properties (Maj 2015), and its combustion in inappropriate installations may entail serious environmental costs associated with excessive emissions of toxic exhaust components.

The determination of emission factors is a way to assess the levels of pollutants emitted from a fuel combustion source. The emission factor is usually defined as the amount of a given pollutant emitted per one unit of the burned fuel mass or per a specific task performed. It is often presented in the form of an emission factor referring to the mass and expressed, for example, in g of pollutant per kg of fuel burned. An alternative representation is the mass of the pollutant per one unit of energy obtained. The determination of emission factors can be performed using two basic methods: the index one and the direct measurements one. The best source of information on the emission of pollutants into the atmosphere are measurements performed on real objects and in conditions similar to real conditions. The emission factors determined on the basis of such measurements reflect their real levels and allow a comparison between different combustion systems. However, it should be borne in mind that the measurements are technically and legally complex, and also expensive.

Periodic measurements of emissions into the air are carried out for fuel combustion installations requiring a permit to introduce gases or dusts into the air or an integrated permit, involving combustion units for fuels for which emission standards are defined. For other installations, not covered by the measurements, for which there is no obligation to carry them out, emission factors developed in the literature should be used (Niemczewska, 2017). This is the case with domestic low-power boilers. The main idea of the index method of calculating the emission of pollutants is based on the use of tabulated values of drift factors and/or emissions estimated for a given pollutant and the type and power of the boiler (installation) used, or other technological and technical data developed for typical processes and technological devices. It is the simplest and cheapest method, but charged with a rather large error.

The values of air pollution emission factors calculated using the index method often differ from the ones based on direct measurements, as they are either overestimated or lowered. This usually occurs in the case of modern devices characterized by low real emissions or in the case of devices with a significant degree of depletion, so that the regulation of their working conditions is not possible or very limited, which results in high real emissions of pollutants (Niemczewska, 2017).

The aim of the work was to compare and assess the emission factors of toxic exhaust components obtained on the basis of direct measurements as well as the factors estimated using the index method, calculated on the basis of relevant drift factors available in the literature. A commercially available automatic pellet boiler with the capacity of 10 kW was used in the study . Combustion tests were carried out for five different materials, including wood pellets, energy plant pellets and agricultural waste. The emission factors were determined for CO, NOx and SO_2 with reference to the unit of fuel mass and calorific value of fuel.

2. Material and methods of research

An empirical evaluation of the emission of toxic exhaust components was made during combustion tests of pellets from various types of biomass in an automatic 10 kW boiler (EG-PELLET Greń), adapted to the combustion of wood pellets. The installation used in the tests was a typical installation used for heating detached houses.

Wood pellets available on the market were obtained, as well as pellets from sunflower husks and rape straw from a local distributor (Zamość distric in Poland) and pellets made from Virginia mallow (*Sida hermaphrodita*) and Miscanthus (*Miscanthus giganteus*), produced in the own laboratory (SJ 25 Brikol) for research purposes.

The boiler used in the tests was equipped with a retort burner, which was fed with fuel from the tank by means of a screw-conveyor feeder. The combustion air was supplied by the fan to the nozzle system in the burner. Boiler operation was controlled by means of a programmed electronic controller. During the combustion tests, the boiler's nominal settings have not been interfered with. Combustion tests were carried out at the set boiler operating conditions at nominal settings. During the test, the boiler worked with rated power. Before starting the measurements the boiler was heated for a period of 1 hour, the combustion tests for individual types of pellets lasted 3 hours. The fuel mass flow was approx. 4 $kg \cdot h^{-1}$. The combustion tests were carried out in triplicate and the arithmetic mean of the three measurements was used for further calculations.

The composition of exhaust gases at the boiler outlet was measured using the SIEMENS analyzer system. The system includes ULTRAMAT 23 type analyzers enabling CO measurement in the ranges of 0-5% and 0-50%, SO_2 in the range of 0-2500 ppm and two NO analyzers with ranges of 0-1000 ppm, including one cooperating with the NO_2 to NO converter. These analyzers use the IR reference method. The gas concentration was measured using the OXYMAT 5 type analyzer, allowing the measurement of O_2 in the 0-25% range, operating on the basis of the reference method using the phenomenon of paramagnetism. The exhaust gases were sampled continuously using a heated probe system with a ceramic filter, a heated hose and a gas-conditioning system. The gas sampling probe was located on a vertical, straight and free of flow disturbances duct of chimney of a constant diameter (the requirement of $L \geq 5$ DH for the measuring cross-section was fulfilled).

To determine the emission factors using the index method, it is necessary to know the physical-chemical characteristics of the biomass used, thus a technical and elementary analysis of the biomass was carried out. The research material was prepared in accordance with the PN-EN 14778 standard. The elemental composition of the combustible substance was determined in the samples in the analytical state. Carbon, hydrogen, nitrogen and sulfur were determined using the CHN628 Elemental Analyzer with the LECO S module. The oxygen content in the fuel was calculated as a supplement to 100%. Moisture determination was performed in accordance with the requirements of the PN-EN ISO 18134 standard, volatile compounds PN-EN ISO 18123 and ash PN-EN ISO 18122. The measurements were carried out with the LECO TGA 701 thermogravimeter. The combustion heat was determined in samples in working condition. The determinations were made in accordance with the PN-ISO 1928 standard, the LECO AC600 calorimeter was used for the measurements.

The emissions of particular chemical compounds were estimated in relation to the mass of fuel burned and energy value.

Estimation of emissions from unconventional energy sources is still an unresolved problem, as there are no unambiguous guidelines in this regard, especially for biomass sources. To estimate the emission levels of individual gaseous pollutants, the method of emission factors was used based on the IPCC/OECD methodology (IPCC/OECD, 1995, Radović, 1997, Borycka, 2008, Zwoździak & Walawska, 2008). The method proposed by the IPCC is a simple and transparent way to determine CO, NOx and SO_2 emissions from the combustion of traditional biomass as fuel. It is based on the estimation of an amount of chemically pure coal separated in the combustion process and appropriate ratios of emission of other gases to carbon emissions. The emission per one unit of biomass combusted (emission factor) was determined according to the following formulas:

CO emission factor

$$WE_{CO}=\frac{28}{12}\cdot WE_{C}\cdot(\mathrm{C\_CO/C}),\ [\mathrm{kg\cdot kg^{-1}}] \tag{1}$$

where:
WE_{CO} – CO emission factor,
$\frac{28}{12}$ – the molar ratio of carbon monoxide and carbon,
C_CO/C – part of the carbon emitted as CO – the average value assumed – 0,06 (Radović, 1997),
WE_C – emission factor of chemically pure coal,

$$\mathrm{WE_C}=\mathrm{c}\cdot\mathrm{u_c},\ [\mathrm{kg\cdot kg^{-1}}] \tag{2}$$

where:
c – carbon content in biomass in working condition,
u_c – part of carbon oxidized in the combustion process – the overall value assumed – 0,88 (Radović, 1997)).

NOx emission factor

In the method used, the NOx emission factor is a summary factor for nitrogen dioxide (NO_2) and nitrogen oxide (NO). The emission per unit of fuel burned was determined according to the following formula:

$$WE_{NO_X}=\frac{46}{14}\cdot WE_{C}\cdot(\mathrm{N/C})\cdot(\mathrm{N\_NO_X/N}),\ [\mathrm{kg\cdot kg^{-1}}] \tag{3}$$

where:
WE_{NOx} – nitrogen oxide emission factor,
$\frac{46}{14}$ – the molar mass ratio of nitrogen dioxide and nitrogen, the molar mass of nitrogen dioxide is taken into account because nitrogen oxide in the air oxidizes very quickly to nitrogen dioxide

N/C – nitrogen to carbon ratio in biomass,
N_NO_X/N – part of the nitrogen emitted as NO_X (the average value assumed – 0,122 (Radović, 1997)).

SO_2 emission factor

In exhaust gases over 90% of sulfur is in the form of SO_2. The sulfur oxide emission factor was calculated by to the following dependence:

$$WE_{SO_2} = \frac{2S}{100}, \ [kg \cdot kg^{-1}] \tag{4}$$

where:
WE_{SO_2} – sulfur dioxide emission factor,
2 – molar mass ratio of SO_2 and sulfur,
S – sulfur content in the fuel.

Emission factors obtained during direct measurements were calculated on the basis of formulas 5-7 (Janka, 2014; Warych, 1999)

The value of excess air coefficient λ was calculated based on the measurement of the oxygen concentration in the exhaust gas using the formula:

$$\lambda = \frac{21}{21\text{-}O_{2\ sp}}, \ [-] \tag{5}$$

where:
λ – excess air coefficient,
O_{2sp} – oxygen concentration in the exhaust gas [%].

The emission factors (E_i) of CO, NO_X SO_2 were calculated by the dependence:

$$E_i = V_s^j \cdot \dot{B} \cdot S_i, \ [kg \cdot kg^{-1}] \tag{6}$$

where:
V_s^j – volume of dry exhaust gases arising from the combustion of 1 kg of solid fuel,
$\dot{B}$ – consumption of solid and liquid fuel,
Si – concentration of the ith pollution in gas,

The conversion into the value of factors in relation to the calorific value of fuel was obtained by the following dependence:

$$E_{Ei}=\frac{E_i}{W_o},\ [kg\cdot GJ^{-1}] \tag{7}$$

where:
E_{Ei} – emission of pollution,
W_o – calorific value of fuel.

3. Results and discussion

The results of tests on the physical-chemical properties of the biomass studied are summarized in Table 1.

Table 1. Physical-chemical properties of the pellets studied [own research]

Parameter	Symbol	Unit	Wood pellets	Pellets from rape straw	Pellets from Virginia mallow	Pellets from Miscanthus	Pellets from sunflower husks
Moisture	W_t^r	%	6.3	9.4	6.4	7.1	9.4
Ash	A^a	%	0.32	10.4	3.8	3.16	9.9
Volatile Matter	V^a	%	73.5	64.7	73.3	72.5	69.3
Carbon	C^a	%	46.8	40.1	44.6	46.3	43.6
Hydrogen	H^a	%	6.2	5.8	6.4	6.4	6.4
Nitrogen	N^a	%	4.3	0.8	0.52	0.49	1.7
Sulfur	$S^a{}_A$	%	0.01	0.31	0.07	0.056	0.17
HHV	Q_s^r	$kJ\cdot kg^{-1}$	18 235	15 972	17 956	17 975	17 956
LHV	Q_i^r	$kJ\cdot kg^{-1}$	16 741	14 476	16 402	16 440	16 457

The results of tests on toxic components emissions during the combustion of the pellets studied are presented in Table 2.

The lowest CO emission was found during the combustion of wood pellets and pellets from Virginia mallow, while the highest NO_X emissions were recorded for these fuels. The highest CO emission took place during the combustion of pellets from sunflower husk and Miscanthus, slightly lower during the combustion of rape straw pellets, the NO_X emission during the combustion tests of these fuels was the lowest (Table 2). SO_2 emission is closely related to sulfur content in fuel (Table 1) (a higher sulfur content in fuel translated into higher SO_2 charge introduced into the atmosphere), the highest emission occurred during the combustion of rape straw pellets, the lowest when burning wood pellets (Table 2).

Table 2. Emission of toxic components of exhaust gases during the test's combustion [own research]

The type of pellets	λ	CO	NO_X	SO_2	CO	NO_X	SO_2
	–	$mg \cdot m^{-3}$			$mg \cdot m^{-3}$ (10% O_2)		
Wood	1.47	87.50	338.89	0.081	70.16	271.73	0.065
Rape straw	1.73	447.50	151.02	0.741	405.21	136.76	0.310
Virginia mallow	1.78	241.25	238.04	0.244	118.85	248.31	0.120
Miscanthus	1.69	613.75	170.00	0.197	273.65	75.79	0.088
Sunflower husks	1.85	983.75	122.65	0.289	470.21	58.62	0.138

The emission factors determined by means of direct measurements and the index method, calculated according to the relationship (1-7) are presented in Table 3. They are expressed in $g \cdot kg^{-1}$ and $g \cdot GJ^{-1}$ to facilitate their confrontation with literature data.

Table 3. Emission factors of CO, NO_X and SO_2 emission determined by the index method and the direct measurement method [own research]

Emission factors	Method	Pellets									
		Wood		Rape straw		Virginia mallow		Miscanthus		Sunflower husks	
		$g \cdot kg^{-1}$	$g \cdot GJ^{-1}$	$g \cdot kg^{-1}$	$g \cdot GJ^{-1}$	$g \cdot kg^{-1}$	$g \cdot GJ^{-1}$	$g \cdot kg^{-1}$	$g \cdot GJ^{-1}$	$g \cdot kg^{-1}$	$g \cdot GJ^{-1}$
Eco	Index	57.00	470.75	48.84	2180.9	54.32	1297.4	56.39	3306.8	53.10	5304.8
	DM	6.57	3473.6	30.48	2976.3	18.09	3310.3	46.12	3436.5	73.98	3236.1
E_{NOx}	Index	1.52	92.43	0.28	17.2	0.18	11.18	0.17	10.53	0.60	36.54
	DM	2.54	154.32	1.03	62.68	1.79	108.79	1.28	77.84	0.92	56.21
E_{SO2}	Index	0.02	1.22	0.62	37.78	0.14	8.531	0.112	6.82	0.34	20.72
	DM	0	1.122	0.002	0.061	0.001	0.061	0.001	0.061	0.001	0.061

DM – Direct measurements

CO emission factors determined using the index method were similar to each other, which results from small differences in the content of initial coal in particular types of biomass (Table 1). On the other hand, the factors determined on the basis of direct measurements showed considerable variation, from 6.57 $g \cdot kg^{-1}$ for wood pellets to 73.98 $g \cdot kg^{-1}$ for sunflower husk pellets. Such large discrepancies result from the combustion conditions. During the combustion of sunflower husk pellets, problems with stabilizing boiler operation were noted, especially during the final test phase. This was related to the caking of slag, which prevented ash from being poured into the ash pan and at the same time hindered the access of air to the retor, thus preventing CO afterburning to CO_2 (Szyszlak-Barglowicz et al., 2017). It should be noted that there are significant differences between the factors determined by the index method and the direct measurement method. The factors obtained by the index method were over 700% higher for wood pellets, 200% for Virginia mallow pellets, and the smallest difference, 22%, was found for Miscanthus pellets, whereas due to the reported combustion problems for the sunflower husk pellets, for them the CO emission factor determined using the index method was lower by nearly 40% than the one determined by the direct measurements method.

As the obtained test results have proved, biomass combustion in low power boilers encounters a number of problems, which are related to different chemical composition of biomass and its variable properties that cause agglomeration of slag and deposit formation on the boiler, resulting in a change of combustion organization (Vamvuka & Kakaras, 2011; Zajac et al., 2017). In view of the above, the determination of CO emission factors based on the index method was charged with a large error. For typical fuels such as wood pellets, these factors were significantly higher compared to the ones obtained on the basis of direct measurements.

It is well known that the CO emission from low-power boilers depends on the type of boiler, burner design, thermal load and excess air coefficient (Lasek et al., 2018). Verma et al. (2011) described the principle of T-3: combustion temperature, turbulence and time. These authors have found that CO emissions may result from low combustion temperature, insufficient oxygen, poor fuel mixing with combustion air and/or too short exhaust gases residence time in the combustion zone. Garcia-Maraver et al. (2015) also noticed that the CO emission depends on the residence time of the gas in the combustion chamber as well as on the temperature and turbulence.

The determined NO_X emission factors for the studied biomass fuels were very diverse. The highest values of gas emission factors determined by both the discussed methods were found for wood pellets: 1.52 $g \cdot kg^{-1}$ by the index method and 2.54 $g \cdot kg^{-1}$ by empirical method. At the same time, NO_X emissions were the highest during combustion tests of this fuel (Table 3). The lowest values of the NO_X emission factor were found, depending on the method of their determination, as: 0.92 $g \cdot kg^{-1}$ and 1.03 $g \cdot kg^{-1}$ for sunflower and rape straw pellets using the empirical method and 0.17 $g \cdot kg^{-1}$ and 0.18 $g \cdot kg^{-1}$ for pellets from Miscanthus and Virginia mallow using the index method. At the same time, the lowest NO_X emissions (Table 2) were found during the combustion tests on sunflower husk pellets and rape straw pellets.

When comparing the NO_X emission factors determined by the direct measurement method and the index method, it was found that the factors determined by the direct measurement method were higher in comparison to the ones determined using the index method. Differences ranged from 35-40% for wood pellets and sunflower husk to 86-90% for pellets from Miscanthus and Virginia mallow, i.e. for the biofuels characterized by lower nitrogen content (Table 1). However, it should not be forgotten that the final level of nitrogen oxide emissions is determined not only by the nitrogen content of the fuel but also by the combustion conditions.

The determination of SO_2 emission factors is a special case. The amount of SO_2 emitted depends on the reflux of sulfur in the fuel. The higher it is, the higher the SO_2 charge introduced into the environment (Ściążko & Zieliński, 2003). Biomass generally contains small amounts of flammable sulfur, which results in SO_2 emission factors even by an order lower in comparison with CO and NO_X emission factors. Higher sulfur content can be found in some of the agribiomas (rape and cereal straw), which corresponds to higher SO_2 emissions during its combustion. This is also confirmed by the results of the tests carried out.

The SO_2 emission factors determined on the basis of direct measurements differed significantly from the ones determined using the index method. In combustion tests SO_2 emissions were very low (Table 2), and empirically determined emission factors for this gas were close to zero (from 0 for wood pellets to 0.002 $g \cdot kg^{-1}$ for rape straw pellets). The SO_2 emission factors determined using the index method were from several dozen to several hundred times higher than the ones determined by the empirical method. It follows that the sulfur contained in the fuel remained mainly in the furnace waste. Using the index method, the lowest SO_2 factors were determined for wood pellets and the highest for sunflower seed pellets (Table 3). The SO_2 factors, both the ones determined by the index method and those determined empirically, correspond with the sulfur content in the burned pellets.

In the literature, one can find works that were aimed at determining emission factors during biomass combustion in low-power installations, but the results presented there are divergent. There are a few reports regarding emissions during biomass combustion in an automatic boiler, but they usually concern research using wood pellets as test fuel.

The emission factors of NOx and CO determined in the studies by means of direct measurements for the studied biofuels were higher than the ranges of these gases emission factors for wood pellets presented in the works (Boman et al., 2011; Johansson et al., 2004; Paulrud et al., 2010 Win and Others, 2012), with the exception of the CO emission factor for wood pellets, which was comparable.

Carvalho et al., (2013) set emission factors for pellets from various types of agricultural biomass and wood pellets. The factors were also significantly lower when burning wood pellets. The highest values of CO emission factors were found for hay pellets (280 $g{\cdot}GJ^{-1}$), wheat bran (224 $g{\cdot}GJ^{-1}$) and straw (223 $g{\cdot}GJ^{-1}$), They were from eleven to fourteen times higher in comparison to emission factors for wood pellets. CO emission factors for corn straw pellets as well as for waste from vineyard and sorghum clearings were relatively low (two to five times higher than CO emissions for wood pellets). NOx and SO_2 emissions were also higher when the boiler was fed with pellets from biomass of agricultural origin.

Zając et al. (2017) found high CO emissions when burning pellets from agrobiomass in a boiler designed for burning wood-based pellets, due to incomplete combustion and poor process organization. The higher CO concentration resulted from the lowering of temperature in combustion chamber due to difficulties in feeding fuel. In the case of wood pellets combustion, this phenomenon was not observed, and the CO emission was lower.

Juszczak (2012) points out that for pellets from various types of agricultural biomass, burners adapted to wood pellets are often used in boilers. Too high temperature in the furnace, however, causes the ash to soften and clump, creating problems in the operation of the burner, increasing the emission of CO and HC and reducing the thermal efficiency of the boiler. To reduce the phenomenon of ash softening, you need to lower the temperature in the furnace. This results in poorer performance and lower thermal efficiency of the boiler, with a slightly lower, but still high, emission of CO and sometimes also HC.

Hrdlička et al. (2016) draw attention to the fact that during the empirical determination of emission factors, the boiler's working conditions, power load and excess air ratio are significant. The emission factors for various biomass fuels presented by these authors were the lowest at 100% nominal boiler load. The lowest emission factors were also found for wood pellets (CO 1.6 $g{\cdot}kg^{-1}$; NOx 1.2 $g{\cdot}kg^{-1}$; SO_2 0.01, $g{\cdot}kg^{-1}$). For pellets from other types of biomass slightly higher factors were noted (for rape straw: CO 27.3 $g{\cdot}kg^{-1}$; NOx 3.9 $g{\cdot}kg^{-1}$; SO_2 0.1 $g{\cdot}kg^{-1}$, for cereal straw CO 3.2 $g{\cdot}kg^{-1}$; NOx 3.8 $g{\cdot}kg^{-1}$; SO_2 0.8 $g{\cdot}kg^{-1}$). At lower boiler load, these factors were higher for all the biofuels tested, and in many cases the differences were very large.

4. Conclusion

The main disadvantage of devices for biomass combustion, especially of low power devices, is the high level of emission variability (Evtyugina et al., 2014). Emissions from biomass combustion depend on such factors as: combustion conditions, properties and quality of biomass, boiler and burner design.

A comprehensive and detailed inventory of biomass combustion, representing the current state, is important to provide the necessary information to manage emissions at the local, regional and global levels. The conducted research allowed to conclude that the values factors and factors determined on the basis of direct measurements differed significantly, which was related to the various combustion conditions of the examined biomass fuels. In particular, it was found that:

1. The CO emission factors determined using the index method for the fuels tested were higher from several dozen to several hundred percent from the factors determined on the basis of direct measurements, with the exception of the factor for sunflower seed pellets, which was lower by several dozen percent from the empirically determined one, due to the problems at the boiler's work. For the basic fuel, which is wood pellets, in the case of the boiler used in the tests, the CO emission factors determined using the index method were significantly higher than the ones obtained on the basis of direct measurements.
2. NOx emission factors determined by the direct measurement method were higher by several dozen percent compared to the factors determined using the index method. The largest differences were found for biofuels characterized by lower nitrogen content (pellets from Miscanthus and Virginia mallow).
3. The SO_2 emission factors determined empirically differed significantly from the factors determined using the index method. Since the SO_2 emission during combustion tests was very low, the emission factors determined on the basis of direct measurements were close to zero. SO_2 emission factors determined using the index method were from several dozen to several hundred times higher.
4. The CO, NOx, SO_2 emission factors determined using the index method were burdened with a large error. In the case of CO and NOx emission factors, this resulted from the course of the combustion process, which for neither of the biofuels ran smoothly and accurately at all times, and this fact inevitably affected the obtained boiler power. During the conducted combustion tests, when the boiler reached the rated power and the maximum load, the CO emission factors determined using the index method were much higher than those determined empirically. On the other hand, the NOx emission factors determined using the index method were significantly lower than those determined empirically. It follows, that setting emission factors for biomass fuels using the index method can be highly erroneous and does not provide reliable information about the actual emissions from low-capacity boilers installed in individual households.

As the combustion process is very sensitive to the conditions in which it occurs, and even a small change in them can cause major changes in emission factors, it cannot be assumed that the emission factors obtained in the conducted tests can be an undisputable source of information about emissions from this type of installations. Further emission tests are needed, taking into account different types of equipment, a wide range of their models and technologies as well as various biomass fuels. The results of the present studies will allow the development of more accurate drift rates for biomass fuels and also more precise estimation of emission factors. It would be difficult to base emission calculations solely on emission measurements, especially due to the costs of research, which should involve a huge number of facilities and devices in the country. The use of available emission factors and calculation methods is advisable, as an empirical determination of individual factors to be used for all the devices/installations would be practically unfeasible.

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Abstract

The assessment of environmental benefits resulting from biomass burning is a complex issue. The most reliable is when there is the possibility of empirical emission assessment using various fuels in energy installations. If no specific emission data is available, it should be estimated using appropriate indicators.

There is still considerable uncertainty in the assessment of the impact of pollutant emissions accompanying the combustion of biomass on air quality on a local scale. This is caused not only by the lack of data on the amount of biomass burned but also by the lack of emission factors that would characterize real combustion. In this context, it is extremely important to expand knowledge about environmental aspects resulting from the use of energy biomass.

The aim of the work was to compare and assess emission factors of toxic exhaust components obtained on the basis of direct measurements and indicators estimated using the index method, calculated on the basis of appropriate fixed-point indicators available in the literature. The work uses a commercially available automatic pellet boiler with a capacity of 10 kW. Combustion tests were carried out for five different materials, including wood pellets, energy plant pellets and agricultural waste. The emission factors were determined for CO, NO_x and SO_2 with reference to the unit of mass of fuel and calorific value of fuel.

The CO, NO_X, SO_2 emission indices determined using the index method were burdened with a large error. In the case of CO and NO_x emission indicators, this resulted from the course of the combustion process, which for the biofuels tested did not always run equally smoothly and without problems, which affected the obtained boiler power. During the conducted combustion tests, when the boiler reached its rated power and maximum load, the CO emission indices determined using the index method were much higher than those determined empirically. On the other hand, the NO_X emission factors determined using the index method were lower than those determined empirically. It follows that setting emission indicators using biomass fuels may be subject to a very large error and not to inform about the actual emissions from low-capacity boilers installed in individual households.

Because the combustion process is very sensitive to the conditions in which it occurs, and their slight change may cause major changes in emission factors, it can not be considered that the emission factors obtained in the conducted research can be an undisputable source of information about emissions from this type of installations. Further emission tests are required, taking into account different types of equipment, a wide range of their models and technologies as well as various biomass fuels. The results of this research will allow the development of more accurate drift rates for biomass fuels and for more precise estimation of emission factors.

Keywords:
pellets, biomass combustion, small scale boilers, emission factor

Porównanie i ocena wskaźników emisji toksycznych składników spalin podczas spalania paliw biomasowych

Streszczenie

Ocena korzyści środowiskowych, wynikających ze spalania biomasy, jest zagadnieniem złożonym. Najbardziej wiarygodna jest wówczas, gdy istnieje możliwość empirycznej oceny emisji z wykorzystaniem różnych paliw w instalacjach energetycznych. Jeżeli brak jest konkretnych danych o emisji, należy ją oszacować, wykorzystując odpowiednie wskaźniki.

Wciąż istnieje znaczna niepewność oceny wpływu emisji zanieczyszczeń towarzyszących spalaniu biomasy na jakość powietrza w skali lokalnej. Spowodowane jest to nie tylko brakiem danych dotyczących ilości spalanej biomasy ale również brakiem współczynników emisji, które charakteryzowałyby spalanie rzeczywiste. W tym kontekście niezwykle istotne jest poszerzanie wiedzy dotyczącej aspektów środowiskowych wynikających z wykorzystania energetycznego biomasy.

Celem pracy było porównanie i ocena wskaźników emisji toksycznych składników spalin, uzyskanych na podstawie pomiarów bezpośrednich oraz wskaźników oszacowanych za pomocą metody wskaźnikowej, obliczonych na podstawie odpowiednich, dostępnych w literaturze wskaźników unosu. W pracy wykorzystano dostępny komercyjnie, automatyczny kocioł na pelety o mocy 10 kW. Testy spalania przeprowadzono dla pięciu różnych materiałów, w tym peletów drzewnych, peletu z roślin energetycznych i odpadów rolniczych. Wskaźniki emisji wyznaczono dla CO, NOx i SO_2 w odniesieniu do jednostki masy paliwa i wartości opałowej paliwa.

Wskaźniki emisji CO, NOx, SO_2 wyznaczone metodą wskaźnikową były obciążone dużym błędem. W przypadku wskaźników emisji CO i NOx wynikało to z przebiegu procesu spalania, który dla badanych biopaliw nie zawsze przebiegał jednakowo sprawnie i bezproblemowo, co wpływało na uzyskiwaną moc kotła. Podczas prowadzonych testów spalania, kiedy kocioł osiągał moc znamionową i maksymalne obciążenie, wskaźniki emisji CO wyznaczone metodą wskaźnikową były o wiele wyższe od wyznaczonych empirycznie. Natomiast wskaźniki emisji NO_X wyznaczone metodą wskaźnikową były niższe niż wyznaczone empirycznie. Wynika stąd, że wyznaczanie wskaźników emisji metodą wskaźnikową dla paliw biomasowych może być obarczone bardzo dużym błędem i nie informować o rzeczywistej emisji z kotłów małej mocy zainstalowanych w indywidualnych gospodarstwach domowych.

Ponieważ proces spalania jest bardzo wrażliwy na warunki w jakich zachodzi, a niewielka ich zmiana może spowodować duże zmiany wskaźników emisji, nie można uznać, że wskaźniki emisji uzyskane w przeprowadzonych badaniach mogą stanowić bezdyskusyjne źródło informacji o emisjach z instalacji tego typu. Niezbędne są dalsze badania emisji z uwzględnieniem różnych typów urządzeń, szerokiej gamy ich modeli i technologii oraz różnych paliw biomasowych. Wyniki tych badań pozwolą na opracowanie dokładniejszych wskaźników unosu dla paliw biomasowych oraz na precyzyjniejsze szacowanie wskaźników emisji.

Słowa kluczowe:
pelety, spalanie biomasy, kotły małej mocy, wskaźniki emisji

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Polybrominated Diphenyl Ethers as the Emerging Contaminants in the Polish Environment

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are organobromine compounds with 209 theoretically possible congeners, including 1 up to 10 bromine atoms, each. They do not occur naturally in the environment but are synthesized as a result of the bromination of diphenyl ether. PBDEs are brominated flame retardants used in products to meet the fire safety requirements (de Wit 2002). Polybrominated diphenyl ethers are so-called emerging contaminants – substances that have recently been detected in the environment, are not included or have been included only recently in the regular monitoring programmes, and yet sufficient information does not exist to determine their potential environmental or public health risk (Naidu et al. 2016).

PBDEs have been used in a range of products:

- plastics, thermoplastic polymers,
- textiles (curtains, carpets, tents, protective clothing, workwear, toys),
- construction materials (insulation panels, insulation foam, wall and flooring panels, foam fillers),
- electric and electronic equipment (computers, office equipment),
- furniture industry (mattresses, upholstered furniture),
- polyurethane foams,
- resins, rubbers, paints, varnishes, impregnates.

Their content in products (polymers, textiles) was on average 5-30% by weight (Alaee et al. 2003).

The commercial mixtures of PBDEs were initially used in the 1960s, and their names are derived from a congener of the highest percentage in the mixture:

- pentabromodiphenyl ether (pentaBDE) – a mixture of, among others, tetraBDE (24-38%), pentaBDE (50-60%) and hexaBDE (4-8%); technical pentaBDE – a total quantity of the following congeners: BDE-47, BDE-99 and BDE-100,
- octabromodiphenyl ether (octaBDE) – a mixture of, among others, hexaBDE (10-12%), heptaBDE (44%), octaBDE (31-35%) and nonaBDE (10-11%); technical octaBDE – a total quantity of the following congeners: BDE-153, BDE-154, BDE-183,
- decabromodiphenyl ether (decaBDE) – a mixture of nonaBDE (< 3%) and decaBDE (97-98%); technical decaBDE – congener BDE-209.

PentaBDE was mainly used in the elastic polyurethane foams (ca. 95% of the applications), which were applied in the furniture and upholstery (60%) and automobile industry (36%) (Alaee et al. 2003). OctaBDE was predominantly used in the ABS plastics (nearly 95% of the applications), in the production of the electric and electronic equipment (office equipment, TV sets). DecaBDE was primarily used in the polymer materials, including the polystyrene parts of the electronic household appliances and in the furniture upholstery.

According to the data from 2010, an annual manufacturing volume of the commercial PBDEs was approximately 67,000 Mg, in that circa 55,000 Mg (82%) decaBDE, almost 9,000 Mg (13%) pentaBDE and 3,000 Mg (5%) octaBDE (Fulara & Czaplicka 2010). Based on the available information, decaBDE is still manufactured in few countries – China, Japan or India (Kukharchyk 2017).

Polybrominated diphenyl ethers have never been manufactured in Poland (Krupanek et al. 2011). The following technical PBDEs mixtures were available for sale: BR 55N, Bromkal 82-ode, DE 83R, Saytex 102 and Tardex 100 (http://www.inchem.org/documents/ehc/ehc/ehc162.htm). The use of pentaBDE and octaBDE in the EU, also in Poland, was prohibited in 2004, and since 2006 a ban on the use of decaBDE in the electric and electronic equipment has been introduced (OJ L 42, 15.2.2003, 45-46; OJ L 37, 13.2.2003, 19-23). Since March 2019, the manufacturing or placing on the market of decaBDE as a substance on its own is prohibited. Pursuant to the Commission Regulation (EU) 2017/227 of 9 February 2017, till 2 March 2027 the ban does not apply to the decaBDE used for the production of spare parts for the machinery produced before 2 March 2019 and for the production of aircraft (OJ L 35 of 10.2.2017, 6-9).

The commercial pentaBDE mixture (tetra- and pentaBDE ethers) and octaBDE mixture (hexa- and heptaBDE ethers) were classified as the persistent organic pollutants and in 2009 included in Annex A (*Elimination*) to the Stockholm

Convention (Journal of Laws of 2009 no. 14, item 76). The use and recycling of the products that contain these compounds were severely restricted. The European Union, as a party to the Convention, registered a specific exemption for hexa-, hepta-, tetra- and pentaBDE, due to a fact, that products, which contain mentioned PBDEs, are still in use and will be recycled in the future. The specific exemptions for PBDEs listed in the Convention will expire in 2030.

Studies related to the PBDEs occurrence in the environmental, food or dust samples show that products containing PBDEs have been and are used in Poland. Analysis of the studies on the occurrence and concentrations of the polybrominated diphenyl ethers in the environment, food, animal organisms, in that humans, will enable to evaluate the PBDEs contamination in Poland and indicate data gaps. Therefore, this study is focused on discussing the results of determination of PBDEs used in commercial mixtures:

- technical pentaBDE (BDE-28, 47, 99, 100),
- technical octaBDE (BDE-153, 154, 183),
- technical decaBDE (BDE-209).

2. PBDEs in the environment

One of the primary emission sources of polybrominated diphenyl ethers to the environment is the use of the products that contain these compounds and subsequent waste management (Krupanek et al. 2011). For Poland, releases to the wastewaters from the industrial sources were estimated, with a great degree of uncertainty, at 1-7 kg/y for pentaBDE and 10 kg/y for decaBDE, and from the municipal wastewater at 0.4 kg/y in the case of pentaBDE and 1.1 kg/y for decaBDE. A volume of the annual release to the environment from the agricultural use of the sewage sludge was estimated at 0.02-0.06 kg for pentaBDE and 43 kg for decaBDE. A deposition volume of pentaBDE from the air, as a result of the use of products, was estimated at 14 up to 20 kg/y, and for decaBDE at 42 up to 130 kg/y, however, these estimations are encumbered with a great deal of uncertainty. The annual emissions of these compounds to the atmosphere and internal air were estimated on the similar levels – 0.08-1.6 kg/y for pentaPDE and 0.4-7 kg/y for decaBDE and 0.07-1.6 kg/y for pentaBDE and 1-23 kg/y for decaBDE, respectively (Krupanek et al. 2011).

2.1. Water and sediments

In Poland, the levels of the following PBDE congeners: BDE-28, 47, 99, 100, 153, 154 are determined in the surface waters and sediments in selected sampling points within the frames of the State Environmental Monitoring (SEM) performed by the Inspection of Environmental Protection (GIOŚ). The PBDEs concentrations in the surface waters can be referred to the environmental quality standards (EQS) for surface waters, expressed by a maximum allowable concentration (MAC-EQS). For PBDEs (the sum of congeners BDE-28, 47, 99, 100, 153 and 154), the MAC-EQS values are (Journal of Laws of 2016 item 1187):

- 0.14 µg/L for inland surface waters (rivers and lakes, and the artificial or significantly changed parts of the waters connected with them),
- 0.014 µg/L for other surface waters.

The PBDEs concentrations in the rivers and lakes' surface waters and sediments detected over a few last years within the frames of the SEM are presented in Table 1.

Table 1. PBDEs (BDE-28, 47, 99, 153, 154) concentrations in the rivers and lakes' surface waters and sediments, determined in 2011-2015 (GIOŚ's unpublished data)

Year	Concentration range (∑PBDEs)			
	Rivers µg/L	Rivers' sediments ng/g dw	Lakes µg/L	Lakes' sediments ng/g dw
2011	*n = 31*		*n = 7*	
	0.00005-0.00127		0.00005-0.00031	
2012	*n = 718*		*n = 17*	
	0.00005-**0.5***		0.00005-0.00025	
2013	*n = 745*	*n =43*	*n = 32*	*n = 22*
	0.000025-0.00036	<50 – < 60000	0.000036-0.00025	<50 – < 50000
2014	*n = 948*	*n = 64*	*n = 52*	
	0 – 0.0018	<0.05 – 64.9	0.000025-0.00025	N/A
2015	*n = 715*	*n = 57*	*n = 68*	*n = 8*
	0.00005-0.00025	<0.05 – 216	0.000025-0.00025	<0.05-86.7
2016	*n =10*	*n = 43*		*n = 1***
	0.011-0.047	<10		<10
2017		*n = 60*		*n = 21*
		< 0.05		< 0.05

* result exceeding the MAC-EQS value for surface waters (0.014 µg/L);
BDE-100 was not included
** sampling point on the Wielkie Dąbie Lake

The data show that over the years 2011-2016, the PBDEs levels in lakes' waters did not exceed MAC-EQS. Regarding rivers' waters, PBDEs concentrations exceeded the MAC-EQS only in 2012 (for 52 out of 718 sampling points). According to the information from the GIOŚ, in the case of sediments, the monitoring of PBDEs started in 2013 in selected rivers and lakes. In 2013, both for rivers and lakes' sediments, PBDE-209 was detected in the highest concentrations (<0.1 - <60,000 ng/g dw in rivers' sediments and <150 - <50,000 ng/g dw in lakes' sediments), as this congener is strongly bonded to sediments (ATSDR

2017). The results for other congeners fluctuated within <50 – <500 ng/g dw. Since the samples were taken in rotational maner (every three years) the possible trend is hard to observe.

In 2010, studies on the occurrence of 7 PBDE congeners in the sediments in the Vistula river estuary, Władysławowskie Fishery and Ustecko-Łebskie Fishery were conducted (Waszak et al. 2012). The fraction <63 μm was used to perform the analysis. The mean concentration of PBDEs in the sediments fluctuated from 0.22 up to 0.61 ng/g dw (Table 2).

Table 2. The mean concentrations of selected PBDE congeners in the sediments, ng/g dw (Waszak et al. 2012)

	Vistula river estuary	Władysławowskie Fishery	Ustecko-Łebskie Fishery
	n = 3	*n* = 1	*n* = 2
BDE-28	0.20 ± 0.03	0.05	0.03 ± 0.02
BDE-47	0.15 ± 0.03	0.06	0.05 ± 0.02
BDE-99	0.11 ± 0.03	0.03	0.03 ±0.03
BDE-100	0.05 ± 0.01	0.004	0.005 ± 0.002
BDE-153	0.03 ± 0.02	0.04	0.03 ± 0.02
BDE-154	0.06 ± 0.03	0.03	0.05 ± 0.04
BDE-183	0.03 ± 0.01	0.02	0.02 ± 0.02
∑PBDEs	0.61 ± 0.10	0.22	0.22 ± 0.05

In the sediment samples from the Vistula river estuary, the PBDE concentrations were higher than in the sediments samples from the fisheries, probably due to a greater anthropogenic stress in the Bay of Gdansk. In case of BDE-28 and BDE-47, their concentrations in samples from Gdansk Bay were higher by circa 33% and 22%, respectively. BDE-47, one of the pentaBDE consituents, accounted for 23 up to 27% of the total quantity of all PBDE congeners studied.

Regular monitoring of organobromine compounds in the Baltic Sea has begun in 2012 (Łysiak-Pastuszak et al. 2013). In 2012-2014, the chemical status of all control points in the West Pomeranian Voivodeship – uniform water bodies (JCW) of the transitional waters (JCW of Szczecin lagoon, JCW of Kamieński lagoon, JCW of Dziwna river estuary and JCW of Świna river estuary) and of the coastal waters (JCW of Dziwna-Świna, JCW of Sarbinowo-Dziwna and JCW of Jarosławiec-Sarbinowo) – were assessed as less than good, what was impacted by, inter alia, the exceedances of the average annual values of pentabromodiphenyl ether (Łysiak-Pastuszak et al. 2013; Łysiak-Pastuszak et al. 2014; Zalewska et al. 2015).

2.2. Wastewater and sewage sludges

Occurrence of pentaBDE, octaBDE and decaBDE in wastewater and sewage sludge was investigated within the frame of "*COHIBA: Control of hazardous substances in the Baltic Sea region"* project (Zielonka et al. 2012). In 2009 and 2010, samples of wastewater and sewage sludges were collected, once per two months, from the municipal and industrial wastewater treatment plants (WWTP). Data on the frequency of the occurrence of pentaBDE, octaBDE and decaBDE are presented in Table 3.

Table 3. The frequency of the occurrence of selected polybrominated diphenyl ethers in studied samples, % (Zielonka et al. 2012)

Mixture	Wastewater from the municipal WWTP	Wastewater from the industrial WWTP	Sewage sludges	Surface runoffs	Landfill leachates
pentaBDE	44.4	16.7	50	-	-
octaBDE	-	-	100	50	50
decaBDE	100	100	100	100	100

In effluent from municipal and industrial wastewater treatment plants, concentrations of decaBDE were in all cases above LOD of the method. Moreover, the results of the screening inventory in the Baltic Sea area show that not only point sources (municipal and industrial wastewater treatment plants) but also dispersed sources (field runoffs and use of sewage sludges in agriculture) are responsible for the surface water contamination by PBDEs.

2.3. Air and dust

Due to the wide use of PBDEs in the textiles, furniture and electronic equipment, ingestion of house dust is considered as one of the main exposure routes to PBDEs, especially in the case of infants and small children (Król et al. 2014). In order to investigate the occurrence of congeners used in commercial pentaBDE and octaBDE mixtures, 30 samples of indoor dust (offices, shops with the electronic equipment, computer servicing points, residential houses) were taken in Lublin in 2009 (Staszowska et al. 2012). Results of the study are presented in Table 4.

Table 4. The concentration of selected PBDE congeners in the indoor dust samples, ng/g dw (Staszowska et al. 2012)

Compound	Single-family houses	Offices	Computer servicing points	Electronic equipment shops
	n = 20	*n* = 6	*n* = 2	*n* = 2
BDE-28	<MDL – 8.7	2.4 – 29.4	25.7 – 41.3	32.3 – 27.6
BDE-47	5.1 – 96	7.4 – 111	18.7 – 544	14.6 – 96
BDE-99	<MDL – 74	5.8 – 49	7.1 – 179	6.2 – 75
BDE-100	<MDL – 59.7	5.1 – 33	19.2 – 155	5.4 – 76.9
BDE-153	<MDL – 21.4	6.3 – 24.7	5.9 – 46	6.6 – 34.4

MDL – *method detection limit*

In the majority of the samples, congeners from two PBDE commercial mixtures, with a prevalence of pentaBDE, were detected. The highest concentrations of BDE-28, 47, 99, 100 and 153 were determined in samples collected from the computer servicing points and shops with electronic equipment. However, the maximum concentrations of BDE-47, 99, 100 and 153 in the house dust were comparable with concentrations determined in the dust from offices and electronic equipment shops, and in the case of BDE-99 and BDE-100 were even higher.

In 2012, dust samples were collected from 12 households in Gdańsk and Gdynia, in order to analyse the occurrence and levels of BDE-47, 99, 100, 153, 154, 183, 209 (Król et al. 2014). Results are shown in Table 5.

Table 5. The median, mean and range concentrations of PBDE congeners analysed in dust collected from Gdańsk and Gdynia households, ng/g dw (Król et al. 2014)

Compound	Median	Mean	Range
BDE-28	3.8	3.4	<MDL – 8.2
BDE-47	5.4	9.9	<MDL – 51
BDE-99	1.4	2.2	<MDL – 4.8
BDE-100	<MDL	<MDL	<MDL
BDE-153	<MDL	<MDL	<MDL
BDE-154	<MDL	<MDL	<MDL
BDE-183	3.9	7.5	<MDL – 22
BDE-209	219	241	7.1 – 615
∑PBDEs	232	264	<MDL – 701

*MDL – *method detection limit*

Due to very low water solubility, PBDEs, particularly higher brominated congeners, are strongly associated with the solid phase. It decreases their mobility in the soil, sediments or water, but increases in the atmosphere, where they are associated with solid particles (and dust) suspended in the air (ATSDR 2017). The above is confirmed by the mentioned results – the highest content in dust samples were obtained for the BDE-209 (around 90% of the total concentration of all studied congeners). Concentrations of BDE-100, 153 and 154 were below the MDLs.

3. PBDEs in food and fish potentially intended for human consumption

Food is another main route of human exposure to PBDEs, especially the one that contains significant quantities of animal fat. Therefore, apart from the section dedicated to PBDEs in food, this part of work is also focused on PBDEs concentration in the fish, as potential nutrition source, caught in Polish rivers, lakes, and in the Polish part of the Baltic Sea.

3.1. Content of PBDEs in food

In Poland, the content of PBDEs in the butter, hen eggs, chocolate products, back fat, beef fat and fish meat (carp, cod, salmon) was studied by Wojtalewicz and Wojtalewicz et al. (2008). The total concentration of PBDE congeners with results above detection limit (the sum of BDE-28, 47, 99, 100, 153, 154) was of similar order of magnitude in all products:

- butter: 55-174 pg/g fat,
- hen eggs: 173-391 pg/g fat,
- lard: 38-71 pg/g fat,
- beef fat: 43-68 pg/g fat,
- chocolate products: 55-260 pg/g fat.

Sum of congeners from tetraBDE and pentaBDE mixtures constituted circa 90% of the total amount of PBDEs in the studied products. A high similarity between a congener profile in the analysed samples was observed: BDE-47 and BDE-99 were determined in the highest concentrations (in both cases 42% of the total amount of PBDE), then BDE-153 (6%), BDE-100 (4%), BDE-154 (4%) and BDE-28 (3%). It matches the composition profile of commercial pentaBDE and octaBDE mixtures, in which tetra- and penta-homologues occur in the highest quantities.

In the fish samples, the highest content of all PBDE congeners was detected in the salmon tissues (0.377-5.340 µg/kg ww), with the BDE-47 being the dominant congener. The higher content of PBDEs in the salmon tissues compared to the cod tissues is related to higher fat content in the salmon. The highest content of tetraBDE (BDE-47 and -49) in all fish species confirms that the lower-brominated PBDEs show high affinity to lipids and tendency to bioaccumulation in the aquatic organisms (Siddiqi et al. 2003).

The content of PBDEs was also studied in the cereal products from the Polish market – groats, flakes, flour, pasta, bran, porridges for children, cereal snacks and bread by Roszko et al. (2014). In 191 samples, the mean total content of PBDEs (BDE-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209) was 112±80 pg/g, while the mean total content without the BDE-209 was 15±6 pg/g. Reported data on concentrations of PBDEs in various food items are provided in Table 6.

The levels of PBDEs in the studied cereal products were low. The congener BDE-209 (on average of 97 pg/g dw) was predominant, followed by the congeners BDE-99 (on average 3 pg/g dw) and BDE-47 (on average 2,8 pg/g). The congener BDE-209 accounted for ca 90% of the sum of PBDEs in bran and cereal snacks and for 65% of the sum of PBDEs in groats and flakes.

The content of PBDEs was also studied in the hen eggs from the free-range hens and conventional farms by Roszko et al. (2014). Each sample was composed of at least 8 eggs. 20 samples from the free-range hens and 19 samples from the conventional farms were subjected to the analysis (Table 7).

Congeners BDE-47, 99, 153 and 183 occurred in the highest concentration. The higher PBDEs content was determined in the eggs from the free-range hens, the medians for both groups were similar.

In 2015, the concentrations of 39 PBDEs congeners were determined in the honey samples collected in Wyszyny, Żołędowo, Wągrowiec, Chojna, Mostki, Miłoradzice, Glinica, Nowy Staw, Nidzica, Zalesie Górne, Radzyń Podlaski, Ulanów and Lubaczów (Roszko et al. 2016). For BDE-47, 99, 100 and 183 the highest concentrations were determined. (Table 8). The congeners BDE-118, 47 and 183 accounted for approximately 26.5%, 22% and 13% of the total quantity of all PBDEs, respectively.

Table 6. The concentration of selected PBDE congeners in different cereal products on the Polish market, pg/g (Roszko et al. 2014)

Compound	Concentration	Cereal products							
		Groats	Flakes	Flour	Pasta	Bran	Porridges for children	Cereal snacks	Bread
		n = 35	*n* = 35	*n* = 27	*n* = 14	*n* = 20	*n* = 25	*n* = 15	*n* = 20
BDE-28	Range	0.0-2.9	0.0-0.0	0.0-7.1	0.0-4.0	0.0-105.1	0.0-1.2	0.0-0.7	0.0-0.8
	Mean	0.4	0.0	0.6	0.4	5.7	0.2	0.4	0.2
	Median	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0
BDE-47	Range	0.0-6.3	0.7-12.6	0.0-15.1	0.0-6.8	0.0-13.0	1.7-6.1	2.5-3.3	0.0-9.8
	Mean	1.7	3.2	2.4	2.6	4.3	2.9	2.8	2.4
	Median	1.4	3.0	1.2	2.5	4.0	2.8	2.8	2.0
BDE-99	Range	0.0-8.0	0.0-4.4	0.0-11.4	0.4-29.5	0.2-11.1	1.3-8.4	2.9-4.3	0.0-5.2
	Mean	1.2	1.7	2.1	7.1	3.7	3.4	3.4	1.5
	Median	1.0	1.6	1.2	3.6	3.1	3.4	3.4	1.4
BDE-100	Range	0.0-2.1	0.0-2.2	0.0-13.5	0.0-5.5	0.0-31.4	0.0-1.3	0.0-0.6	0.0-0.6
	Mean	0.3	0.3	1.3	1.1	1.9	0.3	0.2	0.3
	Median	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.4
BDE-153	Range	0.0-1.5	0.0-2.2	0.0-4.8	0.0-5.2	0.0-4.3	0.0-4.0	1.1-1.7	0.0-1.4
	Mean	0.6	0.7	0.7	1.2	1.6	1.4	1.4	0.4
	Median	0.5	0.5	0.3	0.5	1.5	1.5	1.5	0.2

Table 6. cont.

Compound	Concentration	Cereal products							
		Groats	Flakes	Flour	Pasta	Bran	Porridges for children	Cereal snacks	Bread
		$n = 35$	$n = 35$	$n = 27$	$n = 14$	$n = 20$	$n = 25$	$n = 15$	$n = 20$
BDE-154	Range	0.0-1.9	0.0-3.4	0.0-3.7	0.0-2.2	0.0-1.2	0.0-1.0	0.0-0.8	0.0-0.9
	Mean	0.3	0.4	0.5	0.5	0.4	0.2	0.3	0.3
	Median	0.2	0.3	0.2	0.2	0.4	0.0	0.0	0.2
BDE-183	Range	0.0-9.0	0.5-18.2	0.0-22.1	0.0-5.4	0.0-30.6	0.6-24.1	3.5-7.0	0.1-2.9
	Mean	2.7	3.3	2.0	1.4	6.8	5.5	5.7	1.3
	Median	2.7	2.0	0.5	0.5	4.9	5.6	5.6	1.2
BDE-209	Range	0.0-34.6	0.9-39.2	1.1-961.1	0.5-895.8	17.7-1971.0	23.2-536.8	98.8-163.5	6.7-100.4
	Mean	15.2	18.4	81.0	148.1	248.5	112.8	129.7	22.6
	Median	14.5	19.4	18.3	29.3	59.8	84.4	122.0	17.5
ΣPBDEs	**Range**	8.4-48.6	9.1-59.9	17.4-1002.7	20.0-921.8	37.1-1989.8	34.6-552.4	113.9-178.8	10.2-111.8
	Mean	23.6	29.0	97.2	168.8	274.9	128.4	145.0	29.8
	Median	21.8	28.8	34.2	55.8	88.6	100.5	138.1	25.7

Table 7. The concentration of the sum of PBDEs in eggs, pg/g fat (Roszko et al. 2014)

	Hen eggs from the free-range hens			Hen eggs from conventional farms		
	Mean	Median	Range	Mean	Median	Range
∑PBDEs	164.5	99.4	50.8-735.9	111.1	74.7	21.5-231.6

Table 8. The mean, median and range of concentrations of selected PBDE congeners in the honey samples from Poland, pg/g (Roszko et al. 2016)

PBDE	Mean	Median	Range
BDE-47	3.0	1.9	0.0-12.5
BDE-99	2.7	6.2	0.0-34.6
BDE-100	1.4	4.8	0.0-29.4
BDE-153	0.6	1.8	0.0-10.5
BDE-154	0.9	1.7	0.0-7.5
BDE-183	1.4	1.8	0.0-6.2

The food is the main source of human exposure to organic contaminants, with fish recognized as the most important exposure source (Szlinder-Richert et al. 2010). Therefore, since 2000, the studies on the concentration of PBDEs in the various species of the fresh-water and salt-water fish fished in the Polish waters have been conducted. For brominated diphenyl ethers (the sum of BDE-28, 47, 99, 100, 153 and 154) the environmental quality standard for fish (EQS Flora and Fauna) was determined as 0.0085 µg/kg ww (Journal of Laws of 2016 item 1187), in relation to which the results of presented studies were compared.

Between 2000 and 2008, the studies on the concentration of polybrominated diphenyl ethers (BDE-28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183 and 209) in herrings from Baltic Sea were conducted by Roots et al. (2009). The herring is the species preferred for the purposes of monitoring the PBDEs levels in the Baltic Sea because it is the important commercial species, fished in all parts of the Baltic Sea. The material for the studies was sampled on the open sea, from the Gulf of Finland and the Gulf of Riga. The highest content of PBDEs was detected in the herrings originating from both gulfs. BDE-47, 99, 100, 28, 153 and 154 congeners were detected in the highest concentrations. Over the period 1999-2008, an increase in the PBDEs content in the herrings was not observed. In 2007, the high concentrations of the BDE-209 were determined, however, the reason was not explained.

In 2004-2006, the studies on the PBDEs content (BDE-28, 47, 99, 100, 153, 154, 183) in the fish meat (herring, sprat, salmon) from the southern part of the Baltic Sea were conducted (Szlinder-Richert et al. 2010) (Table 9). The highest content of PBDEs was detected in the salmon meat and the lowest in herring meat. Detected concentrations were similar to the PBDEs content in the herrings originating from the northern part of the Baltic Sea. In the herrings and salmons, the congener BDE-47 which accounted for 55% up to 65% of the total quantity of all PBDEs was detected in the highest quantity. In all studied fishes from the southern Baltic, BDE-183 occurred in the lowest concentrations and accounted for less than 1% of the total quantity of the studied PBDEs. It has to be noted, that all detected concentrations exceeded the EQS level.

In 2010, the studies on the PBDEs content (BDE-28, 47, 99, 100, 153, 154 and 183) in the muscles of the females of flounder species were conducted (Waszak et al. 2012). The study material was collected in the Vistula river estuary, as well as in the area of the Władysławowskie Fishery and Ustecko-Łebskie Fishery. Additionally, in the years 2010 and 2011, the PBDEs concentration in the muscles, liver and gonads of the females of flounder species females fished in the Vistula river estuary were determined. The concentrations of PBDEs in the liver were higher than in the muscles and gonads. Generally, the content of PBDEs was relatively low, the highest in the samples of the flounders from the Vistula river estuary (it results from the higher anthropogenic stress), and the lowest in the samples of the flounders from the Władysławowskie Fishery, however, in the majority of the cases, the environmental quality standard (EQS) was exceeded (Table 10). Similarly, as in the aforementioned studies, the congener BDE-47 occurred in the highest concentrations.

In the years 2010-2012, the studies on the PBDEs concentration, as one of the organic contaminants, in the muscles and liver of the freshwater eel in the Polish waters were performed by Szlinder-Richert et al. (2014). The study material was collected from the Vistula Lagoon ($n = 43$), Szczecin Lagoon ($n = 34$), Bay of Puck ($n = 25$), the lakes: Śniardwy, Mamry, Nidzkie and Jamno ($n = 46$), as well as from the Vistula river near Toruń ($n = 5$). The mean content of PBDEs in the muscles was 1-2 ng/g ww (0.07-8.19 ng/g ww). The content of PBDEs in the muscles of the eels from the Vistula river and Bay of Puck was circa 3-fold higher than in the muscles of the eels from the waters of the Vistula Lagoon, Szczecin lagoon and the lakes. The study results showed the highest content of BDE-47 (0.05-6.4 ng/g w.w.) – it accounted for 50 up to 80% of the sum of PBDEs. The higher content of PBDEs was detected in the liver samples than in muscles (range: 0.19±0.1-1.64±1.6 ng/g w.w.). The highest PBDEs content was determined in the liver of the eel from the Bay of Puck, and the lowest – the eel coming from the lakes. The PBDEs content in the muscles of the freshwater eel fished in the Polish waters significantly exceeded the EQS for fish.

In 2013, the studies on the content of, inter alia, PBDEs in the liver of the Atlantic cod originating from the Baltic Sea were conducted by Roszko et al. (2015). The mean content of the total PBDEs (36 congeners) was 57.857 ng/g fat ($n = 51$, range: 28.592-159.669 ng/g fat). In the profile of the PBDE congeners, the congener BDE-47 prevailed (circa 38% of the total quantity of all PBDEs), and pentaBDE and tetraBDE predominated over the other congeners.

Within the frames of the SEM performed by GIOŚ, data on the content of PBDEs (BDE-28, 47, 99, 100, 153, 154) in the fish from the Polish maritime areas of the Baltic Sea, and from rivers and lakes are collected (Łysiak-Pastuszak et al. 2016). The results are presented in Table 9. In 2015, in the muscle tissue of European flounder fished in the coastal waters of the Gdańsk Basin the lowest content of PBDEs, compared to previous years, was reported – 0.15 ng/g ww. In the case of herring, compared to years 2012-2014, the lower content of PBDEs in the muscle tissues was reported for animals fished in the Gotland Basin and the Bornholm Basin. The content of PBDEs in the muscle tissue of European flounder from the Bornholm Basin was lower than in herring. In the SEM reports, the status of marine waters of the Baltic Sea economic zone regarding the PBDEs concentrations in the years 2012-2015 was qualified as very good. As in 2016, the EQS for fish of 0.0085 ng/g w.w. was introduced, all results from the aforementioned period would qualify the status of the marine waters as poor (exceeding the threshold a few orders of magnitude). It should be pointed out that in the European Union law, this EQS was established already in 2013 (OJ L 226, 24.8.2013).

The results of PBDEs content in the samples of the fish meat (roach, bream, perch, herring and river trout) fished in the Polish rivers, lakes, and transitional and coastal waters, collected within the SEM (GIOŚ unpublished data), are presented in Table 9. Generally, for the same species, for years 2016 and 2017, the lower content of PBDEs was detected in the meat of lake fish compared with the meat of the river fish. For all fish species, fished in the rivers, lakes, and transitional and coastal waters, in 2017 the content of the studied PBDEs was lower compared to the results from 2016. However, results both from 2016 and 2017 exceeded the EQS, and the highest results were obtained for the roach and perch meat fished in the rivers.

Table 9. The mean and range of concentrations of the sum of PBDEs in the fish sampled from Baltic Sea and Polish rivers and lakes, ng/g ww

Sampling site	Sampling year	n	Matrix	Fat content [%]	∑PBDEs – mean (range) [ng/g ww]	Source
Southern Baltic Sea	2004	12	Herring (muscles)	4.2	1.3(*)	Szlinder-Richert J. et al. 2010
	2005	16	Herring (muscles)	4.4	1.2(*)	Szlinder-Richert J. et al. 2010
	2006	15	Herring (muscles)	4.3	1.3(*)	Szlinder-Richert J. et al. 2010
	2004	11	Sprat (muscles)	9.3	2.3(*)	Szlinder-Richert J. et al. 2010
	2005	14	Sprat (muscles)	9.8	1.1(*)	Szlinder-Richert J. et al. 2010
	2006	13	Sprat (muscles)	7.9	1.8(*)	Szlinder-Richert J. et al. 2010
	2004	5	Salmon (muscles)	7.8	4.3(*)	Szlinder-Richert J. et al. 2010
	2005	15	Salmon (muscles)	10.2	2.3(*)	Szlinder-Richert J. et al. 2010
	2006	15	Salmon (muscles)	8.2	2.2(*)	Szlinder-Richert J. et al. 2010
Szczecin Lagoon	2014		Perch (muscles)		0.04(*)	GIOŚ, 2016
	2015		Perch (muscles)		0.07(*)	GIOŚ, 2016
Vistula Lagoon	2014		Perch (muscles)		0.03(*)	GIOŚ, 2016
	2015		Perch (muscles)		0.02(*)	GIOŚ, 2016
Bornholm Basin	2012		Herring (muscles)		0.82(*)	GIOŚ, 2016
	2013		Herring (muscles)		1.39(*)	GIOŚ, 2016
	2014		Herring (muscles)		0.67(*)	GIOŚ, 2016
	2015		Herring (muscles)		0.45(*)	GIOŚ, 2016
	2012		European flounder (muscles)		0.25(*)	GIOŚ, 2016
	2013		European flounder (muscles)		0.20(*)	GIOŚ, 2016
	2014		European flounder (muscles)		0.38(*)	GIOŚ, 2016
	2015		European flounder (muscles)		0.30(*)	GIOŚ, 2016

Table 9. cont.

Sampling site	Sampling year	n	Matrix	Fat content [%]	∑PBDEs – mean (range) [ng/g ww]	Source
Eastern Gotland Basin	2012		Herring (muscles)		0.67(*)	GIOŚ, 2016
	2013		Herring (muscles)		1.29(*)	GIOŚ, 2016
	2014		Herring (muscles)		0.90(*)	GIOŚ, 2016
	2015		Herring (muscles)		0.63(*)	GIOŚ, 2016
Coastal waters of the Gdańsk Basin	2012		European flounder (muscles)		0.22(*)	GIOŚ, 2016
	2013		European flounder (muscles)		0.17(*)	GIOŚ, 2016
	2014		European flounder (muscles)		0.21(*)	GIOŚ, 2016
	2015		European flounder (muscles)		0.15(*)	GIOŚ, 2016
Rivers	2016	115	Roach (muscles)		(0.071-3,5)(*)	GIOŚ.2017 (unpublished)
	2017	301	Roach (muscles)		(0,026-1.146)(*)	GIOŚ,2017 (unpublished)
	2016	30	Bream (muscles)		(0.075-2.7) (*)	GIOŚ.2017 (unpublished)
	2017	95	Bream (muscles)		(0,051-2.48) (*)	GIOŚ,2017 (unpublished)
	2016	8	Perch (muscles)		(0.14-1.8) (*)	GIOŚ,2017 (unpublished)
	2017	54	Perch (muscles)		(0.089-1.276(*))	GIOŚ,2017 (unpublished)
	2017	8	River trout (muscles)		(0.195-.530) (*)	GIOŚ,2017 (unpublished)
Lakes	2016	23	Roach (muscles)		(0.067-0,56) (*)	GIOŚ,2017 (unpublished)
	2017	44	Roach (muscles)		(0,059-0.594) (*)	GIOŚ,2017 (unpublished)
	2016	16	Bream (muscles)		(0.14-0.72) (*)	GIOŚ.2017 (unpublished)
	2017	26	Bream (muscles)		(0.45-0.371) (*)	GIOŚ.2017 (unpublished)
	2016	1	Perch (muscles)		1.6(*)	GIOŚ,2017 (unpublished)
	2017	20	Perch (muscles)		(0.111-0.668) (*)	GIOŚ,2017 (unpublished)

Table 9. cont.

Sampling site	Sampling year	n	Matrix	Fat content [%]	∑PBDEs – mean (range) [ng/g ww]	Source
Transitional and coastal waters	2016	3	Perch (muscles)		(0.11-0.29) (*)	GIOŚ,2017 (unpublished)
	2017	3	Perch (muscles)		(0.091-0.259) (*)	GIOŚ,2017 (unpublished)
	2017	4	Herring (muscles)		(0.804-1.013) (*)	GIOŚ,2017 (unpublished)

(*) result above the environmental quality standard (EQS) – 0.0085 ng/g m.m. (EQS Flora and Fauna)
(**) MDL – method detection limit

4. Human and animal tissues

The samples of the human blood serum, umbilical cord blood serum and human breast milk are the useful biological matrices for the evaluation the adult organism, as well as for the evaluation of a pre- and post-labour exposure to PBDEs of the neonates (Jarczewska et al. 2006). Therefore, the concentrations of selected PBDE congeners in the blood serum and human breast milk were determined during a few studies conducted in Poland. In the years 2002-2005, 89 samples of the umbilical cord blood from the women from Warsaw and the surrounding area were collected, in order to asses the human exposure, inter alia, to PBDEs (BDE-47, 99 and 153) in the prenatal period (Hernik et al. 2013). The average age of the women was 28 years old (16-40 years old), and an average fat content in the blood was of 0.042%. In 2004, the samples of human breast milk from 22 mothers from the Wielkopolska region were collected by Jaraczewska et al. (2006). The average age of the women was 30 years (22-38), and an average fat content in the milk was 2.0%. The results are presented in Table 11.

Table 10. The mean and range of concentrations of individual congeners and the sum of PBDEs in the fish samples from Poland, ng/g (Waszak et al. 2012)

Sampling site	Sampling year	n	Matrix	Fat content [%]	Mean (range) [ng/g w.w.]							∑PBDEs – mean (range) [ng/g w.w.]
					BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	
The Vistula river estuary	2010	23	Flounder (muscles)	1.24	0.03 (0.01-0.06)	0.13 (0.06-0.26)	0.02 (0.006-0.08)	0.05 (0.007-0.15)	0.02 (0.01-0.03)	0.03 (0.01-0.05)	0.01 (0.002-0.02)	0.30 (0.11-0.52)(*)
Władysławowskie Fishery	2010	22	Flounder (muscles)	1.63	0.04 (0.01-0.08)	0.10 (0.03-0.36)	0.02 (0.006-0.06)	0.01 (0.002-0.05)	0.02 (0.01-0.05)	0.03 (0.01-0.06)	0.007 (0.002-0.02)	0.22 (0.08-0.66)(*)
Ustecko-Łebskie Fishery	2010	22	Flounder (muscles)	1.08	0.02 (0.006-0.04)	0.04 (0.01-0.07)	0.009 (0.005-0.02)	0.004 (0.002-0.01)	0.02 (0.008-0.4)	0.02 (0.008-0.3)	0.008 (0.002-0.03)	0.11 (0.08-0.66)(*)
The Vistula river estuary	2010 and 2011	51	Flounder (muscles)	2.0	0.04 (0.01-0.1)	0.2 (0.06-0.4)	0.02 (0.008-0.1)	0.04 (0.008-0.02)	0.02 (0.008-0.03)	0.03 (0.01-0.1)	0.007 (0.002-0.02)	0.3 (0.1-0.6)(*)
The Vistula river estuary	2010 and 2011	39	Flounder (liver)	6.0	0.2 (0.06-0.5)	0.4 (0.1-1.0)	0.07 (0.01-0.5)	0.2 (0.008-0.8)	0.05 (0.01-0.1)	0.06 (0.02-0.1)	<MDL (**)	1.0 (0.3-2.0)(*)
The Vistula river estuary	2010 and 2011	37	Flounder (gonads)	3.0	0.05 (0.007-0.1)	0.1 (0.02-0.2)	0.02 (0.008-0.2)	0.05 (0.008-0.2)	0.03 (0.008-0.1)	0.02 (0.007-0.1)	<MDL	0.3 (0.04-0.6)(*)

(*) result above the environmental quality standard requirements (EQS) – 0.0085 ng/g m.m. (EQS Flora and Fauna)

(**) MDL – method detection limit

Table 11. The mean concentrations (ng/g of fat) of the selected PBDE congeners in the umbilical cord blood (Hernik et al. 2013) and in the breast milk (Jaraczewska et al. 2006) of Polish women

PBDE	Umbilical cord blood (*n* = 89)			Human breast milk (*n* = 22)		
	Mean content	Standard deviation	Maximum value	Mean content	Standard deviation	Maximum value
BDE-28	-	-	-	0.07	0.08	0.33
BDE-47	1.00	1.20	5.00	1.07	1.03	5.62
BDE-99	0.60	2.25	24.60	0.47	0.13	1.43
BDE-100	-	-	-	0.15	0.13	0.55
BDE-153	0.40	0.89	3.80	0.53	0.27	1.12
BDE-183	-	-	-	0.08	0.07	0.32
∑PBDEs	-	-	-	2.5	1.7	8.4

BDE-47 was detected in the highest concentrations, both in the umbilical cord blood, and human breast milk. In the umbilical cord blood it was detected in 90% of the samples and it accounted for circa 48% of the total quantity of the studied PBDEs. In the umbilical cord blood the lowest concentrations had the congener BDE-153 (15% of the total quantity of the studied PBDEs). A correlation between the concentration of PBDEs in the umbilical cord blood and age of the women was not observed, but it was concluded that human exposure to PBDEs begins already during the foetal period. BDE-47 together with BDE-153 was present in all samples of the human breast milk. The congeners BDE-47, 153, 99, 100, 183 and 28 were circa 45%, 21%, 17%, 6%, 3% and 3% of the total quantity of all studied PBDEs, respectively.

In the years 2002-2004, the blood samples from men (age between 18.5-49.7) from Poland, Ukraine and Greenland (Innuits) were collected, in order to test the concentrations of, inter alia, selected congeners of PBDEs: BDE- 28, 47, 99, 100, 153, 154 and 183 in the blood serum (Lenters et al. 2013). The mean concentrations of the congeners together with the frequency of their occurrence are presented in Table 12.

The concentrations of PBDEs were circa 3-15 times higher in the blood serum of the men from Greenland than men from Poland and Ukraine. In all studied groups, BDE-47 and BDE-153 occurred in more than 95% samples. BDE-47, 99, 100, 153 and -154 accounted for, respectively, 40-58%, 9-23%, 7-9%, 19-40% and 1-3% of the total quantity of all PBDEs. BDE-183 was not determined in any sample.

Table 12. The frequency of occurrence (%) and mean concentrations (ng/g fat) of the selected PBDE congeners in the blood serum of men from Poland, Ukraine and Greenland (Lenters et al. 2013)

PBDE	Poland n = 100		Ukraine n = 100		Greenland n = 99	
	Frequency of occurrence %	Mean blood concentration ng/g fat	Frequency of occurrence %	Mean blood concentration ng/g fat	Frequency of occurrence %	Mean blood concentration ng/g fat
BDE-47	100	0.66	99	0.12	98	1.8
BDE-99	23	-	56	-	74	0.5
BDE-100	19	-	19	-	73	0.43
BDE-153	98	0.58	95	0.32	98	2.8
BDE-154	17	-	22	-	36	-

The use of hair as the biomarkers for the evaluation of human exposure to persistent organic pollutants has started relatively recently. Due to an easy collection, a possibility of the long-term storage and a broad range of the information about the short-term and long-term exposure, hair became commonly used study matrix for the evaluation of human exposure to a wide range of product occurring in the environment (Król et al. 2014). In 2012, the hair samples from 12 inhabitants of Tri-City were collected (women and men aged between 25-30), and the concentrations of 8 PBDE congeners – BDE-28, 47, 99, 100, 153, 154, 183, 209 were tested (Król et al. 2014). From women, hair of 10-30 cm length was collected and from men hair of 1-5 cm (illustrating 10-30 months and 1-5 months of the exposure to PBDEs, respectively. In Table 13, median, mean, and range of concentrations of the individual PBDE congeners are presented.

Table 13. The median, mean and range of the concentrations of the individual PBDE congeners in the hair of the Tri-City inhabitants, ng/g dw (Król et al. 2014)

PBDE	Median	Mean	Range
BDE-28	0.4	0.7	<MDL – 2.8
BDE-47	0.4	0.4	<MDL – 0.65
BDE-99	0.21	0.11	<MDL – 0.42
BDE-100	<MDL*	<MDL	<MDL
BDE-153	<MDL	<MDL	<MDL
BDE-154	<MDL	<MDL	<MDL
BDE-183	<MDL	3.8	3.1-4.6
BDE-209	9.5	12	5.5-25

*MDL – *method detection limit*

BDE-209 was detected in the highest concentrations and it accounted for almost 70% of the total amount of all PBDEs. BDE-183, 28, 47 and 99 accounted for ca. 23%, 4%, 2.1% and 0.8% of the total amount of PBDEs, respectively. The content of BDE-100 and BDE-153 was below the method detection limit. The high content of the congener BDE-209, in relation to the other studied congeners, may result from a fact, that as the main constituent of decaBDE was used in the electric and electronic devices used on the daily basis (TV sets, computers, household appliances, hairdryers, cables or wires) and decorative (curtains) or upholstery (furniture) fabrics.

The sum of the mean concentrations of the studied PBDEs in the women's hair was slightly higher than in the men's hair, but for the congener BDE-209 the result was opposite – the sum of the mean concentrations in the women's hair was of 11 ng/g dw, and in the men's hair – 18 ng/g dw. The concentrations of PBDEs in the non-dyed hair were higher than the concentrations of PBDEs in the dyed hair indicating that hair dying decreases their adsorption properties, or some congeners are subjected to the degradation due to an impact of dying.

The studies on the content of ten BDE congeners in the livers of the predatory birds (barn owl, common buzzard, common kestrel, marsh harrier and Northern goshawk) in Poland during period 2007-2008 were conducted by Czerwiński et al. (2010). The study materials were collected in Tarnowskie Góry (barn owl), Warsaw (common buzzard, common kestrel), Mikołów (common buzzard, marsh harrier) and Biała (Northern goshawk). Studied PBDE congeners were determined in all study samples, and the results were assessed as the high ones. The highest contents of PBDEs were detected in the samples of the liver of common buzzard and marsh harrier. BDE-47, 153 and 99 occurred in the highest concentrations. The maximum concentrations of the particular congeners were of, respectively:

- BDE-28 – 203.1 ng/g fat,
- BDE-47 – 1359.3 ng/g fat,
- BDE-99 – 666.7 ng/g fat,
- BDE-100 – 171.9 ng/g fat,
- BDE-153 – 1035.7 ng/g fat,
- BDE-183 – 89.3 ng/g fat.

The high results may indicate the high potential for bioaccumulation and biomagnification of the PBDEs compounds.

5. Summary

Polybrominated diphenyl ethers have never been manufactured in Poland. In spite of the bans and restrictions put on the use of pentaBDE, octaBDE and decaBDE in the commercial products, which entered into force a decade ago, these chemical compounds are determined in the environment, food and animal and human tissues in Poland. Despite the restrictions on manufacturing, distribution and use, in the following years, the products containing these compounds will end up in the waste stream (waste electrical and electronic equipment, upholstery, end-of-life vehicles, construction materials, wire and cable insulations) and will be released into various environmental matrices (air, water, soil). There, they will be a subject of the bioconcentration in the organisms and bioaccumulation and biomagnification in the food chain.

The scientific, technical, socio-economic and environmental data on PBDEs collected over the years, including the impact on the human health, resulted in the introduction of the environmental quality standards for the surface waters and flora and fauna at European Union and national levels. However, such standards are lacking for soils, food and water intended for human consumption or feeds.

Polybrominated diphenyl ethers are studied within the frames of the regular monitoring studies for a few years only and to a limited extent. Therefore, the available data is insufficient for the assessment of the current status of PBDEs contamination in Poland and for determination of the time trends for these contaminants. However, the measured levels of these compounds in food, which is one of the main sources of human exposure to PBDEs, indicate the need for further studies.

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Abstract

The study focus on the occurrence and levels of polybrominated diphenyl ethers (PBDEs) as contaminants of emerging concern in Poland. In the article, their properties, primary uses and emission sources to the environment were discussed. The review of the available studies on the PBDEs content in the samples of different matrices (groundwaters, surface waters, sediments, air and dust, food, animal and human tissues) was conducted and the results exceeding the available limit values were indicated. It enabled to evaluate the problem of the PBDEs contamination in Poland.

Keywords:
polybrominated diphenyl ethers, PBDEs, water, sediments, wastewater, sludge, air, dust, food, fish, human tissues, animal tissues

Polibromowane etery difenylowe jako nowo pojawiające się zanieczyszczenia w środowisku Polski

Streszczenie

W artykule przedstawiono dane dotyczące występowania i stężeń polibromowanych eterów difenylowych jako nowo pojawiających się zanieczyszczeń w Polsce. W artykule przedyskutowano ich właściwości, wykorzystanie oraz źródła emisji do środowiska. Przeprowadzono przegląd dostępnych badań dotyczących zawartości PBDEs w próbkach różnych matryc środowiskowych (wodach podziemnych, powierzchniowych, osadach, powietrzu i kurzu, żywności, tkanach zwierzących i ludzkich) oraz wskazano wyniki przekraczające ustalone wartości graniczne. Pozwoliło to na ocenę problemu zanieczyszczenia środowiska Polski przez PBDEs.

Słowa kluczowe:
polibromowane etery difenylowe, PBDEs, woda, osadu, ścieki, osady ściekowe, powierze, kurz, żywność, ryby, tkanki ludzkie, tkanki zwierzęce

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Applicability of Chemometric Methods for Estimating the Influence of Environmental Factors on the Water Quality on the Example of Some Lakes in Wolin National Park

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1. Introduction

Water, the one of the main elements of the natural environment, mainly surface water, is exposed to numerous contaminating. These pollution has become a growing threat to human society and natural ecosystems in the recent decades (Garizi et al. 2011, Dray & Josse 2015). Frequently, although not the most important, source of pollution of natural waters are thermal inflows and precipitations (e.g. Kulikowska-Karpińska and Kłusewicz 2009, Poleszczuk et al. 2012, Sorokovikova et al. 2015). Also occurring climate changes have certain effects and interactions. Therefore, vulnerability assessment is one of the key tools used to gain knowledge about the degree of impact of threats on aquatic ecosystems and how aquatic ecosystems deal with this threat (e.g. Zurovec et al 2017).

Understanding the phenomena (e.g. Bailey 2012) occurring in natural waters is based on the correct interpretation of analytical data obtained during the experiments. Therefore, ecologists (e.g. Dray & Josse 2015) usually collected and stored various data from multiple sampling sites. Additional information can be recorded to investigate their impact on the observed ecosystems (Dray & Josse 2015).

Multivariete stastistical analysis methods are part of chemometric procedures are methods of extracting information from chemical and biological systems by data-driven means (Wold 1995). They can summarize the main structures of a data containing the measurements of several quantitative variables. Newly detected structures can provide information previously hidden and invisible that can used to assess the quality of water through the standard procedure of prediction methodology such as neural network or fuzzy logic tool boxes (e.g. Sahooa et al. 2015).

This paper attempts to use chemometric methods (PCA, DA, CA) on data collected from the lakes Czajcze and Domysłowskie (Wolin National Park, NW Poland) in vegetation season in 2000-2013 and an attempt was made to assess the impact of selected environmental factors (water level of lakes and monthly sum of precipitation) on some hydrochemical parameters of the lakes.

2. Characteristic of investigated area

Czajcze and Domysłowskie Lake (Fig. 1) are located on the Wolin island, in the territory of Wolin National Park (WNP) in the Warnowo Protection Zone.

Both lakes belong to the type of flow lakes - they are directly fed by the waters of the Lewinska Struga stream. Along the runoff of the stream through the WNP territories, waters go by lakes: Rabiąż, Czajcze, and Domysłowskie. After passing through WPN protected areas runoff goes by further through other lakes of the Warnowsko-Kołczewski district to the Kamieński Lagoon (Wawrzyniak et al. 2012). Basic morphometry of studied lakes are presented in Table 1 after Jańczak (Jańczak 1997).

Table 1. Morphometric characteristic of studied lakes in Wolin National Park, after Jańczak (1997)

Lake Parameters	Lake	
	Czajcze	Domysłowskie
Latitude	$53^0$56.5’	$53^0$56.4’
Longitude	$14^0$34.0’	$14^0$34.6’
Surface (ha)	71.5	43.5
Max. Length (m)	1630	1140
Max. Width (m)	640	550
Length of shore-line (m)	4970	3000
Development of shore-line (m above sea leavel)	1.66	1.28
Altitude	1.3	1.3
Average depth (m)	2.9	2.1
Max. Depth (m)	4.6	3.1
Volume (thousand m3)	2073.5	913.5
Uncover factor	24.7	20.7

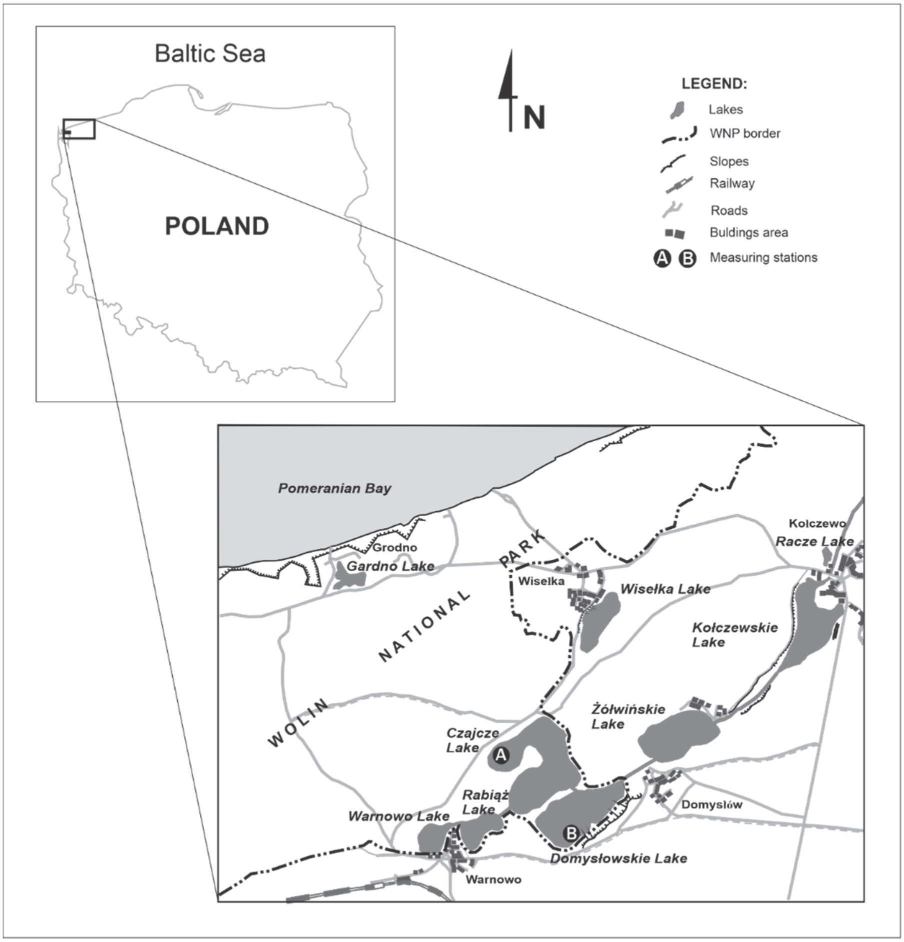


Fig. 1. Czajcze and Domysłowskie Lakes in Wolin National Park

3. Material and methods

In the period of March to October in years 2000-2013 water samples were collected from the surface layer (ca. 25 cm below the water surface) of Lakes Czajcze and Domysłowskie (Fig. 2) (APHA 1998) a frequency of once a month.

Nine selected physicochemical water quality indices were determined i.e. water temperature, pH, concentration of dissolved oxygen (DO), water saturation (WS), five day biochemical oxygen demand (BOD), chemical oxygen demand (COD), concentrations of calcium ions (Ca^{2+}), chloride ions (Cl^{-}) and total alkalinity (HCO_3^{-}). Sampling, sample processing and analytical methods were compatible with APHA (APHA 1998, 2005).

Table 2. Descriptive statistics of environmental factors and selected water quality indices of Czajcze and Domysłowskie Lakes in years 2000-2013

No	Water quality indices (units)	Descriptive statistics									
		Czajcze Lake					Domysłowskie Lake				
		min	$\bar{x}$	max	SD	CV [%]	min	$\bar{x}$	max	SD	CV [%]
Czajcze Lake											
1	Precipitation (mm)	10.70	57.26	259.00	47.19	82	10.70	57.26	259.00	47.19	82
2	Water level (cm)	73.00	100.03	123.00	13.93	14	40.00	60.53	85.00	12.68	21
3	Water temperature (°C)	2.00	13.04	23.60	6.88	53	1.00	12.42	23.10	6.87	55
4	pH (pH units)	6.86	7.68	8.64	0.39	5	5.25	7.65	8.69	0.60	8
5	DO ($mg\ O_2 \cdot dm^{-3}$)	1.80	7.78	26.70	3.93	50	1.50	8.19	19.80	3.98	49
6	Water saturation (%)	20.98	70.69	273.50	40.02	57	15.90	73.86	188.50	37.94	51
7	BOD_5 ($mg\ O_2 \cdot dm^{-3}$)	5.60	8.57	13.80	1.54	18	6.60	9.83	17.20	2.14	22
8	COD-Mn ($mg\ O_2 \cdot dm^{-3}$)	0.10	2.92	7.40	2.02	69	0.00	2.89	7.90	1.89	65
9	Ca^{2+} ($mg\ Ca \cdot dm^{-3}$)	38.00	57.06	84.00	9.52	17	22.00	50.87	72.00	13.04	26
10	HCO_3^- ($mg\ HCO_3 \cdot dm^{-3}$)	105.0	162.93	300.00	46.65	29	128.10	193.30	366.00	55.10	29

Obtained results were subjected to the statistical analysis – basic statistics (descriptive methods, Pearson correlations), time series analysis (Mann-Kendall trend test) and chemometric methods: principal component analysis (PCA), cluster analysis (CA) and discriminant analysis (DA). Before chemometric analyses normal distribution test were performed using Kolmogorov-Smirnov test (Kumarasamy et al. 2014, Thomas et al. 2015). To avoid misclassification due to wide differences in data units and dimensionality – standardization of experimental data to PCA and CA was performed. For DA raw data were used (Basilevsky 2009, Einax 1995). All statistical analyses were done using STATISTICA 13.1PL.

Water level in lakes and precipitation (as month sum) has been obtained from the Management of Wolin National Park and internet sources (http://www.wolinpn.pl/).

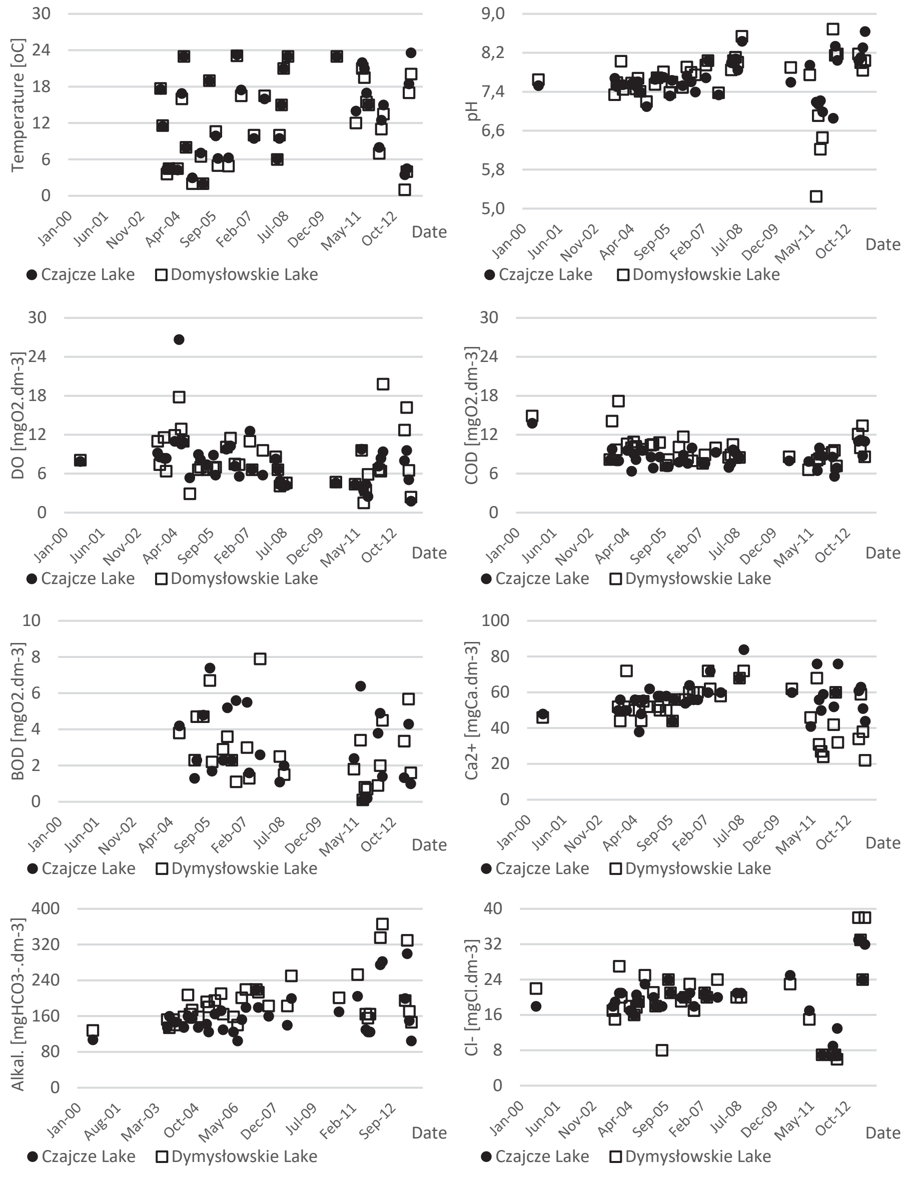


Fig. 2. Changes in concentrations of selected water quality indices for Czajcze and Domysłowskie Lakes

5. Results and discussion

Based on the analysis of collected data, a clear picture of the water quality of investigated lakes and changes of these water quality in period investigated was obtained (Fig. 2). The variability of the studied water quality indices was typical for these lakes, which is indicated by the research carried out so far (e.g. Grzegorczyk et al. 2008, Bucior & Poleszczuk 2013). Attention is drawn to the large variability of the pH parameter in Domysłowkie Lake, observed in particular in the period August-October 2011 (Fig. 2, Table 2). It could be associated with increased processes of decomposition of organic matter of an allochtonic nature, probability of origin from municipal sewage (Pitter 1999). For a more complete description of the experimental data the description statistics were determined (Table 3). The changes of water level in Czajcze Lake and Domysłowskie Lake and precipitation sum in month in period 2000-2013 was presented on Fig. 3.

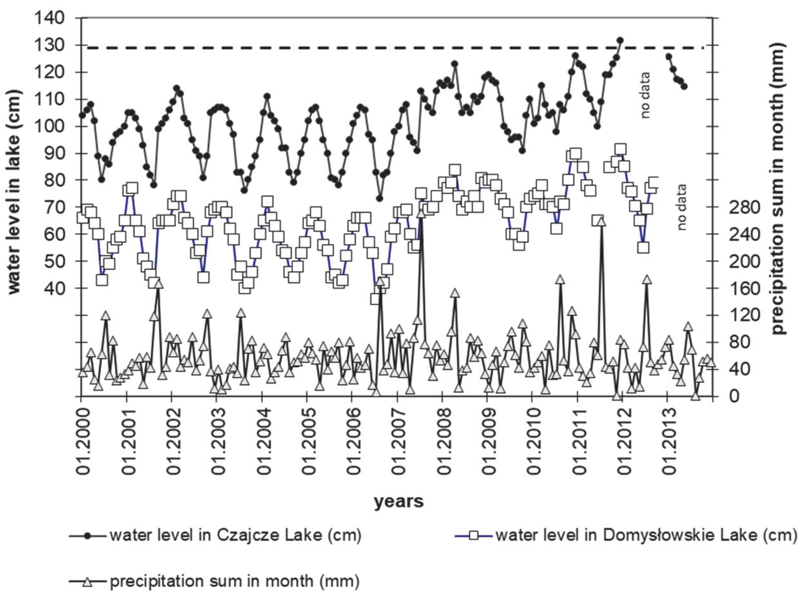


Fig. 3. Changes of water level in Czajcze and Domysłowskie Lakes on background precipitation in years 2000-2013

On the basis of experimental data – time series of selected water quality indices and environmental factor were obtained. This enabled to perform Mann-Kendall trend test to detect whether or not trends are present (Tab. 3).

Table 3. Mann-Kendall trend test for environmental factors and selected water quality indices of Czajcze and Domysłowskie Lake

Examined factor	Domysłowskie Lake			Czajcze Lake		
	Kendall's tau	p	S	Kendall's tau	p	S
Precipitation	-0.019	0.870	-0.001	-0.019	0.870	-0.001
Water level	0.312	**0.005**	**0.015**	0.427	**0.000**	**0.017**
temp.	0.106	0.345	0.001	0.105	0.351	0.001
pH	0.297	**0.007**	**0.000**	0.261	**0.019**	**0.000**
DO	-0.236	**0.035**	**-0.011**	-0.349	**0.002**	**-0.011**
Water saturation	-0.078	0.484	-0.003	-0.220	**0.048**	**-0.017**
COD	-0.211	0.059	0.000	0.018	0.879	0.000
BOD	-0.239	**0.031**	0.000	-0.165	0.139	0.000
Ca	-0.073	0.521	-0.002	0.258	**0.023**	**0.012**
Alkal.	0.330	**0.003**	**0.017**	0.188	0.093	0.001
Cl^-	0.003	0.991	0.000	0.106	0.355	0.001

For Czajcze Lake water level and alkalinity had statistically significant increasing trend when concentration of dissolved oxygen had decreasing trend. Trend for pH and BOD were also detected.

Pearson correlations (Tab. 4), shows the dependence between each investigated water quality indices in the matrix correlation (e.g. Little and Rubin 2014).

The analysis of Pearson's correlation was carried out in order to detect whether the variability of the tested water quality indices is individual or whether it depends on the runoff of the Lewińska Struga stream through the examined lakes. As Table 3 shows only BOD and COD have not shown correlation effect thus, this may indicate the effect of impurities other than by the stream, as well as another composition of microorganisms carrying out the decomposition of organic matter (Mostofa et al. 2013).

On the based the principal components analysis (PCA) eigenvalues of the matrix correlation were appointed (Table 4), which are a measure of the variability of the primary (original) data in the coordinates of the main components. On this basis, a graph was obtained (Fig. 4.) to illustrate which variables (water quality indices) show a similar pattern of changes, and which are clearly distinguished on the background of effect water level in lakes and monthly sum of precipitation.

PCA was performed on the basis of normalized results of hydro-chemical analyses. A similar approach to hydrochemical interpretation of water was presented by Siwek (Siwek et al. 2013).

Table 4. Pearson correlation of selected water quality indices between Czajcze and Domysłowkie Lakes

Water quality indices		Czajcze Lake							
		pH	DO	WS	BOD	COD	Ca^{2+}	Cl^-	HCO_3^-
Domysłowskie Lake	pH	**0.469** *	-0.001	0.046	0.080	0.093	0.278	0.182	**0.452** *
	DO	-0.357	**0.691** ***	**0.469** *	0.140	0.050	0.051	0.144	0.051
	Water saturation	-0.369	**0.575** **	**0.590** **	0.230	0.076	0.099	0.063	0.044
	BOD	-0.086	0.318	0.345	0.417	-0.062	-0.200	0.301	-0.202
	COD	0.154	0.299	0.216	-0.029	0.205	0.115	0.193	-0.077
	Ca^{2+}	0.056	0.292	0.440	0.135	-0.408	**0.601** **	-0.163	0.197
	Cl^-	**0.586** **	-0.105	-0.186	-0.253	**0.545** *	-0.097	**0.944** ***	-0.411
	HCO_3^-	0.014	0.147	0.219	0.365	-0.394	0.097	**-0.576** **	**0.956** ***

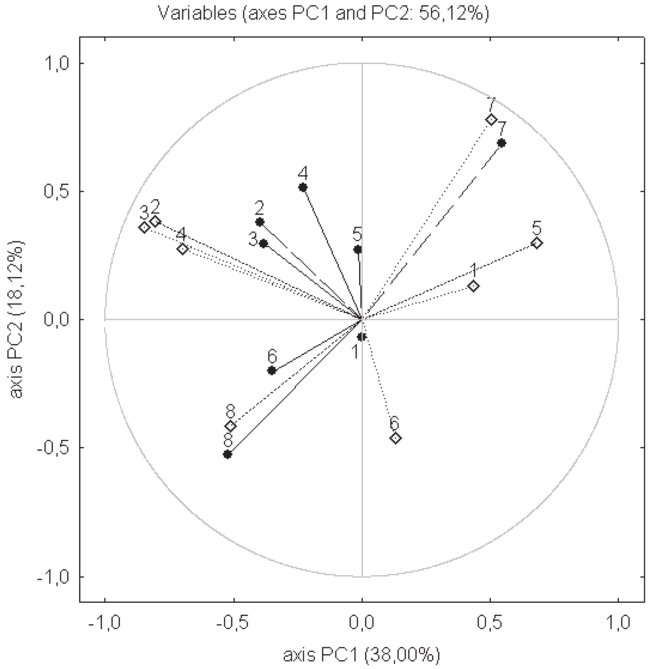
Significant level: *** $\alpha \leq 0{,}001$, ** $0{,}001 < \alpha \leq 0{,}01$, * $0{,}01 < \alpha \leq 0{,}05$

It is clearly shown in Fig. 4, which of the investigated water quality indices have a similar nature of change and which are clearly different from each other. Those of the water quality indices that had higher intrinsic values had the corresponding self-correlated vector values less correlated with the other parameters (Smoliński et al. 2016).

The analysis of the eigenvalues main components > 1 PCA shows that the plane of first and second principal component describes 56.12% of the variance of the primary (original) data (Fig. 4).

According to the above criteria, only principal components (PCs) with values higher than the values of the principal components were considered (Kowalkowski et al. 2006, Kannel et al. 2007). In literature it is assumed that if the percentage explained by the first two dimensions is 64% (e.g. Howaniec & Smoliński 2014) than it is significant statistically.

Those of the investigated parameters-water quality indices that had a higher eigenvalues, had the corresponding to that value eigenvector less correlated with other parameters (Smoliński et al. 2016). Then, using the cluster analysis, hierarchical dendrograms of the surface water quality indices of Lake Czajcze and Lake Domysłowskie were presented in Fig. 5. Water quality indices were grouped into indicators that provide the most and least information about the interactions between the examined indices and environmental factors (e.g. Vega et al. 1998, Singh et al. 2004).



Legend: ◊ Czajcze Lake; • Domysłowskie Lake
1 – pH (pH units); 2 – DO (mg O_2/dm^3); 3 – water saturation by O_2 (mg O_2/dm^3);
4 – BOD_5 (mg O_2/dm^3); 5 – COD-Mn (mg O_2/dm^3); 6 – Ca^{2+} (mg Ca/dm^3);
7 – Cl^- (mg Cl/dm^3); 8 – HCO_3^- (mg HCO_3/dm^3)

Fig. 4. PCA ordination diagrams of investigated water quality indices

Dendrograms based on CA analysis had emerged 3 groups of factors for both examined Lakes (Fig. 5). For the Czajcze Lake the first group with DO, water saturation, BOD and alkalinity as showed oxygen dependent group, second – water temperature and sum of precipitation – and third group with COD, Cl, pH, water level and Ca – as environmental dependent groups.

For Domysłowskie Lake the first group which included Ca, water level, pH and alkalinity was environmental dependent group. Second – as oxygen conduction related group with DO and WS. The third – including precipitation, temperature, Cl, COD, BOD – as environmental group with external contamination risk.

Similarities in variability in precipitation and water temperature may be related to their variability and seasonal dependence. The variability of the water level with respect to the variability of pH and Ca concentrations may provide information on the inflow of alkaline waters with a high content of bicarbonates.

Similarities in the variability of COD and Cl concentrations may indicate organic pollutants of natural origin, but in combination with BOD they reveal the effect of anthropogenic pollution (Miller et al 2016).

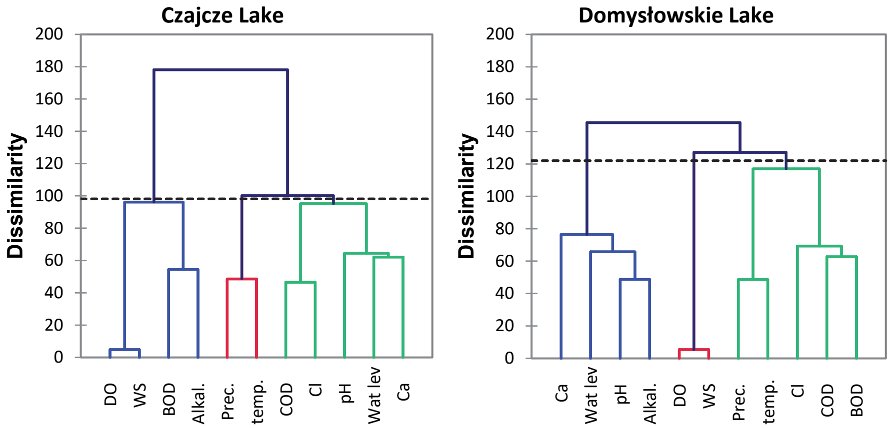


Fig. 5. Dendrograms showing variation in the variability of studied water quality indices for lakes Czajcze and Domysłowskie

The results of the CA confirms and complement the results obtained by using the PCA method (Fig. 4, Tab. 5 and Tab. 2). Similar results have been reported by Zhang et al. (2017) in his research on surface waters of the Ganjiang River (China), who used identical statistical methods for the interpretation of experimental data.

The discriminant analysis results are shown in Table 6 and in Figure 6 (Tab. 6, Fig. 6). In this report, the discriminant analysis was carried out to assess which of the variables (selected water quality indices, environmental factors) discriminated between the subjected lakes. The assumed criterion was belonging to the lake and the season of the year. The analysis showed the correctness of the assumption - the assumed grouping criteria perfectly reflect the differences between the studied seasons and lakes (Fig. 5). Analysis based on seasons shown that most discriminant power among analyzed factors had water level, water temperature, pH, DO, alkalinity and lake from which water were sampled. In the other hand analysis based on the lake criterion shown that only water level, COD and alkalinity had any discriminant power (Tab. 6). As a practical dimension of the analysis, it may be assumed to reduce the number of tests required to distinguish significant differences between the studied reservoirs in different research seasons.

Table 5. PCA results

No.	Water quality indices (units)	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8
Czajcze Lake									
1	pH (jedn. pH)	0,435	0,133	0,697	0,398	-0,349	0,052	-0,152	0,039
2	DO (mg O_2/dm^3)	-0,805	0,383	0,206	-0,305	0,075	0,191	0,008	0,167
3	Water saturation (%)	-0,846	0,360	0,254	-0,192	0,081	0,034	-0,140	-0,162
4	BOD_5 (mg O_2/dm^3)	-0,700	0,276	-0,091	0,480	0,067	-0,433	0,002	0,045
5	COD-Mn (mg O_2/dm^3)	0,682	0,300	-0,138	0,107	0,621	0,035	-0,165	0,031
6	Ca^{2+} (mg Ca/dm^{-3})	0,129	-0,461	0,689	-0,372	0,291	-0,267	0,039	0,012
7	Cl^- (mg Cl/dm^3)	0,504	0,777	0,285	0,040	0,068	0,004	0,228	-0,048
8	HCO_3^- (mg HCO_3/dm^3)	-0,512	-0,415	0,243	0,566	0,325	0,264	0,103	-0,025
Domysłowskie Lake									
1	pH (jedn. pH)	0.000	-0.070	0.570	0.467	0.260	0.203	0.147	-0.055
2	DO (mg O_2/dm^3)	-0.398	0.377	0.088	-0.378	0.424	0.202	0.084	0.131
3	Water saturation (%)	-0.379	0.295	0.050	-0.308	0.452	-0.038	-0.091	-0.261
4	BOD_5 (mg O_2/dm^3)	-0.227	0.512	-0.030	-0.032	-0.044	-0.306	0.136	-0.020
5	COD-Mn (mg O_2/dm^3)	-0.015	0.273	0.254	-0.143	0.186	0.114	-0.332	0.322
6	Ca^{2+} (mg Ca/dm^{-3})	-0.349	-0.202	0.543	-0.251	0.031	-0.293	0.046	-0.279
7	Cl^- (mg Cl/dm^3)	0.546	0.686	0.240	0.026	0.060	0.128	0.266	-0.007
8	HCO_3^- (mg HCO_3/dm^3)	-0.521	-0.527	0.205	0.539	0.145	0.237	0.046	-0.032
	Eigenvalue	3.040	1.449	1.235	0.991	0.718	0.370	0.134	0.062
	Cumulative eigenvalue	3.040	4.490	5.725	6.716	7.434	7.804	7.938	8.000
	Cumulative (%)	38.00	56.12	71.56	83.94	92.92	97.55	99.23	100.00

The cause of a completely different qualitative composition of investigated lakes waters since 2006 than in earlier years was detected in the first place, in climatic conditions. There was an attempt to link them with an increased amount of precipitation.

It has been observed, that since the second half of 2006, the amount of atmospheric precipitation on the territory of the Warnowskie lakes increased slightly. Unfortunately, it was not large enough growth of atmospheric precipitation (with a few exceptions) to give a clear explanation for this state of affairs.

Table 6. Results of discriminant analysis based on different grouping factors

Grouing factor: season				Grouing factor: lake			
Variable	Lambda	F	p-value	Variable	Lambda	F	p-value
water level	**0.932**	**3.695**	**0.049**	**water level**	**0.314**	**146.342**	**< 0.0001**
temp.	**0.602**	**21.804**	**< 0.0001**	season	0.999	0.054	0.818
pH	**0.708**	**13.609**	**< 0.0001**	temp.	0.996	0.238	0.627
DO	**0.907**	**3.369**	**0.040**	pH	0.988	0.802	0.374
WS	0.938	2.191	0.120	DO	0.998	0.148	0.702
COD	0.977	0.775	0.465	WS	0.998	0.122	0.728
BOD	0.993	0.223	0.800	**COD**	**0.919**	**5.917**	**0.018**
Ca	0.967	1.128	0.330	BOD	1.000	0.018	0.895
Alkal.	**0.903**	**3.550**	**0.034**	Ca	0.964	2.495	0.119
Cl	0.975	0.850	0.432	**Alkal.**	**0.860**	**10.894**	**0.002**
Lake	**0.998**	**3.369**	**0.039**	Cl	0.960	2.822	0.098

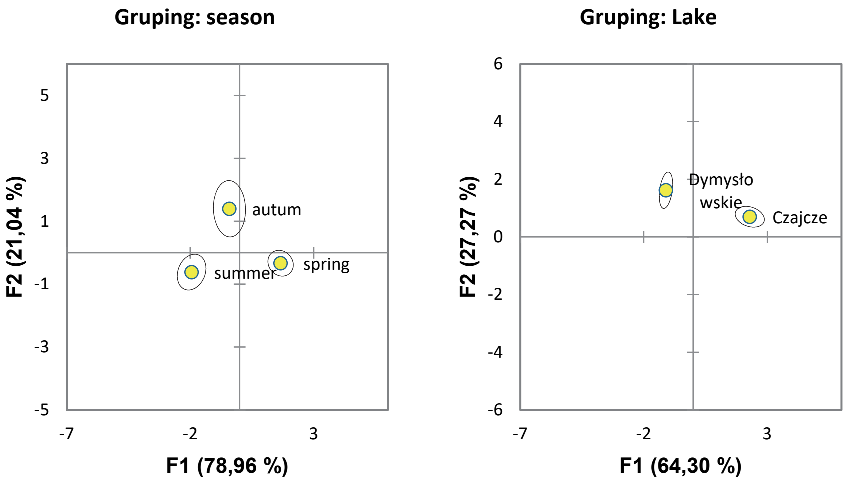


Fig. 6. Relationship between seasons and lakes based on discriminant analysis

Consider, in turn, tributary of the waters from Lake Rabiąż (Eastern Warnowo) which is connected to Lake Czajcze by clearly shore narrow channel-watercourse did not make sense, because at present the channel-watercourse connecting the two lakes is completely overgrown (Dąbrowski 2005) and has bottom sediments. So any water flow from Lake Rabiąż to Lake Czajcze is impossible. So it can be concluded that maybe the insignificant growth of atmospheric

precipitation together with other, unknown to the author of this work, factors influenced to the persistent growth of water level and the new quality composition of water in Lake Czajcze. The Domysłowskie Lake is the last from the WNP lakes, which the waters of Lewińska Stream flow down. Thus water from Czajcze Lake flows down to Domysłowskie Lake. The water of Czajcze Lake to Domysłowskie Lake "the new composition” quantitative the quality of waters. Probably only the rafting of waters from Czajcze Lake is the general cause of new quality and quantity composition of waters in Domysłowske Lake.
Those results confirms presented earlier the analytical results of experimental data analyzed by chemometric and classical statistical methods.

Methods presented in this work are well-developed and often used by researchers as statistical techniques to identify and pre-characterize the different groups of elements in water that exhibit similar seasonal variability and correlations (e.g. Giri & Singh 2014; Krishna & Mohan 2014; Bu et al. 2015, Mao et al. 2017). In addition, this study demonstrates the usefulness of chemometric techniques for a better understanding of seasonal variations (changes) in water quality (Garizi et al. 2011, Arslan 2013, Aksever & Büyükşahin 2017).

The seasonal variability of water quality indices in the surface waters of both investigated lakes undoubtedly depended on many factors (e.g. Siwek et al. 2013). Chemometric analysis indicated have shown statistically significant correlations between selected water chemistry indices and environmental factors i.e. meteorological (e.g. Rafałowska 2008) and hydrological conditions (Krajewska & Fac-Beneda 2016, Lopata et al. 2016) of studied lakes.

6. Conclusions

As is known, chemometric methods have become widely used methods for analysis and inference in the natural sciences. As classification methods, they allow getting better information about relations within dataset (Einax 1995, Kumarasamy et al. 2014). They enable the detection of specific relationships between samples and studied water quality indices, as well as their direct impact on aquatic ecosystems. They enable the determination of naturally occurring groups of factors within large dataset (Einax 1995, Kumarasamy et al. 2014, Thomas et al. 2015). At the same time, the use of these methods allows to reduce the amount of data that is needed to define environmental changes, determining the most important factors shaping its variability over the period considered (Einax 1995, Thomas et al. 2015). Based on the performed chemometric analyzes, it was shown that environmental factors can have a major impact on the shaping of lake water quality on the example of flowable reservoirs, covered by special legal protection and not under strong anthropopressure. It was shown that among the studied water quality indices only the variability of BOD and COD were not dependent on runoff between lakes, which may indicate a different nature of biodegradation of organic matter or illegal discharges of pollutants into lakes. In addition, it was noted that the variability of water quality between the studied reservoirs in long time range was mainly classified by the water level, COD and alkalinity, while analyzing the seasonal variation indices with the highest discriminant power were water level, temperature, pH, and alkalinity. That can be considered as a suggestion to reduce the number of analyzed water quality indices when it comes to show significant differences in the formation of the variability between lakes.

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Abstract

Selected water quality indices collected form Czajcze and Domysłowsie Lakes in Wolin National Park in years 2000-2013 were studied. With the chemometric procedures an attempt was made to assess the impact of selected environmental factors in particular water level of lakes and monthly sum of precipitation on hydrochemistry of the lakes. It has been demonstrated that the level of lake waters can significantly shape the quality of the examined waters on the runoff of a river through lakes.

Keywords:
PCA, DA, CA, Wolin National Park, water quality

Możliwość zastosowania metod chemometrycznych do oceny wpływu czynników środowiskowych na jakość wody na przykładzie jezior w Wolińskim Parku Narodowym

Streszczenie

Oznaczano wybrane wskaźniki jakości wody zebrane z jezior Czajcze i Domysłowskie w Wolińskim Parku Narodowym w latach 2000-2013. Przy użyciu procedur chemometrycznych podjęto próbę oceny wpływu wybranych czynników środowiskowych, w szczególności poziomu wody w jeziorach, jak i miesięcznej sumy opadów, na hydrochemię jezior. Wykazano, że poziom wód jeziornych może znacząco wpłynąć na jakość badanych wód podczas spływu rzeki przez jeziora.

Słowa kluczowe:
PCA, DA, CA, Woliński Park Narodowy, jakość wody

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Analysis of Selected Physicochemical Parameters and Degradation Process Assessment in a Two-Stage Reservoir Jezioro Kowalskie Using Field and Remote Sensing Data

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1. Introduction

Reservoirs play an important role in water management worldwide. The predicted climatic changes will lead to constantly growing importance of retention reservoirs. Water stored in the reservoirs is used for agricultural, industrial and municipal purposes. The main factor limiting the possibility of using water is its quality (Pérez-Gutiérrez et al. 2017, Sojka et al. 2017, Xu et al. 2019). However, water stored in reservoirs is very sensitive to the inflow of pollution from natural and anthropogenic sources (Nicula et al. 2017, Simeonov et al. 2003). The dynamics of the pollutants inflow also depends on natural factors, such as hydrological and meteorological conditions, landform and soil permeability (Álvarez-Cabria et al., 2016, Yu et al. 2016). Currently, studies are being carried out to assess anthropogenic impacts and their effects on water quality (Gao et al., 2016, Hillel et al., 2015, Policht-Latawiec et al. 2016). The growing population, consequent increase of human settlements, and development of agriculture and industry have changed the landscape and raised the pressures on water resources (Dąbrowska et al. 2017, Zhou et al. 2016). Particularly dangerous is the inflow of trace elements, which occurs both in water and reservoir bottom sediments (Frankowski et al. 2009, Siepak & Sojka 2017, Sojka et al. 2019, Sojka et al. 2013, Sojka et al. 2018). However, on agricultural land the inflow of nitrogen and phosphorus is the main factor influencing the eutrophication and overgrowth process (Borek 2018, Huang et al., 2015, Najar et al. 2017, Noori et al. 2018, Sojka 2009, Sojka 2012, Sojka & Murat-Błażejewska 2009, Sojka et al. 2008, Sojka et al. 2019).

Protecting the European water resources is a high priority for the European Union (EU). In 2000 the EU adopted the Water Framework Directive (WFD) (Directive 2000/60/EC). The main purposes of this directive is to establish a framework which prevents further deterioration and protects and enhances the status of aquatic ecosystems, Progressive reduction of pollution of priority substances and phase-out of priority hazardous substances in surface waters and prevention and limitation of input of pollutants in groundwaters, reversal of any significant, upward trend of pollutants in groundwaters and promoting sustainable water uses, based on a long-term protection of the water resources, compliant with other European water Directives. The WFD establishes an innovative approach for water management based on the river basin, the natural geographical and hydrological unit, and sets specific deadlines for Member States to achieve ambitious environmental objectives at water body level.

Traditional monitoring of water physicochemical status and vegetation processes (overgrowing and eutrophication) is based on collecting data from in situ measurements. Recently, remote sensing techniques became one of the most valuable in water resources monitoring. Environmental monitoring is provided on the basis of satellite data from Landsat-7, Landsat-8, MERIS/OLCI, MODIS and Sentinel-2 satellites (Dörnhöfer et al. 2018, El Saadi et al. 2014, González-Márquez et al. 2018). Remote sensing data is defined by spatial, spectral, temporal and radiometric resolution. Due to multi-spectral resolution of satellite data, imagery is used in for agricultural, forestry, natural hazards – droughts and floods (Agutu et al. 2017, Brown 2015, Chen et al. 2017). Additionally, remote sensing techniques are widely used in monitoring dynamics of degradation processes in reservoirs from space (Klein et al. 2017, Matthews et al. 2012, Martins et al. 2019, Murray et al. 2018, Pekel et al. 2016). Identification and mapping of vegetation dynamics is based on vegetation indices (VIs), which are a combination of several bands formulae, mainly representing red and infrared wavelengths (Bohn et al. 2017, Villa et al. 2014). Several indices have been proposed for vegetation dynamics monitoring, but the most often used is the Normalized Vegetation Index (NDVI), originally proposed by Rouse et al. (1974).

Over the years in Poland, single-stage reservoirs were built, then two-stage with a separate initial zone and lateral reservoirs (Sojka et al. 2017). One of the most interesting and promising approaches related to protection of water resources quality is construction of two-stage reservoirs with two separate zones – main and pre-reservoir, also called the upper zone (Bendorf & Pütz 1987a, Bendorf & Pütz 1987b, Bus & Mosiej 2013, Czamara et al. 2008, Dysarz & Wicher-Dysarz 2013, Paul 2003, Paul & Pütz 2008). The results indicated the efficacy of this solution based on two-stage construction in the aspect of water quality protection in the main part of the reservoir and sediment collection

(Dysarz & Wicher-Dysarz 2011, Jaskuła et al. 2018, Pikul & Mokwa 2008). However, there are still not many papers concerning the spatiotemporal changes of the pollution cycle and eutrophication process in two-stage reservoirs using remote sensing data.

The primary objective of the study was to analyse the spatial changes of the physicochemical parameters in the two-stage reservoir Jezioro Kowalskie. The second purpose was to assess the dynamics of the vegetation process on the basis of Sentinel-2 satellite data. The study evaluates the following research hypothesis: (1) the pre-reservoir limits the inflow of the biogenic compounds to the main reservoir and (2) the vegetation process in the pre-dam reservoir is greater than in the main reservoir.

2. Materials and methods

2.1. Sample collection and laboratory analyses

The water quality in the Jezioro Kowalskie reservoir was evaluated on the basis of 13 physichochemical parameters: electrical conductivity (EC), chlorides (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), iron (Fe^{3+}), hardness (Hard), Reaction (Reac), total alkalinity (TAl), total acidity (TAc), ammonium nitrogen ($N\text{-}NH_4$), nitrate nitrogen ($N\text{-}NO_3$), nitrite nitrogen ($N\text{-}NO_2$), phosphate (PO_4^{3-}). The physicochemical parameters were selected on the basis of the Directive of the Minister of Environment of 21sd July, 2016, on the way of classification of surface water bodies and environmental norms of the contents of priority substances. The samples were collected (depth 0.20 m from surface) from 4 points, including two points in the pre-reservoir and two points in the main part (Fig. 1). The measurements were carried out once a month in the years 2015-2016. Laboratory analyses were carried out according to the Polish regulations, presented in Table 1.

On the basis of laboratory analysis results, the minimum, average and maximum values for the pre-dam and the main reservoir were calculated. The spatial variability of the biogenic compounds was presented on the basis of the Inverse Distance Weighting (IDW) interpolation method implemented in ArcGIS 10.6.1 software.

Table 1. Methods and regulations for determining water quality parameters

Parameter	Method	Regulations
EC	conductometric	PN-EN 27888:1999P
Cl^-	argentometric	PN-ISO 9297:1994
Ca^{2+}	titrimetric	PN-C-04554-4:1999
Mg^{2+}	calculation	PN-C-04554-4:1999
Fe^{3+}	absorption spectrometry	PN-ISO 8288:2002
Hard	titrimetric	PN-C-04554-4:1999
Reac	potentiometric	PN-C-04642-7:1999P
TAl	titrimetric	PN-EN ISO 9963-1:2001
TAc	titrimetric	PN-EN ISO 9963-1:2001
$N\text{-}NH_4$	spectrophotometric	PN-ISO 7150-1:2002
$N\text{-}NO_3$	spectrophotometric	PN-C-04576-08:1982
$N\text{-}NO_2$	spectrophotometric	PN-EN 26777:1999
PO_4^{3-}	spectrophotometric	PN-EN ISO 6878:2006

2.2. Satellite imagery

The Sentinel-2 satellite is part of the Copernicus Earth Observation mission. Technical supervision is carried out by the European Space Agency (ESA). It works as a constellation of two satellites; launch of the first satellite (Sentinel-2A) occurred on June 23, 2015, while the second (Sentinel-2B) was launched on March 7, 2017. The main instrument of the satellite, Multi-Spectral Imager (MSI), features 13 spectral bands from the visible and near-infrared (VNIR) to the short-wave infrared (SWIR) in 10, 20 and 60 m spatial resolution with a 5-day repeat cycle.

The Sentinel-2 imagery was acquired from the Sentinel Hub website (https://sentinel-hub.com/). Remote sensing data were selected for the years 2015-2016, which corresponded to the years where field measurements were undertaken. Additionally, satellite data from 2017 and 2018 were used to assess the recent state of the vegetation process. Finally, for the analysis four Sentinel-2, level 1C images acquired on 20th August 2015 (10:00:15 UTC), 3rd September 2016 (10:05:58 UTC), 29th August 2017 (10:00:26 UTC) and 29th August 2018 (10:00:17 UTC) in a tile of 100 km^2 were used. Level 1C products are radiometrically and geometrically corrected (Top of Atmosphere – TOA), including orthorectification and spatial assignment to a global reference system (WGS84, EPSG:4326). In the first step, the satellite composites were created and resampled to 10 m spatial resolution. To scale the Sentinel-2 composites to surface reflectance, the Dark Object Subtraction (DOS) method was carried out (Chavez, 1996) in the Semi-Automatic Classification Plugin. In the second step, vegetation processes in the reservoir were analysed on the basis of the NDVI spectral index. The NDVI is the most recognized and frequently used spectral index for regional and global vegetation assessments. It was first proposed by Rouse et al. (1974). In recent years many researchers have used the NDVI to detect vegetation for environmental purposes (Dlamini et al. 2016, Gao et al. 2012, Zhengjun et al. 2008). The NDVI is expressed as a combination of near-infrared NIR (ρ_{NIR}) and red (ρ_R) bands in the following equation:

$$\mathrm{NDVI} = \frac{\rho_{\mathrm{NIR}} - \rho_{\mathrm{R}}}{\rho_{\mathrm{NIR}} + \rho_{\mathrm{R}}} \tag{1}$$

The values of the NDVI vary from -1 to +1, depending on land cover. Low values (minus or approaching zero) represent water and soil surfaces, while higher values represent vegetation – in an aquatic environment there are seasonal algal blooms and overgrowth areas. In the second step, to assess spatio-temporal changes of the vegetation process, values of the NDVI for each satellite image were extracted to point data for the area of the main and pre-dam reservoir.

The analysis of differences in the values of water quality parameters and NDVI in the pre-dam and the main reservoir was performed using the non-parametric Mann-Whitney U test. The analysis was performed at a confidence level of 0.05 and 0.10.

3. Study area

The Jezioro Kowalskie reservoir (52°28’39.781” N, 17°9’49.022” E) is located on the Główna river in the central part of the Warta river basin (Fig. 1). The Jezioro Kowalskie was built in 1984 as a two-stage reservoir. The pre- dam includes a small sluice and is splitting object into the main and pre-dam reservoir. The area of the reservoir in the normal condition is 203 ha, where the main and pre-reservoir parts are 162.9 ha and 40.4 ha, respectively. The total capacity is $6.58 \cdot 10^6$ m^3, where capacity of the main and pre-reservoir is $5.99 \cdot 10^6$ m^3 and $0.59 \cdot 10^6$ m^3, respectively. The total length of the Jezioro Kowalskie reservoir is 7.1 km, and mean width is 0.27 km. The depth varies from 1.5 m in the pre-reservoir to 6.5 m near the dam in the main part of the reservoir. The mean depth of the pre-reservoir is 1.3 m while for the main part it is 3.1 m. The Jezioro Kowalskie reservoir is multi-purpose and works in the annual cycle.

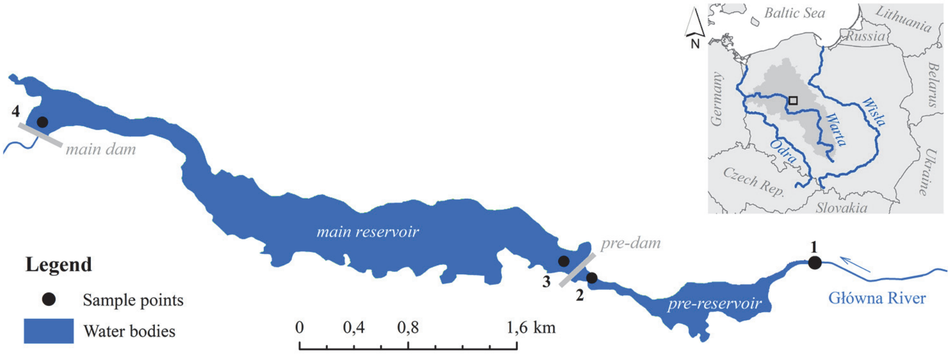

Fig. 1. Study site location

The total area of the Jezioro Kowalskie catchment is 189.35 km^2. Surface water bodies in the Główna River basin were identified as PLRW600025185925. It has lowland character, the absolute altitudes of the terrain varying from 85.52 to 135.02 m a.s.l. with a mean value of 110.27 m a.s.l. The area is mainly covered by arable lands, occupying 67.74% of the total basin area. Other forms of land use are forests (21.46%), artificial surfaces (5.41%) water bodies (3.62%) and pastures (1.77%). In 2016 the percentage of inhabitants who have access to the water supply system varied from 93.8% to 99.9%. The percentage of inhabitants able to use the sanitary sewage system varied from 41.6% to 94.4%.

4. Results and discussion

The values of the water quality parameters in the years 2015-2016 are presented in Table 2.

In the case of the most analyzed parameters, the lowest values occur in the main part of the reservoir, while the highest occur in the pre-dam reservoir. Mean values of the parameters are higher in the pre-dam reservoir, excluding Mg^{2+} and pH. The inflow of biogenic compounds (nitrogen and phosphorus) is the major factor of eutrophication. Jezioro Kowalskie is located in the Pobiedziska commune, which is characterized by the lowest percentage of inhabitants able to use the sanitary and water supply system. Additionally, next to the shoreline there are located leisure areas, where pollutions might flow directly into the reservoir. In Jezioro Kowalskie reservoir the concentration of nitrate nitrogen varies from 0.010 mg·dm^{-3} in the pre-dam reservoir to 5.20 mg·dm^{-3} in the main reservoir. The mean value in the main reservoir is 2.05, while in the upper zone it is 1.45 mg·dm^{-3}.

Table 2. Values of the water quality parameters in the Jezioro Kowalskie reservoir in the years 2015-2016

Parameter	Overall (n=76)	Main part (n=38)	Pre-dam part (n=38)	Statistically significant differences
EC uS·cm^{-1}	421 - 1170 647.94	436 – 840 597.22	421 – 1170 698.66	*
Cl^- mg·dm^{-3}	15 – 105 41.40	15 – 80 40.27	20 – 105 42.53	
Ca^{2+} mg·dm^{-3}	52 – 140 97.36	60 – 132 85.45	52 – 140 109.26	*
Mg^{2+} mg·dm^{-3}	4.86 – 24.32 15.29	4.86 – 24.32 15.48	4.86 – 24.32 15.10	
Fe^{3+} mg·dm^{-3}	0.025 – 0.54 0.120	0.025 – 0.18 0.09	0.025 – 0.54 0.15	*
Hard mVal·dm^{-3}	4.20 – 8.00 6.15	4.20 – 7.40 5.54	5.00 – 8.00 6.76	*
Reac pH	8.02 – 9.98 8.83	8.02 – 9.98 8.88	8.07 – 9.51 8.79	*
TAl mVal·dm^{-3}	2.00 – 6.40 4.32	2.00 – 5.20 3.75	2.60 – 6.40 4.89	*
TAc mVal·dm^{-3}	0.02 – 0.40 0.14	0.02 – 0.40 0.13	0.02 – 0.40 0.15	
$N\text{-}NH_4$ mg·dm^{-3}	0.005 – 3.77 0.51	0.005 – 1.19 0.27	0.005 – 3.77 0.76	
$N\text{-}NO_3$ mg·dm^{-3}	0.01 – 5.20 1.75	0.01 – 3.90 1.45	0.10 – 5.20 2.05	
$N\text{-}NO_2$ mg·dm^{-3}	0.01 – 0.44 0.06	0.01 – 0.35 0.05	0.01 – 0.44 0.07	
PO_4^{3-} mg·dm^{-3}	0.025 – 3.37 0.34	0.025 – 0.74 0.23	0.025 – 3.37 0.44	+

Upper values: minimum-maximum.
Lower values: mean.
Statistically significant differences at the level of 0.05 - * and 0.10 - +

Concentration of nitrite nitrogen is in range 0.01-0.44 mg·dm^{-3} while the average values were similar and were 0.05 and 0.07 mg·dm^{-3} respectively. Average ammonium nitrogen concentrations in the pre-dam reservoir were 0.76 mg·dm^{-3} and in the main reservoir 0.27 mg·dm^{-3}. Concentrations of phosphate are in the range 0.025-3.37 mg·dm^{-3}. Mean concentration in the main part is 0.23 mg·dm^{-3}, while in the upper zone it is 0.44 mg·dm^{-3}. The average value of the NO_3^- to PO_4^{3-} ratio in the initial tank was about 87 mg·dm^{-3} and in the main tank about 61 mg·dm^{-3}. Such values suggest the dominant role of green algae and to a more limited extent blue-green algae.

The statistical analysis performed by means of the Mann-Whitney U test shows the statistically significant differences at the level of 0.05 between concentration of EC, Ca^{2+}, Fe^{3+}, Reac, Hard and TAl in the pre- and main reservoir (Table 2). Moreover, the differences between concentrations of PO_4^{3-} in the reservoirs were statistically significant at the level of 0.10.

Spatial changes of the biogenic compounds' mean concentrations are presented in Figure 2. The highest values occur in the inflow of Główna river to Jezioro Kowalskie reservoir, except nitrite nitrogen. For this parameter, the highest concentration occurs near the dam in the pre-reservoir. High concentrations were also observed in main part of the reservoir, especially near the pre-dam. Spatial analysis of the parameters shows that the main reservoir is characterized by lower concentrations compared to the pre-reservoir. The lowest values of all biogenic compounds were observed near the outflow of the Jezioro Kowalskie reservoir.

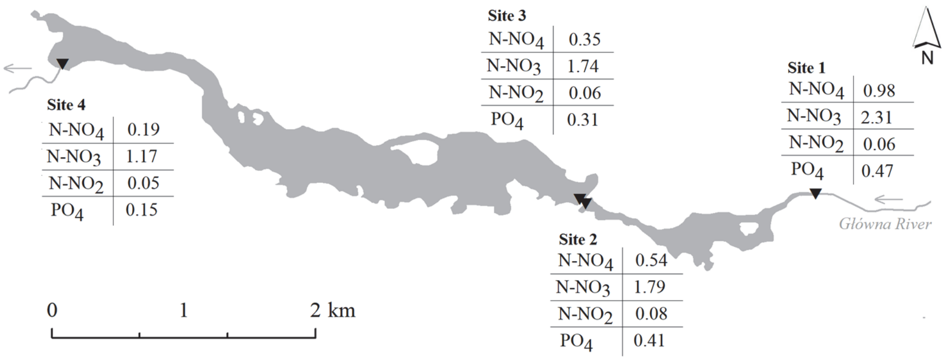

Fig. 2. Spatial changes of biogenic compounds in the Jezioro Kowalskie reservoir (mg·dm^{-3})

The main problem in the Jezioro Kowalskie reservoir is connected with the high inflow of nitrogen and phosphorus compounds, which limits the vegetation processes (Sojka et al. 2016). Figure 3 presents spatiotemporal changes of the NDVI index in August in the years 2015, 2017 and 2018 and September 2016.

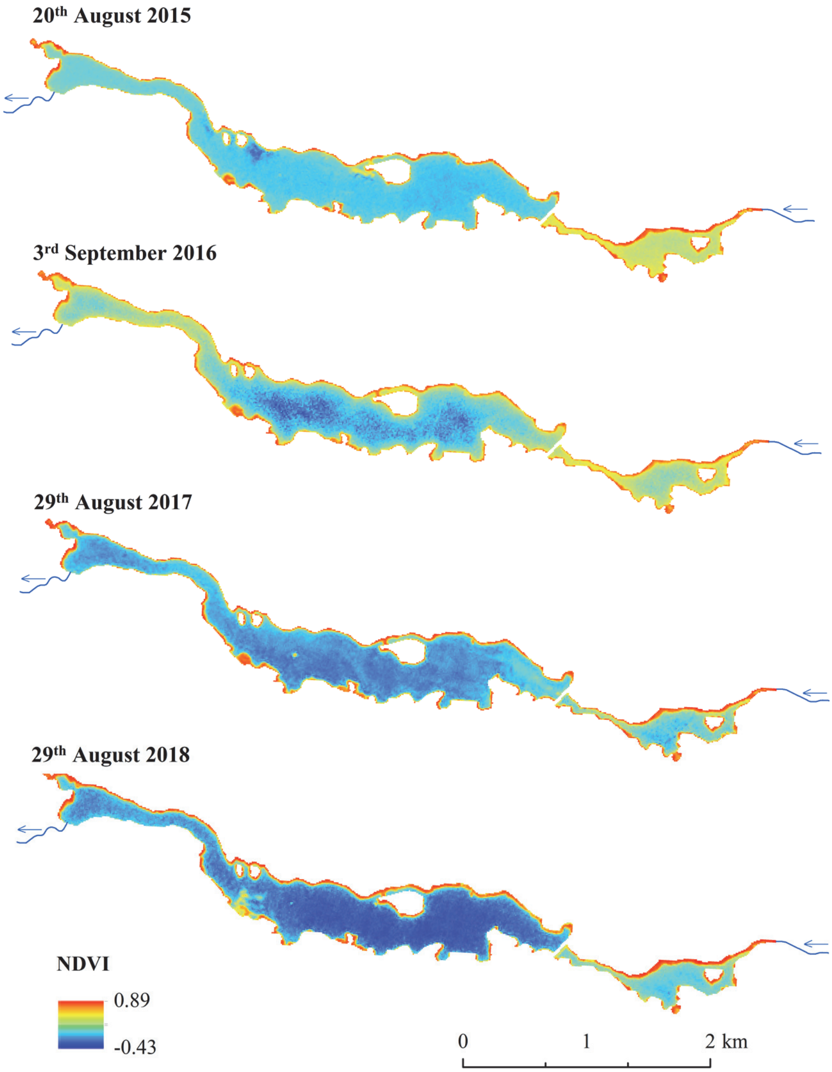

Fig. 3. Spatiotemporal changes of NDVI in the Jezioro Kowalskie reservoir

For the analysed period, the highest values of the NDVI were observed near the banks of the Jezioro Kowalskie reservoir, which is connected with overgrowth areas. In 2015 and 2016 the NDVI values were higher in the whole reservoir area compared to 2017 and 2018. Regardless of the analyzed years, the pre-reservoir was characterized by higher NDVI than the main part.

The NDVI in the Jezioro Kowalskie reservoir in August 2015 varies from -0.28 to 0.86 with the median value of 0.35 (Fig. 4). The lowest NDVI was observed in the main part, while the highest values were comparable between parts of the Radzyny reservoir. The difference between median values in the main and pre-dam reservoir is 0.37. During the first days of September 2016 the values of the NDVI were in range of -0.41 to 0.85. The limit values of the NDVI were observed in the main reservoir. The median value in the pre-reservoir was 0.30, while in the main part it was 0.05. In August 2017, the values of NDVI varied from -0.23 to 0.88. The difference between median values in pre-dam and main reservoir was 0.34. The lowest NDVI was observed in the main part, while the highest values were comparable between parts of the Jezioro Kowalskie reservoir. In 2018, the values of the NDVI were in the range -0.43 to 0.89. The median value in the pre-reservoir was 0.15, while in the main part it was -0.20. The Mann-Whitney U test shows that the NDVI value in the pre-dam reservoir was greater than in the main reservoir in all years. The differences were statistically significant at the level of 0.05.

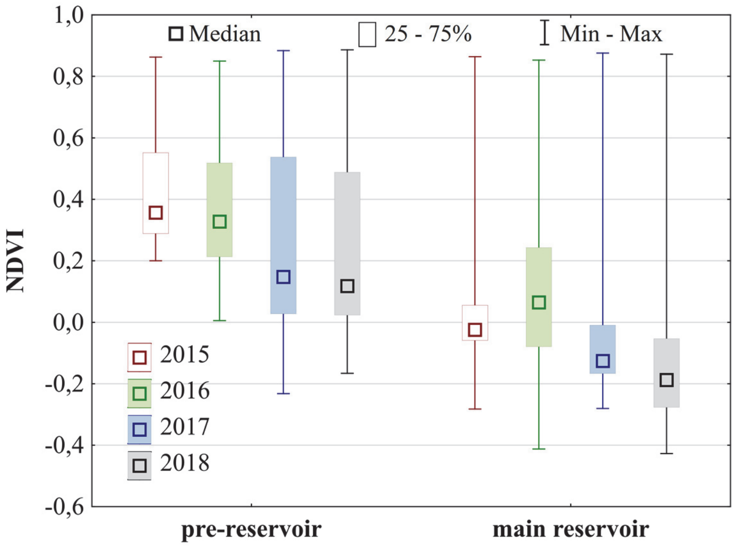

Fig. 4. Values of NDVI in the Jezioro Kowalskie reservoir in the years 2015-2018

The highest biogenic concentrations and NDVI values occurring in the pre-reservoir indicate that the two-stage construction of the reservoir is an effective solution in protection of water quality. The results presented in this paper confirmed the results obtained in the previous studies which indicated that the pre-reservoir protects water resources in the main part of the reservoir, including degradation processes – algae blooms, eutrophication and sedimenta-tion (Dąbrowska et al. 2016, Dysarz & Wicher-Dysarz 2011, Jaskuła et al. 2018, Jaskuła et al. 2019, Mazur 2013, Pikul & Mokwa 2008). The vegetation process may result from supply of biogenic compounds, hydrometeorological conditions as well as water management in reservoir (Dysarz et al. 2006, Nicula et al. 2017). The combination of these factors determines the spatio-temporal changes of the eutrophication process in the reservoir.

5. Conclusion

On the basis of the obtained results, the following conclusions can be made:

1. The results of this study confirm the efficacy of the solution based on two-stage construction in protection of quality of water stored in the main reservoir.
2. The pre-dam reservoir mainly reduces the inflow to the main reservoir of Ca^{2+}, Fe^{3+} and PO_4^{3-}. Also in the main reservoir there were lower values of EC, reaction, hardness and total alkalinity.
3. Higher values of the NDVI were observed in the pre-dam reservoir, which indicates greater degradation in relation to the main reservoir.
4. The highest values of the NDVI observed near the reservoir shoreline are related to overgrowth process of emergent plants.
5. Sentinel-2 satellite imagery allow to assess the spatial variability of the reservoir degradation process. Due to its spatial resolution, the Sentinel-2 satellite should not be used to assess vegetation areas whose width is less than 10 m.
6. Open-access satellite data are more effective source to water monitoring in terms of time and space than traditional in situ measurements.

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Abstract

The paper presents the results of changes of water quality parameters in a two-stage reservoir, observed in the period 2015-2016. The primary objective of the study was to analyse the spatial changes of the water quality parameters in the two-stage reservoir Jezioro Kowalskie. The second purpose was to assess the dynamics of the vegetation process on the basis of Sentinel-2 satellite data. The study adopts the following research hypotheses: 1) the pre-reservoir limits the inflow of the biogenic compounds to the main reservoir, 2) the vegetation process in the pre-dam reservoir is greater than in the main reservoir.

The Jezioro Kowalskie reservoir has two-stage construction – the main and the pre-dam zone. The main role of the pre-dam reservoir is to store sediments and water pollutants.

In this study, 13 water quality parameters were analyzed: electrical conductivity (EC), chlorides (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), iron (Fe^{3+}), hardness (Hard), pH, total alkalinity (TAl), total acidity (TAc), ammonium nitrogen ($N\text{-}NH_4$), nitrate nitrogen ($N\text{-}NO_3$), nitrite nitrogen ($N\text{-}NO_2$), phosphate (PO_4^{3-}). The samples were collected from 4 points, including two points in the pre-reservoir and two points in the main part. In order to determine parts of the reservoir which are exposed to the degradation process, the spatio-temporal changes were analyzed on the basis of the Normalized Difference Vegetation Index (NDVI) spectral index. The analyses showed that the NDVI values in the period 2015-2018 in the pre-dam reservoir were higher than those recorded in the main reservoir. In the main reservoir, NDVI values were lower and characterized by similar variability.

The study confirms the research hypothesis: the pre-reservoir protects the main part, limiting inflow of biogenic compounds which have an impact on the degradation process (overgrowth, eutrophication). The obtained results confirm that Sentinel-2 satellite imagery allows analysis of the vegetation process in retention reservoirs in terms of time and space.

Keywords:
water quality, biogenic compounds, reservoir, NDVI, Sentinel-2

Analiza wybranych parametrów fizykochemicznych i procesu degradacji w dwustopniowym zbiorniku Jezioro Kowalskie na podstawie pomiarów in-situ i danych satelitarnych

Streszczenie

W pracy przedstawiono zmiany wartości parametrów jakości wody w dwustopniowym zbiorniku retencyjnym w latach 2015-2016. Podstawowym celem pracy była analiza przestrzennych zmian jakości wody zachodzących w zbiorniku Jezioro Kowalskie. Drugim celem była ocena dynamiki degradacji zbiornika (zarastania, eutrofizacji) na podstawie danych satelitarnych Sentinel-2. W pracy przedstawiono hipotezy badawcze: 1) zbiornik wstępny ogranicza dopływ zanieczyszczeń do głównej części, skupiając związki biogenne we wstępnej części, 2) procesy degradacji (zakwitów, eutrofizacji) występują w zbiorniku wstępnym.

Zbiornik Jezioro Kowalskie ma dwustopniową konstrukcję, wydzielono w nim część główną oraz wstępną. Do podstawowych zadań zbiornika wstępnego należy ograniczenie dopływu związków biogennych oraz sedymentacji do części głównej.

Przeanalizowano wartości 13 parametrów jakości wody: przewodność elektr. (EC), chlorki (Cl^-), wapń (Ca^{2+}), magnez (Mg^{2+}), żelazo (Fe^{3+}), twardość og. (Hard), pH, zasadowość og. (TAl), kwasowość og. (TAc), azot amonowy (N-NH_4), azot azotanowy (N-NO_3), azot azotynowy (N-NO_2), fosforany (PO_4^{3-}). Próbki pobierane były łącznie z 4 punktów pomiarowo-kontrolnych, dwa z nich zlokalizowane były w części wstępnej oraz dwa w zbiorniku głównym. Woda dopływająca do zbiornika retencyjnego charakteryzowała się wysokimi stężeniami związków biogennych. W celu dokładnego określenia części zbiornika narażonych na proces degradacji, do analizy zachodzących zmian wykorzystano indeks NDVI obliczony na podstawie zdjęć satelitarnych Sentinel-2. Przeprowadzone analizy wykazały, że wartości wskaźnika NDVI w miesiącach wegetacyjnych 2015-2018 były wyższe w zbiorniku wstępnym. Część główna zbiornika charakteryzowała się niższymi wartościami i większą stabilnością wskaźnika NDVI.

Na podstawie uzyskanych wyników, potwierdzono, że część wstępna pełni funkcję ochronną zbiornika głównego, m.in. ogranicza dopływ związków biogennych, powodujących procesy degradacji (zarastania, eutrofizacji). Uzyskane wyniki potwierdzają możliwość zastosowania danych satelitarnych Sentinel-2 do analizy procesu wegetacji w zbiornikach retencyjnych w ujęciu czasowym i przestrzennym.

Słowa kluczowe:
jakość wody, związki biogenne, zbiornik retencyjny, NDVI, Sentinel-2

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Disintegrating Influence of Sonication on the Excess Sludge Liquification and their Microbiological Indicator

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1. Introduction

Sewage sludge is created at various stages of wastewater treatment as a result of physical, chemical and biological processes. Due to the sanitary hazard and high degree of hydration, they are treated as hazardous waste and require proper management (Wolski, & Małkowski 2014, Wolski 2016, Podedworna & Umiejewska 2008). The variety of chemical composition and different properties of sewage sludge impose the necessity of applying various technological solutions during the disposal and processing of sewage sludge (Pietraszek & Podedworna 1990, Wolski, & Wolny 2011). As part of the activated sludge stream, excess sludge is directed in the technological process of wastewater treatment to separate closed fermentation chambers. This sludge is formed as a result of the growth of microorganisms during the removal of dissolved and colloidal pollutants from sewage. Depending on the applied treatment methods, excess sludge contain about 97% of water and from 30% to 50% of mineral substances. In addition, they are characterized by a large number of facultative bacteria, which affects their low susceptibility to degradation under anaerobic conditions. The application of a properly selected disintegration technique before the stabilization process contributes to the destruction of the structure of sludge, the breakdown of cell membranes of microorganisms and the release of intracellular substances into the supernatant liquid, and thus the initiation and increase of biological degradation (Podedworna & Umiejewska 2008, Zhang et al. 2007) As a result of this process, the organic components of the cell become potentially available as a substrate of the living heterotrophic mass. The released organic compounds contained in the sludge are easier to undergo anaerobic stabilization processes. This has the effect of shortening the hydrolytic phase of methane fermentation and accelerating and intensifying the processes taking place in subsequent phases.

The introduction of disintegration techniques also causes an increase in the degree of dry organic matter reduction, and also influences the intensification of biogas production during methane fermentation (Wójtowicz 2006, Bień 2005). According to Penaud and others (Penaud 1999) in the case of disintegration conditions considered optimal, the highest percentage of soluble chemical oxygen demand (SCOD) in total chemical oxygen demand (TCOD) of the substrate should be obtained. However, complex hard-decomposition compounds may form under certain conditions. Consequently, the optimal conditions determined to obtain the SCOD maximum may be different from those that are appropriate to achieve the highest biodegradability of the substrate.

The criterion for the effectiveness of disintegration is the increase in the content of organic matter in the supernatant liquid expressed in the value of SCOD and the disintegration degree of sludge. The use of disintegration methods prior to the methane fermentation process contributes to an increase in the amount of hydrolysates rich in soluble fractions of chemical oxygen demand (Zielewicz-Madej, 2001, Bień & Szparkowska 2004). The use of ultrasonic technology in anaerobic stabilization of sewage sludge leads to the improvement of the sedimentation properties of the digested sludge, increased enzyme activity, metabolic intensification, increased organic matter decomposition and biogas production (Wolny & Kamizela 2003). The use of ultrasonic techniques in the sewage economy requires the optimization of operational parameters such as: frequency, vibration amplitude, wave intensity, input energy and duration of impact (Zielewicz et al. 2008, Kidak et al. 2009, Nanzai et al. 2009). According to Tiehm et al. (Tiehm et al. 1997), the use of ultrasound at 31 kHz prior to the stabilization process contributes to shortening the duration of methane fermentation and leads to increased biogas production intensity. Conducting research in the frequency range of 10-30 kHz and with increasing ultrasound power values, the highest degree of disintegration was recorded at 30 kHz (Zielewicz- Madej & Fukas – Płonka 2002). The most intensive process took place with low frequency values of around 20 kHz. Gonze et al. (Gonze et al. 2003) showed that the operation of ultrasonic field with low frequency and high intensity ultrasonic field affects the effective breakdown of sludge particles and degradation of microbial cells, leading to a clear modification of the structure of sludge. In the initial stage of sonication, no significant changes are observed in the structure of sludge. The short duration of ultrasound action causes scattering of the sludge flocs, without disturbing the cell structure. As a result of the longer action of the ultrasonic field, permanent damage to the cells of microorganisms contained in the sludge occurs. Cichowicz (Cichowicz 2007) reports that sowing of sewage sludge in a short time, a high-power ultrasonic field, results in higher efficiency of sludge biodegradation than the use of ultrasonic field of low power and long duration of ultrasound.

The phenomenon of ultrasonic cavitation is also used for hygienization of sewage sludge.

The aim of the study was to determine the disintegrating influence of sonication on the excess sludge liquification expressed as the increase in the soluble chemical oxygen demand (SCOD). value of the modified excess sludge as well as estimating of the microbiological indicators of sonicated sludge.

2. Experimental part

2.1. Substrate

Excess sludge, sampled from the municipal wastewater treatment plant with a capacity of 90 000 m^3d^{-1}, was the main substrate of the research. The characteristics of selected physico-chemical parameters of excess sludge are presented in Table 1.

Table1. Selected physico-chemical parameters of excess sludge

Indicators	Excess sludge
Total Solids (TS)	11.29 g L^{-1}
Volatile Suspended Solids (VSS)	8.02 g L^{-1}
Soluble Chemical Oxygen Demand (SCOD)	132 mg O_2 L^{-1}

Microbiological analyzes performed for non-modified and disintegrated sludge concerned the number of mesophilic and psychrophilic microorganisms, *Salmonella spp* bacteria and *Escherichia coli* type bacteria, which is a pathogenic species. The characteristics of selected groups of microorganisms of excess sludge are presented in Table 2.

Table 2. Markings of selected groups of excess sludge microorganisms

Microbiological indicators	Excess sludge
Mesophilic microorganisms, JTK/cm^3	$30 \cdot 10^4$
Psychrophilic microorganisms, JTK/cm^3	$80 \cdot 10^4$
Type of bacteria *Escherichia coli*, count	10^{-5}
Salmonella spp	*it was not isolated*

2.2. Methodology

During the first stage of research, the process of excess sludge disintegration was carried out. The most favorable conditions for the sludge sonication were determined, i.e. disintegration time and the value of ultrasonic field vibration amplitude. While in the next stage the process of conventional methane fermentation and methane fermentation of sludge modified by ultrasonic field was conducted (Fig. 1).

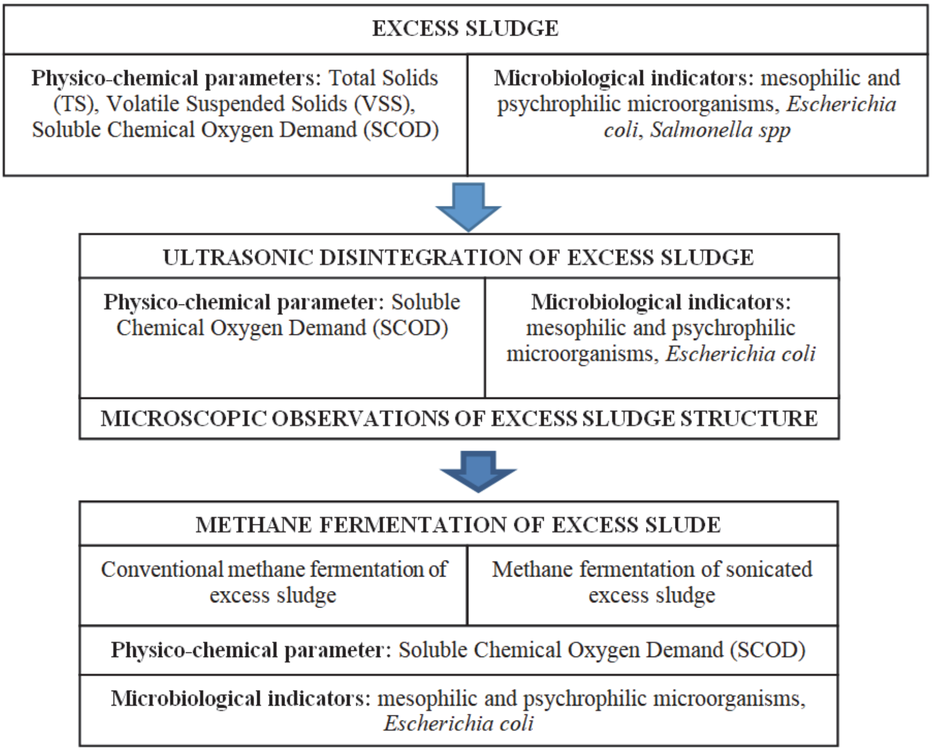


Fig. 1. Diagram showing the stages of research

In the study the following physico-chemical parameters were made: the volatile suspended solids (VSS) (PN-EN-12879) and soluble chemical oxygen demand (SCOD) by dichromate method, using a colorimetric spectrophotometer Hach Dr 400 (PN-EN ISO 7027).

In the case of microbiological analysis a solid medium called nutrient agar was used for the cultivation of mesophilic and psychrophilic microorganisms. For the *Escherichia coli* culture, however, the Eijkmana liquid medium was used and, in order to confirm the presence of microorganisms, the culture was performed on a permanent Endo medium. Salmonella - Shigella (SS) agar medium was used to detect *Salmonella spp*. Before starting the tests, a series of dilutions from 10^{-8} to 10^{-1} were prepared from the collected sludge samples.

The process of disintegration of excess sludge with the ultrasonic field was carried out with the use of a disintegrator type UD-20 produced by "Techpan" with a vibration frequency of 22 kHz and a maximum output power of 180 W. The energy of electric vibrations using a transducer was transformed in the system into the energy of mechanical vibrations, and then, via the sonotrode, transferred to the tested system in the form of an acoustic wave. Disintegration was carried out in glass vessels in a non-flow system. The active volume of the excess sludge was 0.5 L. The sonotrode in the tested sludge was placed at a depth of 2 cm from the bottom of the vessel. Investigations of disintegration of excess sludge with ultrasonic field were carried out in the time interval 30-360 s, for amplitudes of ultrasonic field vibrations in the range of 8-16 μm and ultrasonic wave intensity in the range of 3-10 Wcm^{-2}.

Microscopic observations of excess sludge structures were carried out using the Olympus BX 41 microscope with instrumentation for taking pictures. The micrographs were taken using a 500-fold magnification, and the assessment of excess sludge structure changes was performed by a visual method taking into account selected morphological features of the sludge.

Periodic methane fermentation of excess sludge was carried out for 10 days in specially constructed methane fermentation systems, which are models of fermentation chambers with an active volume of 0.5 L. The sludge was stabilized at a constant temperature of 37°C, characteristic of conducting the process in a mesophilic temperature regime. Fermentation chamber models were placed in a laboratory incubator with constant shaking. In the case of methane fermentation processes, in order to initiate the process, excessive sludge was mixed with digested sludge in a volume ratio of 10 to 1, respectively. Volatile Suspended Solids (VSS) content of the sludge mixture was 8.79±0,18 g L^{-1}.

Anaerobic stabilization was carried out on:

- untreated excess sludge,
- excess sludge disintegrated by an ultrasonic field with an vibration amplitude of 16 μm and a sonication time of 300 s.

3. Results and discussion

3.1. Impact of the ultrasonic field on the changes of soluble chemical oxygen demand

Research on the modification of excess sludge by ultrasonic field was carried out in order to determine the degree of their susceptibility to biodegradation by determining the increase in the concentration of organic substances in a dissolved form. The values of SCOD were measured. It was assumed that the effectiveness of the disintegrating action of the ultrasonic field on excess sludge depends on the operating conditions used for the process. Obtained results of research on the influence of ultrasonic field on the increase of disintegration of excess sludge expressed in the value of SCOD are presented in Figure 2.

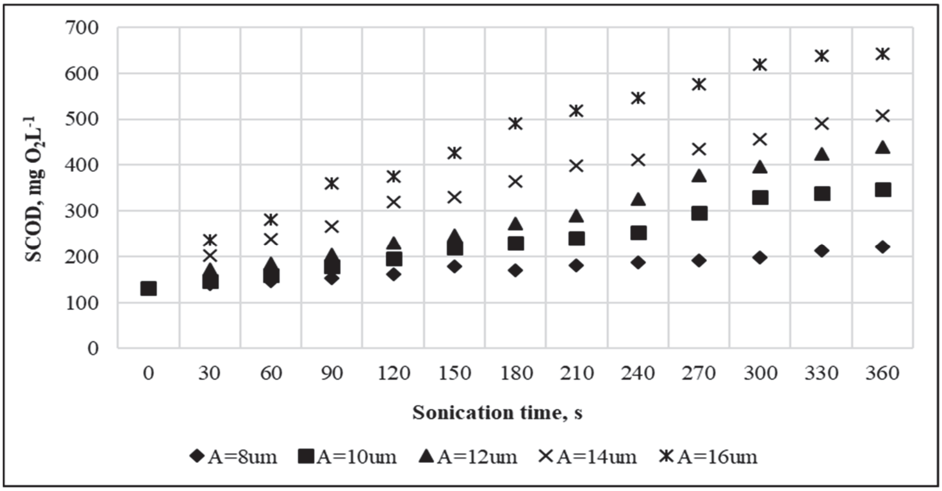


Fig. 2. Influence of ultrasonic disintegration on the SCOD values, depending on the disintegration time of excess sludge and the amplitude of ultrasonic field vibrations

Based on the obtained values of SCOD of excess sludge disintegrated by an ultrasonic field, along with the increase in the value of applied ultrasonic field vibration amplitudes, an increase in the concentration of organic matter in the supernatant liquid was observed. Increase in value of SCOD was also noted along with the extension time of sonication of the prepared sludge. Increase of SCOD value was determined with reference to the value of SCOD of excess sludge unmodified in relation to the obtained values of this index for sludge after the disintegration process. The increasing SCOD value was the effect of the destruction process of cell walls of excess sludge microorganisms and the subsequent sonolysis of organic substances released into the supernatant liquid. Ultrasonic modification of excess sludge used to increase the SCOD value in the leachate has been observed by many scientists. The SCOD increase in the range from 10 to 90% was observed when specific energy was used in the range from 1000 to 100000 kJ kg TS^{-1} (Lehne et al. 2001, Müller et al. 1998). The highest increase of the value of SCOD for individual vibration amplitudes, we obtained for different values of the time of sonication, which was defined as the most favourable disintegration time, as shown in Table 2.

Table 2. Determination, of the most favorable exposure time of the ultrasonic field, based on the increment of the SCOD value

Amplitude of ultrasonic field vibrations, μ m	The most favorable exposure time, s	SCOD $_{\text{of non-modified sludge}}$, mgO_2 L^{-3}	SCOD $_{\text{of modified sludge}}$, mgO_2 L^{-3}	Ratio of SCOD $_{\text{of non-modified sludge}}$/ SCOD $_{\text{of modified sludge}}$
8	300	132	198	1/2
10	300	132	331	1/3
12	270	132	378	1/3
14	330	132	490	1/4
16	300	132	619	1/5

Disintegration of excess sludge with an ultrasonic field with an amplitude of 8 μm caused a two-fold increase of the value of SCOD in relation to the initial value. This result was obtained for an exposure time of 300 s. A threefold increase of the SCOD value was obtained in the case of the use of 10 μm and 12 μm vibration amplitudes at ultrasonic field exposure times of 300 s and 270 s, respectively. Using an ultrasonic field with 14 μm vibration amplitude and 330 s sonication time, a fourfold increase of the index value was obtained. The highest, fivefold increase of the value of SCOD was noted as a result of using an ultrasonic field with a vibration amplitude of 16 μm and a sonication time of 300 s. For technological reasons, the above disintegration conditions were considered the most favourable. Extending the disintegration time, due to the energy consumption of the sonification process, is not indicated. Moreover in the case of ultrasonic wave propagation with the value of ultrasonic field vibration amplitude in the range of 8-16 μm, the wave intensity in the range of 3-10 Wcm^{-2} was obtained. The value of 1 Wcm^{-2} is considered in the literature (Stępniak 2006) to be threshold, above which in the modified medium the cavitation phenomenon is initiated. In addition, according to Gronroos et al. (Gronroos et al. 2005) during ultrasonic treatment of sludge, the degree of liquefaction increases with the passage of sonication time and the increase of the wave intensity.

In the methane fermentation process of non-modified excess sludge, it was observed that the SCOD value gradually increased to the third day of fermentation. For non-treated excess sludge, the SCOD value was 132 mg O_2 L^{-1}, while the value of 934 mg O_2 L^{-1} was recorded in the third day of methane fermentation. In the last day of anaerobic stabilization, the SCOD value was 591 mg O_2 L^{-1}.

In the process of methane fermentation of excess sludge disintegrated with an ultrasonic field, an increase in the concentration of organic substances in the supernatant liquid expressed of SCOD increase was noted. It was observed the increase of SCOD value from the value of 794 mg O_2 L^{-1} up to the value of 1532 mg O_2 L^{-1} determined on the 4th day of the process, followed by a decrease in the value of this indicator to 657 mg O_2 L^{-1} in the 10th day (Fig. 3).

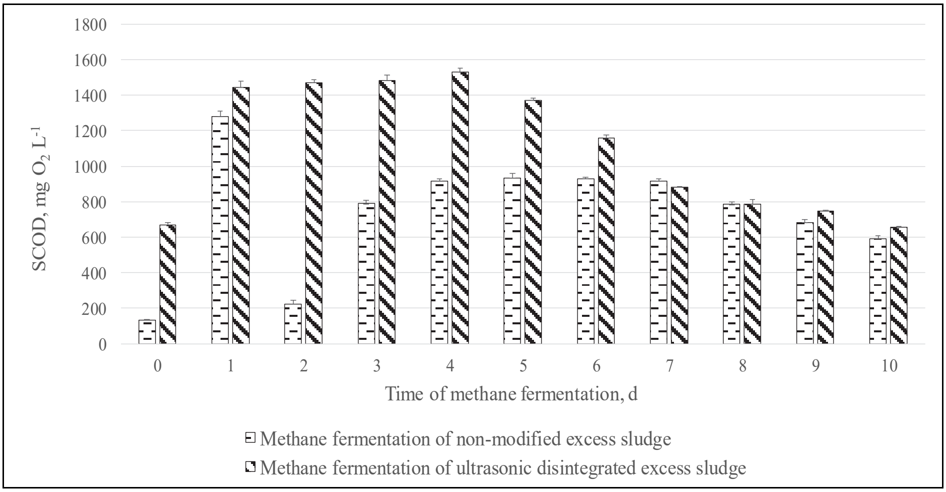


Fig. 3. Changes in the SCOD value of excess sludge in the process of conventional methane fermentation and methane fermentation supported with an ultrasonic field

3.2. Impact of the ultrasonic field on the structure of excess sludge

On the basis of microscopic tests, the structure of excess sludge not subjected to the modification process was evaluated as well as changes occurring in the structure of sludge modified by ultrasonic field, Fenton reagent and combined method. The unmodified excess sludge was characterized by a homogeneous structure, uniform dispersion of fine solid phase particles was observed throughout the liquid phase (Figure 4). The analysis of microscopic preparations of modified sludge showed a clear change in the structure of sludge. As a result of the impact on the sludge with the ultrasound field, along with the prolongation of the exposure time and the increase of the vibration amplitude value of the ultrasonic field, the solid phase particles gradually formed a compact structure. In the field of view of the preparation presenting the structure of overexpressed excess sludge, as compared to unprocessed sludge, there was an increase in the liquid phase space (Fig. 5a-f). The highest efficiency of the dispersive effect of the active ultrasonic field on excess sludge was obtained for a time of 300 s using a vibration amplitude of 16 μm. A similar trend was noted by Hogan et al. (Hogan et. al.) stating that during ultrasonic treatment of sludge, the degree of liquefaction increases with the passage of sonication time and the increase of ultrasonic field intensity.

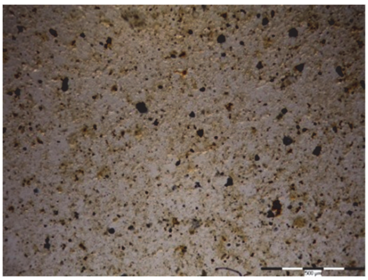
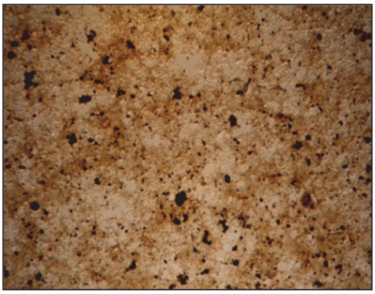
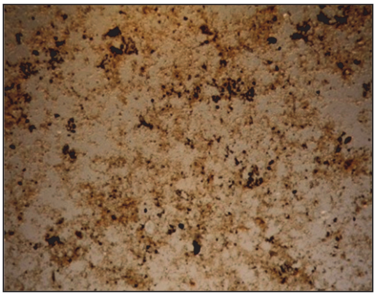


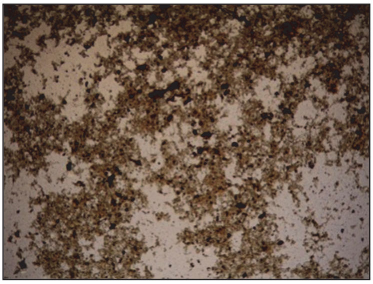
Fig. 4. Structure of non-modified excess sludge



a) t = 300 s, A = 8 μm

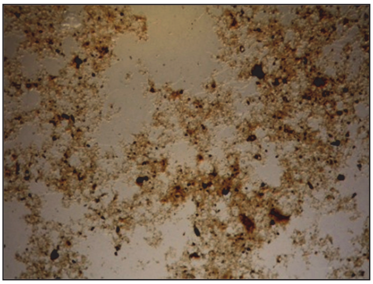


b) t = 300 s, A = 10 μm



c) t = 270 s, A = 12 μm

d) t = 330 s, A = 14 μm



e) t = 300 s, A = 16 μm

Fig. 5. Structure of excess sludge disintegrated by ultrasonic field with different modification time and variable vibration amplitude; a) t = 300 s, A = 8 μm, b) t = 300 s, A = 10 μm, c) t = 270 s, A = 12 μm, d) t = 330 s, A = 14 μm, e) t = 300 s, A = 16 μm

3.3. Effect of ultrasonic disintegration of excess sludge on microbiological indicators

The analysis involved microbiological changes occurring in excess sludge disintegrated by an ultrasonic field. It has been found that the use of sonication influences microbial cells in a destructive manner. The effect of this action is a decrease in the number of examined groups of microorganisms present in the prepared sludge. The phenomenon of ultrasonic cavitation is used to hygienie sewage sludge. The effectiveness of ultrasonic disinfection depends on the parameters of sonication, duration of sonication, as well as the type and number of bacteria destroyed (Goznze et al. 2003). The use of disintegration of excess sludge with an ultrasonic field did not cause a significant reduction in the number of microorganisms of the type *Escherichia coli*. Ultrasonic wave propagation has been effective in reducing the viability of other groups of microorganisms, i.e. mesophilic and psychrophilic microorganisms. During the sludge modification, an increase in the degree of reduction of mesophilic microorganisms from $49 \cdot 10^6$ JTK cm^{-3} to $16 \cdot 10^5$ JTK cm^{-3} and psychrophilic microorganisms from $61 \cdot 10^6$ JTK cm^{-3} to $48 \cdot 10^5$ JTK cm^{-3} was observed.

Table 4. Microbiological analysis of excess sludge subjected to ultrasonic disintegration

Disintegration conditions	Type of microorganisms					
	Mesophilic		Psychrophilic		*Escherichia coli*	
	The number of microorganisms, JTK cm^{-3}		The number of microorganisms, JTK cm^{-3}		Count	
	Non-modified excess sludge	Modified excess sudge	Non-modified excess sludge	Modified excess sludge	Non-modified excess sludge	Modified excess sludge
A = 16 µm, t = 300 s	$49 \cdot 10^6$	$16 \cdot 10^5$	$61 \cdot 10^6$	$48 \cdot 10^5$	10^{-4}	10^{-3}

As the time of sonication increases, the effect of inactivation of microorganisms increases. According to Woszczyk-Cierzyńska et al. (Woszczyk-Cierzyńska et al. 2007), using a longer sonication time of 15 minutes and a frequency of 22 kHz, the degree of destruction of psychrophilic bacteria was achieved, amounting to 97.9% for digested sludge, approximately 98.6% for primary sludge, degree of mesophilic bacteria destruction from 94.3% for primary sludge, up to 94.9% for digested sludge.

The aim of the microbiological analysis was to determine the effect of ultrasonic disintegration of excess sludge subjected to methane fermentation to the number of individual groups of microorganisms present in modified excess sludge. In the stabilization process, a decrease in the number of mesophilic, psychrophilic bacteria as well as *Escherichia coli* bacteria determined by means of count was noted. A decrease in the number of psychrophilic microorganisms from $45 \cdot 10^5$ JTK cm^{-3} to $20 \cdot 10^5$ JTK cm^{-3} occurred in the initial stabilization period, during the first 5 days of the process. In subsequent days of methane fermentation, the amount of microorganisms decreased slightly to $15 \cdot 10^5$ JTK cm^{-3}. The Escherichia coli count equal to 10^{-3} in sludge during the entire stabilization cycle increased to 10^{-2}. The lowest decrease in numbers from $16 \cdot 10^5$ JTK cm^{-3} to $10 \cdot 10^5$ JTK cm^{-3} was observed in the case of mesophilic bacteria. Microbiological changes occurring in the process of methane fermentation of sludge disintegrated by an ultrasonic field are presented in Table 5.

Table 5. Microbiological analysis of ultrasonically disintegrated excess sludge subjected methane fermentation

Methane fermentation		Type of microorganisms		
		Mesophilic	Psychrophilic	*Escherichia coli*
		The number of microorganisms, JTK cm^{-3}	The number of microorganisms, JTK cm^{-3}	Count
Time of the process, d	1	$16 \cdot 10^5$	$45 \cdot 10^5$	10^{-3}
	5	$14 \cdot 10^5$	$20 \cdot 10^5$	10^{-3}
	10	$10 \cdot 10^5$	$15 \cdot 10^5$	10^{-2}

As a result of methane fermentation of unmodified sludge, a slight decrease in the number of psychrophilic bacteria was noted. Mesophilic microorganisms were also characterized by high resistance to anaerobic conditions. After stabilization, a slight decrease in the amount of this group of microorganisms was found. Based on the microbiological analysis performed during the methane fermentation of sonicated excess sludge, a high level of *Escherichia coli* removal was found, the titer of these microorganisms before the 10^{-5} process increased in the methane fermentation process to 10^{-2}.

The described technology based on the process of ultrasonic disintegration is a promising process solution that does not cause secondary pollution of the sludge environment, effectively affecting the methane fermentation process, both in terms of the value of physical and chemical indicators conditioning the process, as well as microbiological. Therefore, there is a potential possibility of implementing the proposed technology into the sewage sludge processing string.

4. Conclusions

Obtained results of research on sonication of excess sludge allow to formulate the following conclusions:

1. The excess sludge modification caused by the effect of the ultrasonic field influenced the increase of disintegration of the modified excess sludge, expressed by an increase of the value of dissolved chemical oxygen demand. The most favorable conditions for the disintegration of excess sludge with the ultrasonic field were considered as the amplitude of 16μm vibrations and sonication time of 300 s. About 5-fold increase of SCOD values in relation to initial values was obtained.
2. On the basis of the microscopic analysis of the structure of disintegrated excess sludge, it was found that the use of an active ultrasonic field causes a clear change in the flocculating structure of excess sludge, affecting the increase of their degree of liquefaction.
3. It was found that the use of ultrasonic disintegration had a destructive effect on microbial cells. The effect of this action was a decrease in the number of examined groups of microorganisms present in the prepared sludge. The use of disintegration of excess sludge by ultrasonic field did not significantly reduce the number of *Escherichia coli* microorganisms. Propagation of ultrasonic wave effectively reduced the viability of other groups of microorganisms, i.e. mesophilic and psychrophilic microorganisms. During the sludge sonication, an increase in the degree of reduction of mesophilic microorganisms from $49 \cdot 10^6$ JTK cm^{-3} to $10 \cdot 10^5$ JTK cm^{-3} and psychrophilic microorganisms from $61 \cdot 10^6$ JTK cm^{-3} to $10 \cdot 10^5$ JTK cm^{-3} was observed.

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Abstract

The rate of decomposition of organic matter during methane fermentation is limited by the speed of the first phase of this process, called hydrolysis, during which liquefaction process of organic compounds takes place. For the pre-treatment of sludge before methane fermentation, disintegration techniques are used, which depending on the type of energy supplied to the system, can be divided into four groups: chemical, thermal, mechanical, biological methods. An effective method of mechanical disintegration of sewage sludge is the technology associated with the use of ultrasound. The impact of ultrasonic waves distorts the state of balance in the system, leads to better spatial packing of molecules, changing the structure of sewage sludge and their physico-chemical properties. The aim of the study was to determine the disintegrating influence of sonication on the excess sludge liquification expressed as the increase in the soluble chemical oxygen demand (SCOD). value of the modified excess sludge as well as estimating of the microbiological indicators of sonicated sludge.

The process of disintegration of excess sludge with the ultrasonic field was carried out with the use of a disintegrator type UD-20 with a vibration frequency of 22 kHz and a maximum output power of 180W. Microbiological analyzes performed for non-modified and disintegrated sludge concerned the number of mesophilic and psychrophilic microorganisms, *Salmonella spp* bacteria and *Escherichia coli* type bacteria, which is a pathogenic species. Periodic methane fermentation of excess sludge was carried out for 10 days, in the temperature of 37°C. As a result of subjecting the excess sludge to disintegration with an ultrasonic field, an increase in the degree of liquefaction of sludge was noted, expressed as an increase in the value of soluble chemical oxygen demand (SCOD). For the vibration amplitude of 16μm and sonication time of 300 s about 5-fold increase of SCOD values in relation to initial values was obtained. The highest degree of elimination of the studied groups of microorganisms was noted on the 10th day of the methane fermentation process of modified excess sludge.

Keywords:
excess sludge, ultrasonic field disintegration, soluble chemical oxygen demand (SCOD), methane fermentation, microbiological indicators

Dezintegrujący wpływ sonifikacji na upłynnienie osadów nadmiernych oraz ich wskaźniki mikrobiologiczne

Streszczenie

Szybkość rozkładu substancji organicznych podczas fermentacji metanowej jest ograniczona szybkością pierwszej fazy tego procesu zwanej hydrolizą, podczas której następuje upłynnienie związków organicznych. W celu wstępnej modyfikacji osadów przed fermentacją metanową stosuje się techniki dezintegracji, które w zależności od rodzaju energii dostarczanej do układu można podzielić na cztery grupy: chemiczne, termiczne, mechaniczne, biologiczne. Skuteczną metodą mechanicznej dezintegracji osadów ściekowych jest technologia związana z zastosowaniem ultradźwięków. Oddziaływanie fal ultradźwiękowych zakłóca stan równowagi w układzie, prowadzi do lepszego przestrzennego upakowania cząsteczek, zmieniając przy tym strukturę osadów ściekowych oraz ich właściwości. Celem badań było określenie dezintegrującego wpływu sonikacji na upłynnienie osadów nadmiernych wyrażone wzrostem wartości rozpuszczo-nego chemicznego zapotrzebowania na tlen ($ChZT_{rozp.}$), a także oszacowanie wskaźników mikrobiologicznych sonifikowanych osadów. Proces dezintegracji osadów nadmiernych polem ultradźwiękowym przeprowadzono przy użyciu dezintegratora typu UD-20 o częstotliwości drgań 22 kHz i maksymalnej mocy wyjściowej 180 W. Analizy mikrobiologiczne przeprowadzone dla osadów niemodyfikowanych i dezintegrowanych dotyczyły określenia liczebności mikroorganizmów mezofilnych i psychrofilnych, bakterii *Salmonella spp* i bakterii typu *Escherichia coli*, która jest gatunkiem patogennym. Okresową fermentację metanową osadów nadmiernych prowadzono przez 10 dób, w temperaturze 37°C. W wyniku poddania osadów nadmiernych modyfikacji za pomocą pola ultradźwiękowego odnotowano wzrost stopnia upłynnienia osadów, wyrażony wzrostem wartości rozpuszczonego chemicznego zapotrzebowania na tlen. Dla amplitudy drgań 16 μm i czasu sonikacji 300 s uzyskano około 5-krotny wzrost wartości $ChZT_{rozp.}$ w stosunku do wartości początkowych. Najwyższy stopień eliminacji badanych grup mikroorganizmów odnotowano w 10 dobie procesu fermentacji metanowej modyfikowanych osadów nadmiernych.

Słowa kluczowe:
osady nadmierne, dezintegracja ultradźwiękowa,
rozpuszczone chemiczne zapotrzebowanie na tlen ($ChZT_{rozp.}$), fermentacja metanowa,
wskaźniki mikrobiologiczne

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Irrigation in the Reclamation of Municipal Waste Landfills

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1. Introduction

Storage in landfills is the oldest and still the most popular method of waste disposal. Deposited waste as a result of biochemical transformation processes undergo decomposition and mineralisation, transforming into anthropogenic material harmless to humans. Landfills must comply with the recently tightened provisions of Polish law, primarily resulting from the necessity of their adaptation to the requirements of the European Union (Regulation of the Minister for the Environment of March 24, 2003 with detailed information concerning the siting, construction, operation and closure to be fulfilled by certain types of landfills (Journal of Laws No. 61 item 549, as amended). In the field of waste management, the European Union has issued as many as nine directives. They have imposed numerous obligations for Poland, of which the most important are: achieving min. 60% of recovery and 55% of recycling for packaging waste in 2014, and at least 25% of recovery for biodegradable waste by 2010 so as not to deposit it in landfills (Rosik-Dulewska 2011).

In practice, the majority of organised municipal landfills in use in Poland do not have any technological solutions for managing leachate, which arises during their operation. Approximately 35% of landfills recirculate leachate to the landfill surface in order to reduce the disposal cost. (Żakowicz, Hewelke 2012). At the same time, for economic reasons, the distribution of leachate on the landfill surface is very rarely carried out with the use of irrigation systems. Not only should these systems support the development and proper maintenance of landfill vegetation by continuous ensuring adequate moisture in the plant root layer, but also favour microbiological processes and consolidate the cover layer of the landfill. It is therefore appropriate to apply an adequate irrigation technology by administering optimal irrigation doses at the appropriate frequency, similar to evapotranspiration. It should cover the water demand of vegetation growing in landfills, inhabited primarily by perennials, including grasses and annual plants (Dyguś et al. 2012, Łuniewski, Łuniewski 2011, Rosik-Dulewska 2011, Skibniewska 2011). Reclamation of landfills as the final process of its operation is divided into two stages: technical reclamation i.e. preparation of conditions for biological reclamation and biological reclamation i.e. introduction of specific plant species to the reclaimed area. The concepts of biological development of the above-ground municipal waste landfills have been the subject of numerous research. The studies also included the technology and size of irrigation doses. The properly developing vegetation layer in the landfill canopy enriches the landscape and creates a friendly microclimate. Especially given the fact that the cover layer of the landfill is not soil, is exposed to water and wind erosion, and characterises with unfavourable physic-water properties. Maintenance of grassy vegetation, trees and shrubs, which in the initial phase of landfill reclamation is not sufficiently developed, depends on the supply of additional water by irrigation. The treatment must be accurate, since the use of too high irrigation dose drains water from the sealed surface of the landfill and accumulates it locally, adversely affecting the structure of the landfill canopy (Żakowicz, Hewelke 2005). In order to maintain the best moisture conditions of the top layer, the most suitable irrigation technology is to provide small doses of water with high frequency, corresponding to evapotranspiration. Application of irrigation should be an indispensable procedure used for efficient and quick landfill reclamation. Specifically that approx. 35% of landfills use the recirculation of leachate to the canopy surface to reduce the cost of its disposal. The distribution of collected leachate to the landfill surface should be carried out with the use of irrigation systems. Well-growing vegetation on the canopy surface protects it, creates a good microclimate and allows it to blend in with the landscape by blurring landscape differences.

2. Material and methods

The aim of the study was to present an irrigation solution (sprinkler and slope) as a necessary element in the biological reclamation and management of the municipal waste landfill in Boduszewo, the commune of Murowana Goślina in the Wielkopolska province (Fig. 1). The scope of work included the presentation of landfill irrigation technologies, selection of irrigation doses, determination of water consumption by vegetation on scarps with different exhibition, selection of the amount of water needed for irrigation along with the applied irrigation doses (net). Determination of the average daily water demand (gross) for irrigation and evapotranspiration.

Fig. 1. Location of the village of Boduszewo in the background of the commune of Murowana Goślina and the area of the reclamated waste landfill; 1 – water reservoir, 2 – ditch, 3 – receiver, (source: http://www.murowana.pl/ogminie/img/mapy/gmina.gif)

Water easily accessible to plants was maintained within the range from the value of field water capacity to the beginning of plant growth inhibition (pF 2,0-2,7). Plants for planting were selected according to the recommendations for similar facilities in Poland. In the first stage (up to 3 years from the start from 2012 to 2014) the reclamation included island planting, trees and shrubs (black locust, Norway maple, bird cherry, black lilac). In the second stage of reclamation from 2015, the islands were enlarged with grassy vegetation and merged into green corridors as biological barriers performing anti-erosion and windbreak functions. Sprinkler irrigation solutions were implemented in the vegetative period of 2015, and the system was supplemented with a slope irrigation technology (in 2016). The value of water consumption in the balance method, from the soil layer with controlled moisture, was calculated for individual months of the vegetative period (IV-IX), depending on the average air temperature. The values of water consumption by vegetation was differentiated between: I reclamation phase (2012-2014) and II reclamation phase (from 2015), taking into account the type of exhibition of the irrigated surface, i.e.: the canopy, southwest, north and east scarps. The precipitation level and average air temperature were obtained from the nearest meteorological station in Zielonka. For calculations the value of real precipitation (up to 3 years after planting trees and shrubs) was decreased due to interception (by 1 mm with precipitation less than 3 mm, by 2 mm with precipitation more than 5 mm). In the period of more intensive growth of trees and shrubs (more than 3 years after planting), the study did not take into account the precipitation level lower than 3 $mm \cdot d^{-1}$.

3. Results and discussion

The village of Boduszewo is located entirely in the buffer zone of the "Puszcza Zielonka" Landscape Park, approx. 3km from Murowana Goślina. From the east and south Boduszewo is surrounded by forests of the Zielonka Forest. These are very valuable natural areas, containing objects of nature conservation. The municipal waste landfill in Boduszewo was built as an above-ground landfill, surrounded by a protective wall formed from local soil. The landfill is shaped similarly to a rectangle with an area of 5,58 ha and the volume of accumulated waste is 837500 m^3. Taking into account the characteristics of the reclaimed landfill in Boduszewo, a sprinkler system equipped with a reel-operated sprinkler RV5 manufactured by Aqua-Rol was applied on island plantings (Tab. 1).

During the first three vegetative periods of field tests and observations (from 2012 to 2014) additional irrigation was not necessary due to the favourable distribution and rate of precipitation. It was also the result of optimal moisture of the top layer of the landfill caused by higher than average long-term atmospheric precipitation values in the winter half-years and longer persistent melt-water occurring in years preceding the research period. During the vegetative period of 2015, with the total precipitation of 242 mm (lower by 78 mm than the multi-year average for this season), precipitation shortages appeared (from 17 mm in May to 77 mm in August) (Fig. 2). Deficiencies were supplemented by sprinkling with irrigation doses net ranging from 18 mm to 25 mm. The irrigation doses were calculated for the grass root layer, (volume 0-15 cm), with the planned maintenance of moisture for water easily accessible to plants (pF 2,0-2,7).

Table 1. Technical and operational characteristics of Aqua-Rol RV5 sprinkler (source: Aqua-Rol Sp. z o.o.)

Model / hose diameter (mm) / length (m)	Sprinkler	Nozzle size (Ø mm)	Flow ($m^3 \cdot h^{-1}$)	Pressure (bar)	Maximal / optimal irrigation area (m)	Efficiency (in ha) in a work cycle	Winding speed For 10 mm dose ($m \cdot h^{-1}$)
RV5 / / 100 / / 500	RANGER	22/24/ /26/28	31.3 - - 62.4	5.0 - - 11.2	100 / / 59-80	4.51	53-78

In addition, the top of the landfill was sown with a mixture of grasses, recommended for dry habitats, which consisted of more than 50% of red fescue (*Festuca rubra L.*) and its varieties with an admixture of white clover (*Trifolium repens L.*). As a result of the calculation with the use of the balance method, recommended by Zakowicz and Hewelke (2005), the water consumption by grasses was determined depending on the average daily air temperature. It was varied and depended on the location of the layer, with controlled moisture, in the landfill. The water consumption on the southwest scarp ranged from 78 mm (IV) to 160 mm (VII). The average water consumption in the vegetative period of 2015 (IV-IX) was 124 mm. During the same period, the water consumption on the northeast scarp was lower (by 46%) and fluctuated from 48 mm (in April) to 123 mm (in July). During the vegetative period of 2016, there was necessary to irrigate shrubs and trees with the use of a slope solution (common oak *Quercus robur L.,* field maple *Acer campestre L.*, bird cherry *Prunus padus L.*, dog rose *Rosa canina L.*). It resulted from the unfavourable distribution of precipitation and, above all, its rate (255 mm), lower than the average by 65 mm as well as air temperature, higher than the average (by 1.0°C).

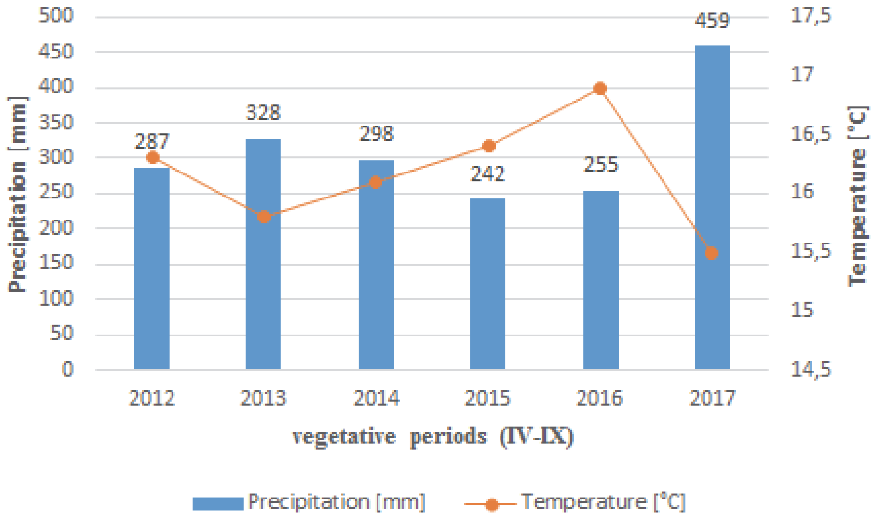

Fig. 2. Total precipitation and average air temperature in vegetative periods 2012-2017

Sprinkler irrigation combined with slope irrigation was carried out in the root layer (0-35 cm) with irrigation doses ranging from 25 mm (in April) to 35 mm in the remaining months of the growing season. During the vegetative period of 2017 irrigation was not conducted due to the total precipitation (459 mm) higher than the multi-year average (139 mm), which retained optimal moisture in the root layer of grasses, trees and shrubs in the landfill (Fig. 3).

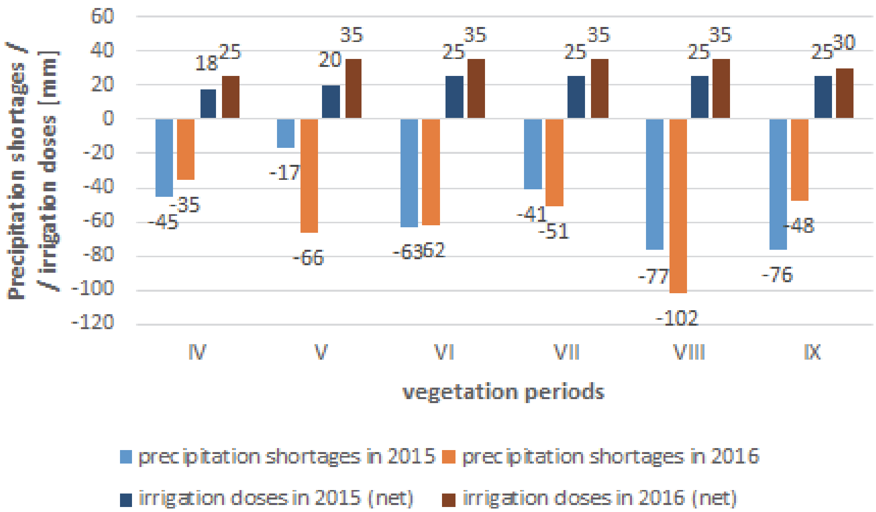

Fig. 3. Precipitation shortages and irrigation doses used in irrigation of the landfill in vegetation periods in 2015 and 2016

4. Conclusion

In the biological reclamation of above ground landfills, adequate maintenance of grass, trees and bushes on their surfaces, particularly in the initial phase, is an important factor conditioning the proper course of the process. The study described irrigation (sprinkler and slope) as a necessary component in the biological reclamation and management of the municipal waste landfill in Boduszewo, the commune of Murowana Goślina in the Wielkopolska province. Irrigation was carried out in the vegetative periods during which, due to the rate and distribution of precipitation (2015 and 2016), it considered necessary. There were determined adequate irrigation doses corresponding to the water consumption by plants covering the landfill. It was indicated that precise irrigation with the use of two complementary systems: sprinkler and slope, allows for accurate and controlled retaining of the moisture in the root layer of vegetation in the landfill. After applying irrigation solutions, significant growth and development of trees and shrubs was observed in the periods with high precipitation deficiencies. Field observations confirmed faster and much wider development of root systems in irrigated plants (in the canopy and on the southwest scarp) compared to plants on the north scarp that was devoid of irrigation. The affected by sprinkling plants on this landfill bloomed (i.e. black lilac and bird cherry), and there was observed a significant height gain comparing to plants planted at the same time but not irrigated. Poplars and maples also developed faster, and their growth was 30-40% higher after applying irrigation. The conducted research and field observations demonstrated that the use of plant irrigation in municipal waste landfills is an indispensable procedure contributing to its effective and fast reclamation.

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Abstract

The study identifies irrigation (sprinkler and slope) as a critical component in the biological reclamation and management of the municipal waste landfill in Boduszewo, the commune of Murowana Goślina in the Wielkopolska province. Irrigation was carried out in the vegetative periods during which, due to the rate and distribution of precipitation (2015 and 2016), it was considered necessary. The irrigation doses were determined corresponding to the water consumption by the vegetation covering the landfill. Results show that precise irrigation with the use of two complementary systems: sprinkler and slope, allows for the prevention and accurate control of the drought, resulting in continuous and uninterrupted growth and development of vegetation in the landfill.

During the vegetative period of 2015, when the total precipitation (242 mm) was lower by 78 mm than the multi-year average for this season, rainfall deficiencies were supplemented by means of irrigation with doses from 18 mm to 25 mm. These were varied depending on the vegetation water consumption. On the southwest scarp of the landfill, the water consumption was 124 mm on average, whereas in the same period on the northeast scarp it was 46% lower. During the vegetative period of 2016, there was identified an additional need for irrigation of shrubs and trees. Sprinkler irrigation combined with slope irrigation was carried out with doses ranging from 25 mm to 35 mm, depending upon the water consumption by plants. During the vegetative period of 2017, there was no additional irrigation due to the favourable distribution of precipitation and its high rate (459 mm), higher than the multi-year average (by 139 mm), which retained optimal moisture in the root layer of grasses, trees and shrubs in the landfill. The use of irrigation of plants in the municipal waste landfill proved to be an indispensable process contributing to its effective and fast biological reclamation.

Keywords:
irrigation in waste landfills, irrigation doses, biological reclamation

Nawadnianie w rekultywacji składowisk odpadów komunalnych

Streszczenie

W pracy przedstawiono nawodnienie (deszczowniane i stokowe), jako jeden z elementów niezbędnych w przeprowadzeniu rekultywacji biologicznej, składowiska odpadów komunalnych we wsi Boduszewo, gmina Murowana Goślina w województwie Wielkopolskim. Nawodnienia prowadzono w okresach wegetacyjnych: 2015 i 2016 roku, w których ze względu na wysokość a przede wszystkim rozkład opadów występowała potrzeba nawadniania. Określono dawki polewowe, odpowiadające zużyciu wody przez rośliny pokrywające składowisko. Wykazano, że precyzyjne nawadnianie, przy pomocy dwóch uzupełniających się systemów: deszczownianego i stokowego, pozwala uniknąć i zapobiegać okresom suszy, wpływając tym samym na niezakłócony wzrost i rozwój roślinności na składowisku.

W okresie wegetacyjnym 2015 roku, w którym suma opadów (242 mm), była niższą o 78 mm od średniej z wielolecia, występujące niedobory opadów uzupełniono

nawadnianiem dawkami w ilości od 18 mm do 25 mm. Były one zróżnicowane w zależności od zużycia wody przez rośliny. Na skarpie południowo-zachodniej składowiska, zużycie wody wynosiło średnio 124 mm, podczas gdy w tym samym okresie na skarpie północno-wschodniej było o 46% niższe. W okresie wegetacyjnym 2016 roku, wystąpiła dodatkowo potrzeba nawadniania krzewów i drzew. Nawodnienie deszczowniane połączone ze stokowym przeprowadzono dawkami w ilości od 25 mm do 35 mm, uzależnionymi od zużycia wody przez rośliny. W okresie wegetacyjnym 2017 roku, nawodnień nie prowadzono, z powodu wystąpienia opadów o dużej wysokości (459 mm), wyższych od średniej z wielolecia (o 139 mm), a przede wszystkim korzystnego ich rozkładu. Spowodowały one optymalne uwilgotnienie w warstwie korzeniowej roślin trawiastych oraz drzew i krzewów na składowisku. Zastosowanie nawodnienia roślin na składowisku odpadów komunalnych, okazało się niezbędnym zabiegiem, przyczyniającym się do efektywnej i szybkiej jego rekultywacji biologicznej.

Słowa kluczowe:
nawadnianie na składowisku odpadów, dawki polewowe, rekultywacja biologiczna

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Waste Management in the Region of Płock – Declarations of Residents

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1. Introduction

The paper discusses waste management on the territory of local governments belonging to the Union of Płock Region Communes and as its members involved in joint waste management. During a review of the waste management system, in the first stage a selection was made of a local governments with values as close to the mean level as possible. Afterwards local governments were chosen characterised by the biggest disparities with respect to population density and the number of registered residents per one declaration related to waste submitted by inhabitants. It was decided that the Czerwińsk nad Wisłą Commune was the most representative local government; the highest population density was recorded for the Stara Biała Commune, and the lowest one – in the Szczawin Kościelny Commune. The biggest number of registered residents per one declaration was recorded for the Pacyna Commune, and the smallest number in the Łąck Commune. Next a comparison was made of changes to amounts of generated waste in selected local governments in six-month periods.

2. Act of 1 July 2011

On 25 July 2011 a new act was announced on amendment of the act on maintaining cleanliness and order in communes and of certain other acts of 1 July 2011 (Polish Journal of Laws/Dz. U. 2011 No. 152 item 897). This act incorporated certain vital changes to the act on maintaining cleanliness and order in communes of 13 September 1996 (Polish Journal of Laws/Dz. U. of 2005 No. 236, item 2008, as later amended). The act came into life gradually, and came into effect fully on 1 July 2013. One of the most significant changes was releasing property owners from responsibility for waste management in favour of local governments (Zmysłowski & Biedugnis 2013). The Act reflects activities of the

European Union with respect to the impact that humans have on the environment. The EU institutions have published numerous documents and reports related to urbanization (Baran S., i in. 2014).

The Act, diverse publications and other documents promote recycling and are oriented at reducing the amount of deposited waste. In 2012 waste was neutralized by storing 62% of the total amount of waste collected. Mixed municipal waste accounted for almost 90% of all municipal waste deposited (Gaska K. & Generowicz A.).

3. Union of Płock Region Communes

The Union of Płock Region Communes (ZGRP) was registered in the Office of the Council of Ministers on 14 April 1994. Statutory tasks of the Union that are of key importance for waste management are as follows:

- “Joint resolving of problems of supra-commune nature” (Union of the Płock Region Communes 2015),
- “Representing joint interests of communes comprised by the Union” (Union of the Płock Region Communes 2015),
- “Taking up integration measures connected with plans of the establishment and functioning of the Płock County” (Union of the Płock Region Communes 2015),
- “running a waste management system on the area of communes being Union members, such as: Bielsk, Brudzeń Duży, Czerwińsk nad Wisłą, Drobin, Gąbin, communes: Gostynin, Łąck, Nowy Duninów, Pacyna, Słupno, Stara Biała, Staroźreby, Szczawin Kościelny, Wyszogród” (Public Information Bulletin 2015),
- “launching and implementing a programme of ecological education of the society” (Public Information Bulletin 2015).

Given the changes incorporated by the act on amendment of the act on maintaining cleanliness and order in communes and of certain other acts of 1 July 2011 (Polish Journal of Laws/Dz. U. 2011 No. 152 item 897), as of 1 July 2013 the Union of Płock Region Communes has taken over the responsibility from a part of local governments comprised by Union, which have consequently waived in its favour their liability for waste management.

Fig. 1. Local governments participating in joint waste management system as members of the Union of Płock Region Commune (own study based on data provided by the Union of the Płock Region Communes)

The Union of Płock Region Communes lies in the north-western part of the Mazovian Province, and associates 18 communes of a total area of 12088.79 km^2, with 236000 inhabitants [1]. Local governments being a part of the Union are in three counties: the County of Gostynin – 3 communes, the County of Płock – 14 communes, and the County of Płońsk – 1 commune.

The joint waste management system under the Union of Płock Region Communes comprises 13 local governments, and namely: the Bielsk Commune, the Brudzeń Duży Commune, the Czerwińsk nad Wisłą Commune, the City and the Drobin Commune, the City and the Commune Gąbin, the Gostynin Commune, in the Łąck Commune, the Pacyna Commune, the Słupno Commune, the Stara Biała Commune, the Staroźreby Commune, the Szczawin Kościelny Commune, the Commune and the city of Wyszogród. The location of particular local governments has been presented on the below figure, with local governments marked red. In 2013 the Union of Płock Region Communes comprised an area of 171800 ha with 102520 inhabitants under the joint waste management system (Table 1) (Central Statistical office 2013).

The average area of local governments participating in the joint waste management system within the Union equalled in 2013 to 13215.38 ha, with the largest local government comprising the area of 27037 ha being the Gostynin Commune, while the smallest local government was the Słupno Commune, which comprised an area of 7493 ha. (Table 1)

The average number of inhabitants of local governments participating in the joint waste management system under the Union equalled in 2013 to 7886.15 people, coming up to average population density of 62.69 persons/km^2. The highest number of inhabitants was recorded in the Gostynin Commune – 12185 people (the population density equalled to 45 persons/km^2), while the lowest number of inhabitants amounting to 3795 people (the population density equalled to 42 persons/km^2) was recorded by the Pacyna Commune. The highest population density in 2013 was recorded in the Stara Biała Commune (the population density was 101 persons/km^2), which came up to 161.11% of the mean population density in the analysed region. The Szczawin Kościelny Commune was characterised by the lowest population density (the population density equalled to 40 persons/km^2), which came up to 63.81% of the mean population density of the analysed region (Table 1.)

Table 1. Local governments participating in joint waste management system under the Union of Płock Region Communes (own study based on data provided by the Union of the Płock Region Communes and the Central Statistical Office)

Item	Commune	Area (ha)	Number of inhabitants (persons)	Population density (person/km^2)
1	Bielsk	12517	9133	73
2	Brudzeń D	15984	8189	61
3	Czerwińsk	14411	7896	55
4	Drobin	14350	8316	58
5	Gąbin	14421	11101	76
6	Gostynin	27037	12185	45
7	Łąck	9399	5288	56
8	Pacyna	9029	3795	42
9	Słupno	7493	6874	92
10	Stara Biała	11112	11245	101
11	Staroźreby	13766	7553	55
12	Szczawin	12716	5092	40
13	Wyszogród	9565	5853	61
Total		171800	102520	
Average		13215.38	7886.15	62.69

4. Declarations of inhabitants pertaining to waste

The Union of Płock Region Communes imposed charges for waste management on the inhabitants of local governments, for the waste management of which it is responsible. Fees were charged to households on the basis of declarations submitted by them. Furthermore, charges collected from uninhabited property were calculated based on the amount of collected waste, with charges depending on the number of containers.

The total number of declarations submitted on the area of local governments that participate in joint waste management system came up to 28181; typically there were 2167.77 declarations per local government. On average there were 6.44 ha of local government area per one declaration and 3.68 inhabitants (registered residents). The biggest number of declarations have been submitted in the Gostynin Commune – 12185 pcs., which comes up to 8.14 ha of local government area per one declaration and 3.67 registered residents per declaration; the lowest number of declarations was received from the Słupno Commune – 7493 pcs., which came up to 3.25 ha of local government per declaration, with 2.98 registered residents per one declaration (Table 2).

A determinant pertaining to the number of declarations may be obtained by adopting an average based on the registered residents per one submitted declaration. The mean number of registered residents in the analysed region per one submitted declaration equalled to 3.68. The highest number of persons per declaration was recorded in the Pacyna Commune 4.02, and the smallest one in the Łąck Commune – 2.38. Also in the Słupno Commune a low number per one declaration was recorded – 2.98, which may arise from the fact of robust economic relations with Płock (Table 2). The number of submitted declarations may be directly correlated with the social structure of the population on the area of the given local government, because in most cases one declaration corresponded to one family or one property.

5. Representative local governments

Further analyses were based on representative local governments. A local government demonstrating values most similar to the mean one as regards social structures and location was the Czerwińsk nad Wisłą Commune. Also the most differentiated local governments were considered as representative ones. Local governments with biggest disparities with respect to the number of registered residents per one declaration included the Pacyna Commune and the Łąck Commune. As regards population density, such local governments comprised the Stara Biała Commune and the Szczawin Kościelny Commune.

Table 2. Local governments participating in joint waste management system as members of the Union of Płock Region Communes (own study based on data provided by the Union of the Płock Region Communes and GUS [Central Statistics Office])

Item	County	Commune	Area	Population	Submitted declarations	Hectares per declaration	Population per declaration
			ha	persons	pieces	ha/ declaration	persons/ dec-laration
1	Płock County	Bielsk	12517	9133	2317	5.40	3.94
2	Płock County	Brudzeń Duży	15984	8189	2192	7.29	3.74
3	Płońsk County	Czerwińsk nad Wisłą	14411	7896	2031	7.10	3.89
4	Płock County	Drobin	14350	8316	2124	6.76	3.92
5	Płock County	Gąbin	14421	11101	2933	4.92	3.78
6	Gostynin County	Gostynin	27037	12185	3323	8.14	3.67
7	Płock County	Łąck	9399	5288	2222	4.23	2.38
8	Gostynin County	Pacyna	9029	3795	943	9.57	4.02
9	Płock County	Słupno	7493	6874	2304	3.25	2.98
10	Płock County	Stara Biała	11112	11245	3108	3.58	3.62
11	Płock County	Staroźreby	13766	7553	1979	6.96	3.82
12	Gostynin County	Szczawin Kościelny	12716	5092	1350	9.42	3.77
13	Płock County		9565	5853	1355	7.06	4.32
		Total	171800	102520	28181		
		Average	13215.38	7886.15	2167.77	6.44	3.68

5.1. Amount of waste per declaration

The average value related to the mean monthly amount of waste per one declaration in five selected local governments was 0.04 Mg; the same amount was recorded for the Czerwińsk nad Wisłą Commune and the Szczawin Kościelny Commune. The value of 0.03 Mg of waste per one declaration was recorded for the following local governments: the Pacyna Commune and the Łąck Commune. A value that considerably exceeded the average one, amounting to 0.06 Mg, was recorded in the Stara Biała Commune. No relation may be formulated for the amount of waste per one declaration and the amount of registered residents per one declaration, similarly as it is impossible to relate it to the population density.

5.2. Share of half-year periods in total amount of waste collected in particular years

Waste collected in the first six-month period in the Łąck Commune, the Pacyna Commune, the Szczawin Kościelny Commune and the Stara Biała Commune amounted on average to 39% of all waste deposited in 2013. The smallest share was recorded in the Szczawin Kościelny Commune at the level of 31%, and the highest one in the Łąck Commune at the level of 49%. The average increase in the amount of waste collected in the second half of 2013 as compared to the first half of 2013 equalled to 65%. The highest increase was found to have taken place in the Szczawin Kościelny Commune and equalled to 121%, and the lowest one in the Łąck Commune and amounted to 5% (Fig. 2).

The average share of the first six-month period in the amount of collected waste equalled to 52%, which was the same amount as in the Łąck Commune. For the Pacyna Commune this value equalled to 56%, for the Szczawin Kościelny Commune the share was 50%, and for the Stara Biała Commune – 49%. It may be assumed that the volume of deposited waste in particular six-month periods amounted approximately to half the amount of generally collected waste in 2014 (Fig. 3).

A comparison of the share of the first six-month period in collected waste in 2014 as compared to 2013 depicts changes of the mean value of 39% in 2013 that grew to 52% in 2014.

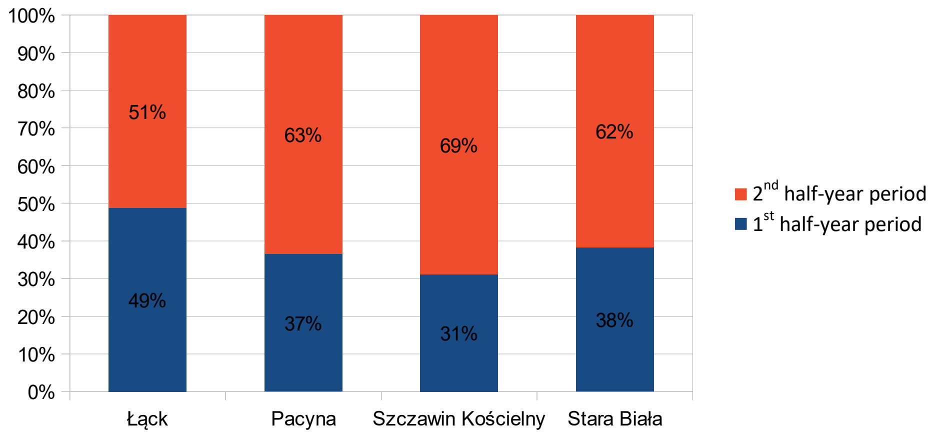

Fig. 2. Share of particular six-month periods in the total amount of waste collected in 2013 (own study based on data provided by the Union of the Płock Region Communes)

The Łąck Commune was found to differ from the remaining communes, because the value for the first half of 2013 amounted to 49%, while for the first half of 2014 it equalled to 52%. Such a minor difference may arise from the fact that the collected waste was removed in the second half-year period of 2013, which could be connected with removal of deposited waste.

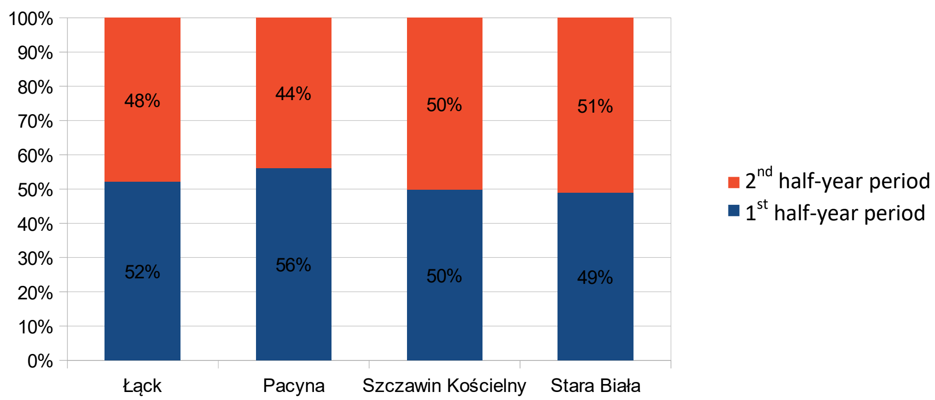

Fig. 3. Share of six-month periods in the total amount of waste collected in in 2014. (own study based on data provided by the Union of the Płock Region Communes)

6. Changes in volume of collected waste as compared to corresponding periods

The conducted comparison of changes that have been recorded in the amount of waste obtained in the process of separate waste collection in the representative self-government authority (Czerwińsk nad Wisłą) in the first six-month periods of 2013 and 2014 and in the second half-year periods of 2013 and 2014 have pointed to the existence of significant differences.

Changes in the volume of waste collected in the second half-year period of 2013 as compared to the second six-month period of 2014 were found to be distinct. Comparisons of the volume of collected waste in particular months point to noticeable yet slight disparities. It may be presumed that those disparities arise from factors that are not directly connected with the generation of waste, such as public holidays, collecting waste on pre-agreed dates with their volume differing in particular months. The amount of waste collected from non-inhabited houses remained on a constant level. A quite significant difference has been recorded as compared in particular months for July 2013 and 2014, which may be a result of coming into effect of the Act of 1 July 2011 (Fig. 4).

The volume of waste collected in the first half of 2013 is much lower as compared to the volume of waste collected in the first half of 2014 (Fig. 5).

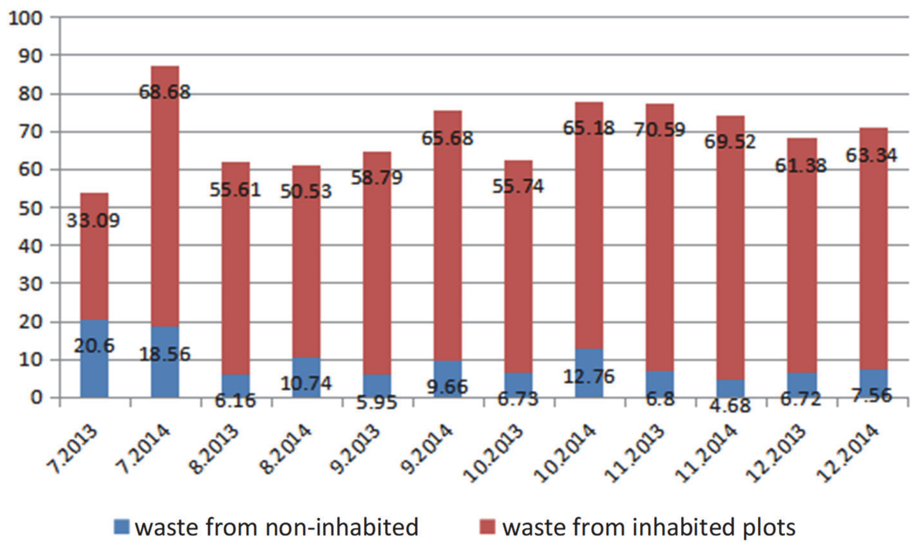

Fig. 4. Amount of waste collected in the Commune of Czerwińsk nad Wisłą for the second six-month period of 2013 and 2014 (Compiled on the basis of data submitted by the Union of the Płock Region Communes)

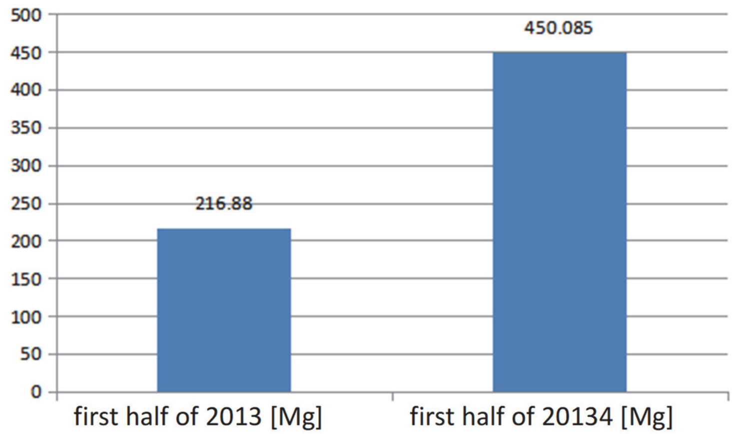

Fig. 5. Volume of waste collected in the Commune of Czerwińsk nad Wisłą for the first half of 2013 and 2014 (Compiled on the basis of data submitted by the Union of the Płock Region Communes)

The noticeable difference arises from the adoption of the Act on 1 July 2011.

A comparison of changes with respect to the volume of waste obtained from separate collection in the first three months following the adoption of the act as compared to the same period of 2012 shows that a significant increase is visible in the volume of collected waste (Fig. 6).

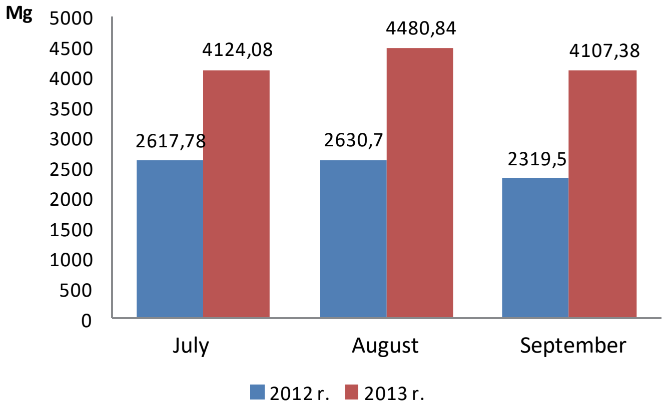

Fig. 6. Volume of waste delivered to the waste segregation facility in July, August and September 2012 and 2013. (Change in the quality of waste upplied to the Waste Management Plant in Poświętne after 1 July 2013)

A conclusion may be drawn that adoption of the act of 1 July 2011 has caused a considerable increase of obtained waste.

7. Changes in volume of waste obtained from separate collection

The adoption of the act of 1 July 2011 caused an increase in the volume of waste obtained in the process of separate collection. A comparison of corresponding periods that followed the adoption of the act has indicated that values were similar. Proof may be found by making a comparison of the share of half-year periods relating to self-governments characterised by the most profound differentiation between each other (Fig. 3) and a comparison of monthly amounts of waste collected by the representative self-government authority in comparable periods (Fig. 4).

The determination of a representative self-government authority allows simplifying analyses of ongoing changes, because it has to be borne in mind that self-government authorities differ highly from each other in several ways, and consequently adopting parameters that pertain only to an extreme self-government authority is not likely to reflect a more extensive aspect of the above discussed changes.

8. Conclusions

1. The lower the number of registered residents per one declaration, the more similar the share of particular six-month periods in the general amount of waste generated in the given year.
2. The population density had no significant impact on the distribution of shares of particular six-month periods in the total volume of generated waste.
3. Coming into effect of the act caused an increase in the amount of waste collected during separate waste collection.
4. In 2014, which may be considered the full functioning cycle of the act, no marked differences have been observed as to the volume of deposited waste during separate collection.
5. As it turned out the most important indices used to compare local governments for waste management comprised the population density and the number of registered residents per one declaration.
6. It is possible to determine the representative local government reflecting mean values for a group of local governments.
7. Adoption of the act resulted in a considerable increase in the amount of waste obtained during separate collection process.

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Abstract

The text of the article pertained to waste management in local government in the region of Płock. In my article described were changes to waste management after 1 July 2013, as well as methods of comparing local governments.

Keywords:
waste, management, Union of Płock Region Communes (ZGRP), Płock region, declaration, act, 2013, 2014, population density, Mazovian province

Gospodarka odpadami w ramach regionu płockiego – deklaracje mieszkańców

Streszczenie

Tekst artykułu dotyczy gospodarki odpadami w samorządzie w regionie płockim. W artykule opisano zmiany w gospodarce odpadami po 1 lipca 2013 r., a także metody porównywania samorządów.

Słowa kluczowe:
odpady, gospodarka, ZGRP, region płocki, deklaracje, ustawa, rok 2013, rok 2014, gęstość zaludnienia, mazowieckie

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The Use of Natural Mineral Sorbents (Zeolite, Bentonite, Halloysite) for Decolorization of Corn-sugar Beet Molasse's Vinasse

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1. Introduction

The molasse's vinasse (beet and cane) is one of the most difficult to neutralize wastewater because it has a low pH, high temperature, dark brown color and contains large amounts of ash (ash) and dissolved organic and inorganic substances (Pant and Adholeya 2007). The molasse's vinasse is a dark brown, viscous liquid with a characteristic, pungent and unpleasant odor and acidity (pH 3.5) (Wagh and Nemade 2015). It is wastewater with a high biological oxygen demand (BOD_5) of 45-100 g/dm^3 and chemical oxygen demand (COD) of 90-210 g/dm^3 (Mane et al. 2006).

The presence of three groups of colored compounds, i.e., melanoidins, hexose alkaline degradation products (HADP) and sucrose caramelization products (Bharagava and Chandra 2010, Chandra et al. 2008, Mane et al. 2006) give the color of the vinasse. The caramel and melanoidins are responsible for 80% for the color of beet juice, and thus the sugar beet molasse vinasse (Coca et al. 2004, Satyawali and Balakrishnan 2007). The antioxidant properties of these compounds cause the vinasse to be toxic to many microorganisms associated with wastewater treatment and the aquatic environment (Sirianuntapiboon et al. 2004). The utilization of the vinasse by pouring on the arable fields is dangerous for plant vegetation. It reduces soil alkalinity and reduces the availability of manganese, inhibiting seed germination. It also affects the quality of groundwater, causing a change in their physicochemical properties. The high COD value of the vinasse and the high content of total nitrogen and phosphate in vinasse may, in turn, lead to the eutrophication of natural waters (Mohana et al. 2009).

Color compounds must be removed from the vinasse before it is discharged into the natural environment (Onyango et al. 2011), because it may cause a decrease in the activity of plant photosynthesis (Pazouki et al. 2008). Color compounds are resistant to conventional biological treatment methods ((aerobic and anaerobic), anaerobic digestion, anaerobic lagoon, activated sludge process), which do not allow complete removal of the color from the waste stream (Yadav and Chandra 2018). During these processes, there may even be an increase in color due to the repolymerization of melanoidins (Pena et al. 2003). Conventional vinasse purification methods achieve melanoidin degradation by about 6-7%. It is, therefore, necessary to apply an additional decolorization process for molasse vinasse. Physicochemical methods are often used for this purpose (Mohana et al. 2009). To remove the colorants from the vinasse there are used different methods with different success: adsorption (Ojijo et al. 2010), coagulation (Liang et al. 2009), UV/H_2O_2 oxidation (Dwyer and Lant 2008; Reis et al. 2019), electrochemical methods (Kobya and Delipinar 2008), ozonation (Coca et al. 2007), membrane techniques (Apollo et al. 2014, Satyawali and Balakrishnan 2008), reverse osmosis (Silva et al. 2019) and evaporation (Liakos and Lazaridis 2016).

Among the physicochemical methods for decolorization and removal of organic pollutants, adsorption on activated carbon is very often used due to its actively developed surface, microporous structure, high adsorption capacity and a high degree of surface reactivity (Satyawali and Balakrishnan 2007). Both commercially available activated carbon, as well as specially prepared types such as those made from sugar cane expeller, were used in the research (Onyango et al. 2011). The use of activated carbon to remove color compounds from vinasse is expensive due to the high price of the sorbent itself and the necessary reagents (Coca et al. 2005). Therefore, there is a need for further research to develop materials that will be efficient, cheap and effective in decolorizing the vinasse (Onyango et al. 2011).

Previous studies on decolorization in most cases concerned mainly sugar cane molasse’s vinasse (Pant and Adholeya 2007). There are few references to the decolorization of sugar beet molasse’s vinasse with the use of natural sorbents (Krzywonos and Szymańska 2011). There is no study on the use of these sorbents for the decolorization of corn-sugar beet molasse's vinasse (CBMV).

The work aimed to remove color compounds from corn-sugar beet molasse’s vinasse with the use of five natural mineral sorbents (two types of halloysite (PJC and KR), two types of zeolite differing in grain thickness and bentonite).

2. Materials and methods

2.1. Decoction and natural sorbents

The corn-sugar beet molasse vinasse (CBMV) was from the Ruskie Piaski distillery, located in the Nielisz commune in the Lublin Voivodeship (Poland). The specificity of ethanol production technology in the Ruskie Piaski distillery consists of using sugar beet molasses and corn as raw materials.

Before use, the vinasse was filtered on paper filters to separate the solids. The supernatant was stored at 20°C.

Five natural mineral sorbents were used in the research: active halloysite KR 0-1 mm with gray color, bulk density 0,65 kg/m^3, pH = 5 to 6, (Intermark, Gliwice, Poland); halloysite PJC 0-1 mm with gray color, bulk density 0.80 kg/m^3, pH = 8 (Intermark, Gliwice, Poland); zeolite I (0.0-0.2 mm) and zeolite II (0.2-0.5 mm, gray-green color, volume density 1600-1800 kg/m^3, pH = 11 (Subio Eko, Chałupki, Poland); bentonite (0-0.056 mm) with a white-gray color, bulk density 0.8-1.0 mg/m^3, pH = 10 (Zakłady Górniczo-Metalowe "ZIĘBIEC", Starachowice, Poland).

2.2. The approach of the decolorization process

The sorbents used in the experiments (halloysite KR, halloysite PJC, zeolites I and II, bentonite) before the tests were dried at 105°C. The dose of 10 g of each sorbent was added to 100 cm^3 of vinasse in a 300 cm^3 conical flask. Each experiment was performed in duplicate. The flasks were placed in a Certomat S shaker (B.Braun Biotech International). Samples for analysis were taken every 15 minutes, and the entire experiment runs for 180 minutes at 100 rpm. The samples were centrifuged before analysis (centrifuge 3722L, Fisher Scientific) at 5000 rpm for 5 minutes. The supernatant was frozen (-20°C) and stored in this state for further analysis. The presented results are mean values from replicates.

2.3. Measurement of the decolorization removal

The decolorization removal was measured by the light absorbance at the wavelength λ = 475 nm, using a DR 5000 spectrophotometer (Hach Lange). For measurement, centrifuged and previously diluted vinasse samples were used. Decolorization (D) was calculated according to formula 1:

$$D(\%) = \frac{A_0 - A_t}{A_t} \cdot 100\% \tag{1}$$

where:
A_0 – initial absorbance,
A_t – absorbance at time t.

2.4. Analytical methods

The melanoidins, sucrose caramelization products, and hexose alkaline degradation products (HADP) was determined spectrophotometrically, using the method of Iwanow-Sapronow (Krzywonos et al. 2016; Sapronov 1963). For chemical oxygen demand (COD), total organic carbon content (TOC), total phosphate content was determined spectrophotometrically using the Hach Lange cuvette tests (Anon. 2000). The 5-day biochemical oxygen demand (BOD_5) was determined using a manometric method using the OxiTop kit (WTW). Removal of TOC, BOD_5 and phosphate phosphorus was determined only for the vinasse samples for which the highest decolorization was observed.

The content of glucose, glycerol, the content of organic acids (lactic, tartaric, succinic, pyroglutamic, acetic and isobutyric) was determined by the HPLC method. The Knauer HPLC kit was used, with refractometric and UV/VIS detectors, equipped with a Rezex ROA Organic Acids column (eluent: 2 mM H_2SO_4, flow rate: 0.5 cm^3/min). Tests were carried out at 65°C, at a wavelength of 210 nm.

The content of betaine was determined by high-performance liquid chromatography (HPLC). Knauer HPLC kit with a UV/VIS detector was used for the measurement, equipped with a Venusil SCX column. The eluent was a mixture of 5 mM H_2SO_4 + 5% methanol, and a flow rate was 1 cm^3/min. Analyses were carried out at 30°C, at a wavelength of 206 nm.

3. Results and discussion

The specificity of the ethanol production technology in the Ruskie Piaski distillery, from which the tested vinasse originated, consists of using sugar beet molasses and corn as raw materials. The dark brown vinasse was characterized by [g O_2/dm^3]: chemical oxygen demand (COD) 77.2; glycerol 21.26; lactic acid, 22.2; pyroglutamic acid 6.33; tartaric acid 5.18; succinic acid 10.6; hexose alkaline degradation products (HADP) 10.9; sucrose caramelization products 2.04; melanoidins 1.79 and betaine 25.3. The pH was 4.87, and the density was 22ºBlg.

Figure 1 shows the changes in the degree of color reduction of CBMV depending on the sorbent used.

The highest decolorization of CBMV was obtained for a sample decolorized by bentonite. For this carrier the process took place in two stages. Color removal by more than half (57%) was obtained already after 15 min and remained at this level up to 150 min. Then the decolorization increased to 74% and remained at this level until the end of the process (180 minutes). A similar two-stage process was observed for the decolorized vinasse by halloysite PJC. The reduction rate for this sorbent in the first stage was lower than in the case of bentonite and amounted to almost 50%. In 135 minutes the degree of decolorization increased but was lower than obtained for bentonite (62%). In the case of zeolites I and II, a much lower removal of colored compounds was observed, approx. 15-20% and the equilibrium was obtained after 75 minutes of shaking. When the halloysite KR was used to decolorization of vinasse, the highest decolorization (21%) was observed after 45 min. Unfortunately, in the final phase of this process (last 30 minutes), a significant increase in color was noted.

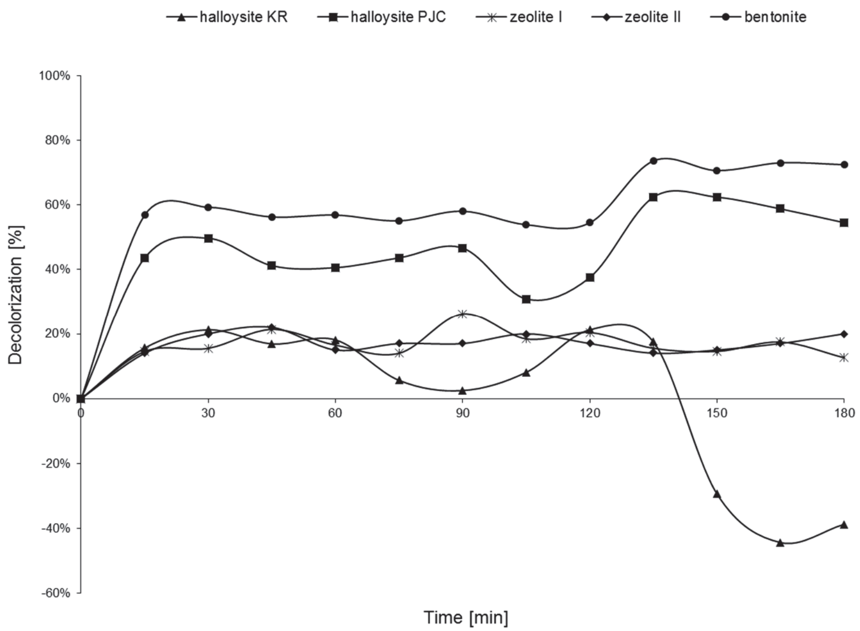

Fig. 1. Decolorization process of corn-sugar beet molasse's vinasse depending on the used sorbent

In a review of existing literature on the subject, no mention was made of the decolorization of corn-sugar beet molasse's vinasse with mineral sorbents.

When the vinasse decolorized with halloysite clay (Krzywonos and Szymańska 2011), after 0.5 hours of the process for a vinasse concentration of 5%, 25%, and 50%, the degree of decolorization was 80%, 98% and 43% respectively, while no decolorization was observed at higher vinasse concentrations. In this study, when the KR and PJC halloysite were used to decolorization corn-sugar beet molasse vinasse, a lower degree of decolorization was obtained (21% and 62% respectively). It should be emphasized that in the presented studies, experiments were carried out on an undiluted (100%) vinasse. Therefore, the used halloysite more effectively decolorized the 100% corn-sugar beet molasses vinasse than sorbents used in the studies of Krzywonos and Szymańska (2011) for decolorization of sugar beet molasses vinasse.

A high initial level of decolorization of the vinasse was observed, similar to the studies of Apollo et al. (2014), in which the natural zeolite was the carrier for the catalyst in the form of titanium dioxide. In the initial phase of the process, particles could be quickly absorbed due to a large amount of free space on the surface of the sorbent. With time, the surface of the sorbent became saturated, and the degree of decolorization stabilized in the following hours of the process. Also in the studies of Prasad and Srivastava (2009) on the use of fly ash for the decolorization of cane vinasse, color removal increased with the increase of the sorbent dose due to the greater availability of the adsorption surface. As in the presented studies, the 50% color reduction was achieved in these studies after only 15 minutes of the process. At a similar dose of sorbent (10 g per 100 cm^3 of vinasse) a degree of color removal of 91% was obtained. However, a 10% dilution of vinasse was used in these studies.

3.1. Content of colored compounds in the experiments

During the experiments, the content of colored compounds (HADP, melanoidins, and sucrose caramelization products) in the samples before and after decolorization of corn-sugar beet molasse's vinasse with the addition of all sorbents was determined (Table 1).

Table 1. The content of colored compounds and pH value of the vinasse before (0 min) and after the decolorization process (180 min) with the use of tested sorbents

		halloysite KR		halloysite PJC		zeolite I		zeolite II		bentonite	
Parameter	Time [min]	0	180	0	180	0	180	0	180	0	180
melanoidins	[g/dm^3]	3.30	3.60	3.22	1.09	3.02	2.21	2.93	2.27	3.31	1.79
HADP*	[g/dm^3]	16.80	22.70	16.50	17.98	16.90	16.20	16.35	15.18	16.86	10.90
caramels	[g/dm^3]	2.11	1.31	2.15	1.63	2.08	1.90	2.05	1.98	2.21	2.04
pH	[-]	4.87	3.55	4.82	5.18	4.87	4.92	4.86	4.93	4.81	5.09

* hexose alkaline degradation products

A slight increase in the content of melanoidins after the decolorization process was observed only for the decolorized vinasse using the KR halloysite.

In other processes, the content of this colored compound decreased (up to 46% for bentonite). On this basis, it can be concluded that this sorbent was the most effective in removing melanoidins from the vinasse.

Analyzing the content of hexose alkaline degradation products, a decrease in their content was observed in the decolorization process of vinasse with zeolite I, zeolite II and with bentonite. The most significant decrease was recorded for the last carrier (by 35%), so also in this case bentonite proved to be the most effective carrier in removing HADP.

In the case of caramels, a drop in their amount was found in the vinasse after the decolorization process in all experiments. The two types of halloysites KR and PJC were more efficient in removing this group of compounds, respectively 38% and 24%.

Unlike in the studies of Krzywonos and Szymańska (2011), where HADP was largely removed, in the presented study the highest removal of melanoidins with bentonite (46%) was observed.

The initial pH of the vinasse (before decolorization) was 4.85 on average. For the vinasse decolorized by halloysite KR, final pH was the lowest and amount to 3.55. The highest final pH of 5.18 was obtained for PJC halloysite decolorized vinasse.

When the halloysite and the activated carbon for decolorization were used, it was found that for the initial pH of 5 (approximately corresponding to the pH of the natural vinasse) the degree of removal of color compounds did not exceed 25% (Krzywonos and Szymańska 2011). In the presented studies, for the initial pH of the vinasse amounting to 4.85, the degree of decolorization was much higher in the case of PJC halloysite (about 50%), and for the halloysite KR, the degree of decolorization was at a similar level (about 18-20%), how in the study of Krzywonos and Szymańska (2011). On the other hand, in the research of Hadavifar et al. (2016) on the decolorization of cane vinasse with the use of, inter alia, granular activated carbon, it was found that the degree of decolorization is strongly dependent on the pH of the vinasse: the higher pH value, the lower the decolorization. When the pH changed from 2 to 10, the degree of color removal decreased from 68% to 31%.

3.2. Degree of removal of chemical oxygen demand (COD)

The chemical oxygen demand was tested for all samples of corn-sugar beet molasses vinasse decolorized using sorbents. The measurements were made for zero time and final samples (Figure 2).

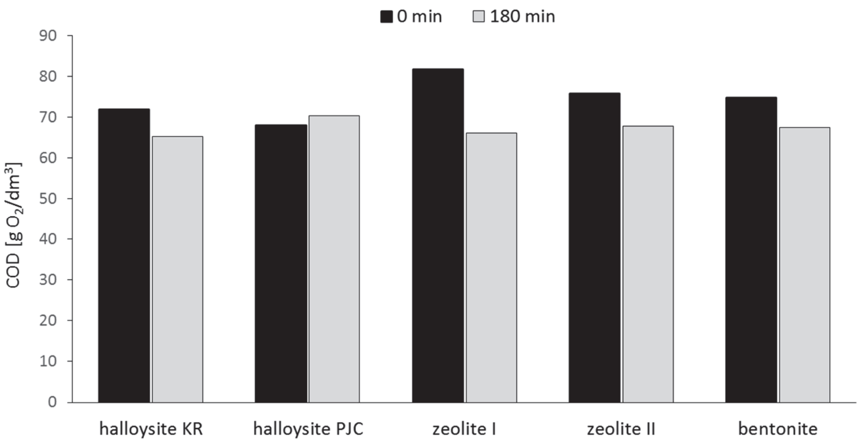

Fig. 2. Chemical oxygen demand for treated CBMV at time 0 and 180 minutes

Only for the decolorized vinasse sample using PJC halloysite, the COD content increased by 3% after three hours of shaking. In other cases, the chemical oxygen demand decreased by about 9-10%. The highest COD removal rate was obtained in the process using zeolite I, and it was 19.2%.

Satyawali and Balakrishnan (2007) obtained a decrease in COD of the vinasse (probably from sugar cane) by 23.6% with the use of active carbon produced from subject bagasse to phosphoric acid. A similar level of removal of COD was also noted in the work of Krzywonos and Łapawa (2012), in which strong alkaline ion exchange resins were used to decolorization sugar beet molasse vinasse. The most substantial removal of COD in undiluted vinasse was achieved using the Dowex 2 resin (23.09%).

The lower level of COD reduction compared to the degree of decolorization may result from the fact that melanoidins present in the vinasse during decolorization are broken down into other organic compounds that also need oxygen for their final degradation (Apollo et al. 2014). It should also be mentioned that in the tests carried out the vinasse was not diluted. Lakshmikanth and Virupakshi (2012) showed that increasing the concentration of the solution reduces color, which results from the higher saturation of the adsorption places.

In the presented studies, the degree of removal of total organic carbon (TOC), five-day biochemical oxygen demand (BOD_5) and phosphate phosphorus were determined only for vinasse samples with the addition of bentonite, in which the highest degree of decolorization was observed. The results obtained during the experiments are presented in Table 2.

Table 2. The content of colored compounds and pH value of the vinasse before (0 min) and after the decolorization process (180 min) with the use of bentonite

Parameter	Unit	Vinasse before decolorization (0 min.)	Vinasse after decolorization (180 min.)
TOC	[g/dm^3]	31.23	33.45
BOD_5	[$g\ O_2/dm^3$]	28.00	28.00
Phosphate phosphorus	[mg/dm^3]	513.00	300.00
Succinic acid	[g/dm^3]	13.94	10.81
Lactic acid	[g/dm^3]	22.71	21.56
Pyroglutamic acid	[g/dm^3]	12.61	6.52
Tartaric acid	[g/dm^3]	9.47	9.47
Glycerol	[g/dm^3]	21.26	brak
Glucose	[g/dm^3]	1.87	brak
Betaine	[g/dm^3]	25.30	17.70

Based on the data from table 2, it can be concluded that the decolorization process caused an increase in the total organic carbon content by about 7%. The BOD_5 value for samples before and after decolorization has not changed, from which it can be concluded that sorbents both before and after the decolorization process needed to oxidize organic compounds with the same amount of oxygen.

It can also be seen that the content of phosphate phosphorus was higher for vinasse before decolorization than about decolorized vinasse by about 215 mg/dm^3, and the phosphate phosphorus removal rate is 41%. It can be concluded that as a result of the absorption process, the content of succinic, lactic and pyroglutamic acid decreased. The highest decrease in the content (almost 50%) was noted in the case of pyroglutamic acid of almost 6.1 g/dm^3. The tartaric acid content remained unchanged. Both glycerol and glucose were removed by bentonite absorption. The content of betaine decreased after 180 minutes of shaking with bentonite by about 8 g/dm^3, i.e., by about 30%.

4. Conclusions

The most effective corn-sugar beet molasse's vinasse discoloration was obtained in the process using bentonite and halloysite PJC, respectively 62% and 74% discoloration. Melanoidins and alkaline products of invert degradation were most effectively removed with the participation of bentonite, while the caramels in the presence of halloysites KR and PJC. After the decolorization process, the content of COD and the content of phosphate phosphorus decreased in almost all samples, while the content of TOC increased. The content of individual acids decreased after the decolorization process of the vinasse using bentonite.

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Abstract

The molasse's vinasse, because it contains three groups of color processes in it, i.e., melanoidins, hexose alkaline degradation products, and sucrose caramelization products, is one of the most difficult to treat wastewater. Vinasse is toxic to various microorganisms, harmful to soil, groundwater, and vegetation. The aim of the study was using five natural sorbents: halloysite (PJC and KR), two types of zeolites differing in grain thickness and bentonite.

The highest decolorization (74% and 62%) was obtained in the process with bentonite and halloysite PJC. Melanoidins and hexose alkaline degradation products were removed when KR and PJC were dosed. After decolorization, in almost all experiments COD and phosphate phosphorus contents were reduced. When bentonite was tested, the organic acids were removed.

Keywords:
decolorization, vinasse, mineral sorbents, zeolite, bentonite, halloysite

Zastosowanie naturalnych sorbentów mineralnych (zeolit, bentonit, haloizyt) do usuwania związków barwnych z wywaru kukurydziano-melasowego

Streszczenie

Wywar melasowy, ze względu na zawarte w nim trzy grupy związków barwnych tj. melanoidyn, produktów alkalicznego rozkładu inwertu oraz produktów karmelizacji sacharozy, jest jednym z najtrudniejszych do unieszkodliwienia ścieków. Wywar jest toksyczny dla wielu mikroorganizmów, szkodliwy dla gleby, wód podziemnych i roślinności, dlatego przed odprowadzeniem wywaru do środowiska naturalnego substancje barwne muszą zostać z niego usunięte.

W pracy sprawdzono jak do usuwania związków barwnych z kukurydziano-melasowego wywaru gorzelniczego nadaje się pięć naturalnych sorbentów mineralnych: haloizyty PJC i KR, dwa zeolity różniące się grubością ziarna oraz bentonit.

Najbardziej efektywne odbarwienie (na poziomie 74% i 62%) uzyskano w procesie z zastosowaniem bentonitu oraz haloizytu PJC. Melanoidyny i produkty alkalicznego rozkładu inwertu najskuteczniej zostały usunięte przy udziale bentonitu, natomiast karmele w obecności haloizytów KR oraz PJC. Po procesie dekoloryzacji prawie we wszystkich próbach zmalała zawartość ChZT oraz zawartość fosforu fosforanowego, natomiast wzrosła zawartość ogólnego węgla organicznego. Po procesie dekoloryzacji wywaru z wykorzystaniem bentonitu zmalała również zawartość poszczególnych kwasów.

Słowa kluczowe:
dekoloryzacja, wywar, sorbenty mineralne, zeolit, bentonit, haloizyt

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Changes in Ecological State and Quality of Rów Wyskoć Waters

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1. Introduction

Small watercourses in agricultural landscape are less studied natural ecosystems, although they play significant role in environment. Small water basins and watercourses can be used as retention systems, have economic functions, elevate esthetic value of the landscape and provide habitats for a number of plants and animals. They are part of ecological islands and corridors connecting areas of particular natural importance and stimulate diversity of species (Dudzińska et al. 2016). The river Rów Wyskoć is localized in Wielkopolskie voivodeship and the study sites were selected inside the General Dezydery Chłapowski Landscape Park. The river collects water from smaller watercourses and from the surrounding arable lands and meadows with different intensity of use. The Landscape Park was established in 1992 in order to protect the rural landscape with the characteristic infield afforestations introduced in the 19th century by Chłapowski (Uglis et al. 2012). The catchment area of Rów Wyskoć watercourse, similarly as the entire Wielkopolska region, is characterized by low precipitation and water deficits (Kozaczyk et al. 2016). Such a watercourses are very important in water management and freshwater protection, agricultural retention, including the soil and landscape retentions. Increase of the soil retention in the microcatchment of Rów Wyskoć by only 1% would reduce the annual outflow from this microcatchment by 4%, which would make 8.9% of the outflow in the vegetation period (April-September) (Jankowiak et al. 2011).

Analysis of the ecological status of surface waters, including watercourses, apart from other factors, takes into account biological indices based on different tolerance of organisms to environmental variables such as water trophy, pH reaction, salinity, rate of flow and others. A number of indices characterizing the ecological status and trophy of flowing waters is based on the condition of macrophytes. In Poland, starting from 2008 the Macrophyte River Index (Makrofitowy Indeks Rzeczny in Polish, MIR) designed at the Department of Ecology and Environmental Protection in Poznań University of Life Sciences, has been in force and this index was used in our study (Directive of the Minister of Environment 2008, Szoszkiewicz et al. 2010).

2. Aim and methods of the study

Studies were undertaken to establish the direction of changes in the ecological state and trophy of Rów Wyskoć on the basis of biological indices and selected parameters describing water quality.

The field study needed for determination of the macrophyte indices were carried out in June and July 2017. The indices determined included the Macrophyte River Index (MIR) used in Poland for evaluation of ecological status (Szoszkiewicz et al. 2010) and Mean Trophic Rank (MTR) used in Great Britain and other countries (Poland, Ireland) for evaluation of trophy of flowing waters (Dawson et al. 1999, Holmes et al. 1999, Szoszkiewicz et al. 2002, Staniszewski et al. 2006, Staniszewski, Jusik 2013). In the field studies carried out along the section of 100 m at each study site, the coverage with particular taxa of vascular plants, ferns and macroscopic algae. Only the plants that have contact with water for over 90% of their vegetation period were taken into account. Each species was assigned with a specific degree of coverage. The MIR and MTR indices were calculated according to accepted procedures (Dawson 1999, Szoszkiewicz 2010):

Macrophyte River Index

$$MIR = \frac{\sum_{i=1}^{N}(L_i \cdot W_i \cdot P_i)}{\sum_{i=1}^{N}(W_i \cdot P_i)} \cdot 10$$

where:
N – the number of species,
Li –index number for a given species,
Wi – weigh coefficient of a given species,
Pi – coverage coefficient.

Mean Trophic Rank

$$MTR = \frac{\sum_{i=1}^{N}(STR_i \cdot SCV_i)}{\sum_{i=1}^{N} SCV_i} \cdot 10$$

where:
STR_i – the trophic index for a given species
(from 1 – hypertrophy to 10 – oligotrophy),
SCV_i – coverage coefficient.

Obtained results were compared with earlier studies, which were carried out in Wyskoć channel (Szoszkiewicz et al. 2006, Gołdyn et al. 2009).

In the sites covered with compact patches of water vegetation of areas greater than 10 m^2, the phytosociological releves were taken and the macro-phyte associations were identified (Braun-Blanquet 1928). The trophy of flowing water was evaluated on the basis of concentrations of total phosphorus, dissolved phosphates and nitrate nitrogen, using the Chemical Index of Trophy (CIT) (Staniszewski 2001, Staniszewski et al. 2019).

The catchment area of the Rów Wyskoć river was determined on the basis of the Raster Map of Hydrographic Divisions in Poland (the abbreviation in Polish MPHP) in the scale 1:50000 (2010) supplied by the National Water Management Authority (KZGW). The physiographic characteristics of the catchment was made on the basis of topographic maps in the scale of 1:10000 and the Digital Model of the Land (NMT) offered by Main Centre of Geodetic and Cartographic Documentation (CODGiK) The structure of the catchment area use was described on the basis of the Corine Land Cover Project realized by the General Inspectorate of Environmental Protection (GIOŚ).

The physico-chemical state of water was characterized on the basis of a set of data including 8 parameters describing water quality: dissolved oxygen (O_2), BOD5, conductivity at 20°C (µS cm^{-1}), pH reaction, ammonium nitrogen ($N\text{-}NH_4$), nitrate nitrogen ($N\text{-}NO_3$), nitrite nitrogen ($N\text{-}NO_2$) and soluble reactive phosphates (PO_4).

The classes of surface water quality were assumed according to the Act of Law in the Journal of Laws of August 5th 2016 on the classification of the state of uniform areas of surface waters and environmental norms of quality for priority substances. The sites of studies were three control sites in villages Racot (1), Wyskoć (2) and Rogaczewo (3) (Fig. 1).

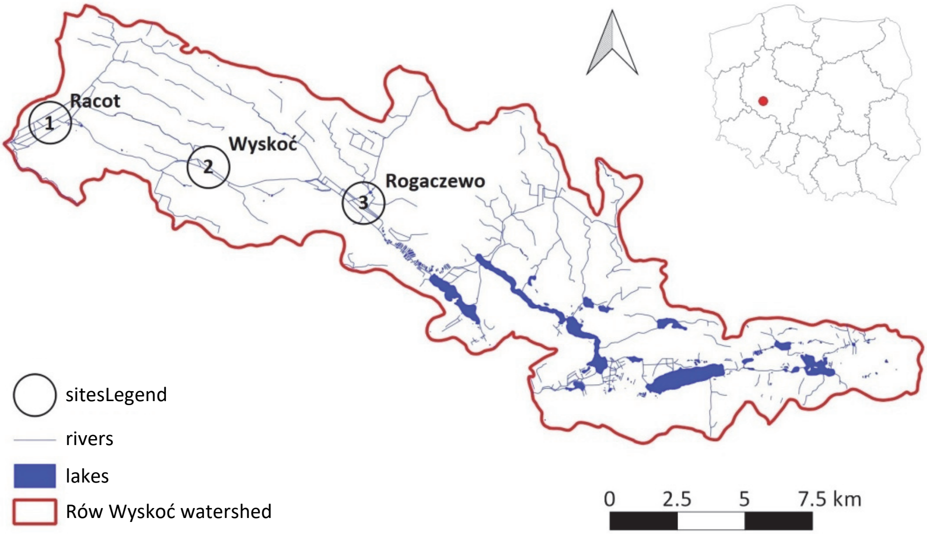

Fig. 1. Rów Wyskoć watercourse with marked sites of study

3. Characteristics of the study area

The catchment area of Rów Wyskoć spreads at 40 km south of Poznań, to the east of Kościan. It has typical lowland features and belongs to the mesoregion of Równina Kościańska (Kościan Plaine). The area in this part of Rów Wyskoć is under intensive agricultural use, where arable land occupies about 70% of the area, meadows and pastures about 10.5%, forests cover 15.5% (Kędziora et al. 1989).

Rów Wyskoć is the right tributary of the Kościan Channel of the Obra river, its length is 36.6 km and it joins this Channel at the 8th kilometer. The total area of Rów Wyskoć catchment is 174.3 km^2. Because of a considerable diversity of the landscape, agricultural use and geomorphology of the area, the catchment can be divided into two parts: region Turew and region Dolsk. The border between them was assumed to be the road connecting the villages Wyrzeka and Jerka. Region Turew (western part) is the area occupied mainly by arable land and has no water basins. This region is entirely within the Kościan Plaine and the area of this part of the catchment is 10 135 ha. Taking into account the administrative division, the whole catchment of Rów Wyskoć belongs to 6 communes. The area that was studied in detail is located within the Kościan commune (Fig. 2).

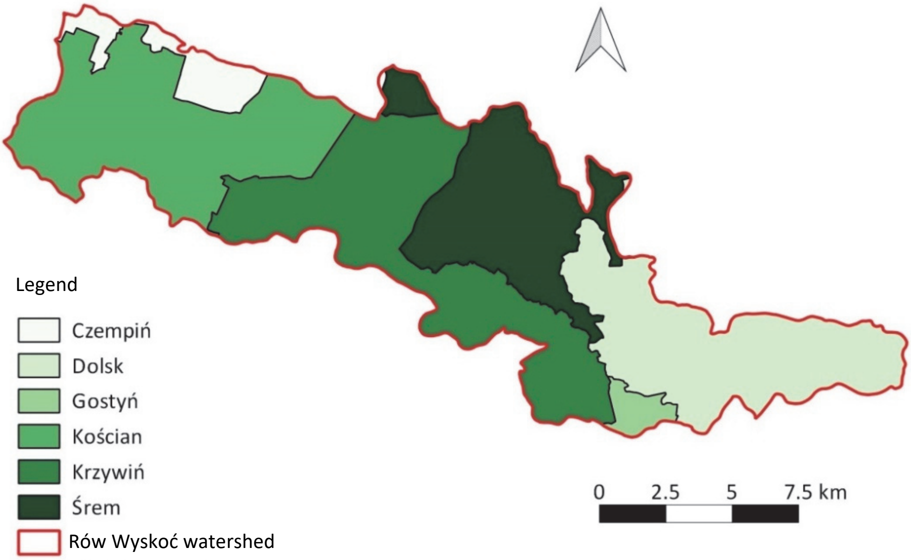

Fig. 2. Rów Wyskoć basin on the background of the administrative division

The structure of land use over the analyzed part of Rów Wyskoć catchment area is similar and arable land covered 74% of the area, while forests 14.1% (Fig. 3).

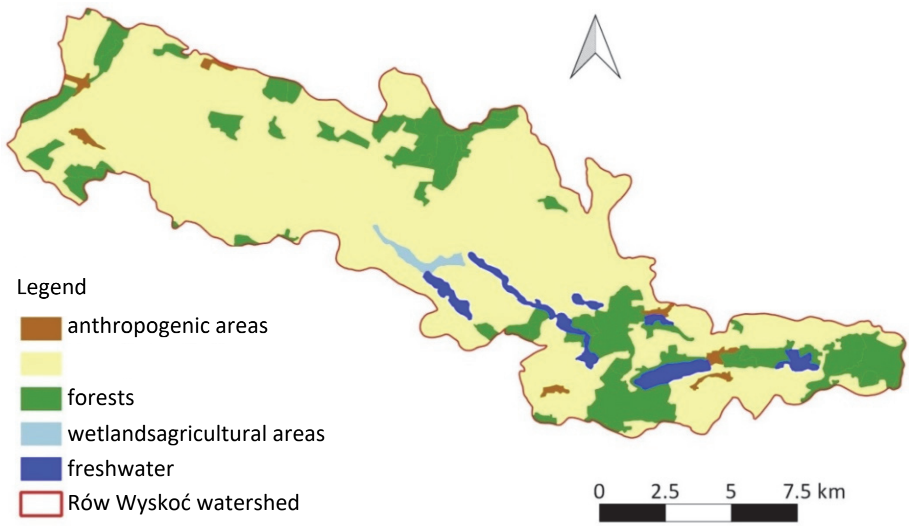

Fig. 3. Structure of land use in the Rów Wyskoć watershed

Ecological status of surface waters, including watercourses, was evaluated using a number indices, among others biological ones based on different tolerance of living organisms to different environmental factors such as water trophy, pH reaction, salinity, rate of water flow and others. The presence of aquatic plants (macrophytes) is the basis for biological indices characterizing the ecological state of watercourses.

4. Results of the study

The three 100 m long sections of Rów Wyskoć were built of sandy sediments with a certain contribution of the organic fraction (abiotic type 17 – lowland sandy stream) and in the period of study the character of flow in the Rów Wyskoć was observed.

In the year 2017 the level of trophy and ecological state at the three surveyed sites were similar (Table 1-5). The macrophyte indices were diversified however, at site 1 in Racot the trophy was higher and the ecological status was lower than at the other two sites. Moreover, at this site patches of *Urtica dioica* were noted, which suggests existinf of point source of nitrogen (Table 2). At site 1, the structure of water vegetation was studied also in 2003 (Szoszkiewicz et al. 2010) and a similar results were obtained. For site 2 it was possible to compare results with the data collected at four other seasons (Table 3) and each time the results corresponded to a good ecological status, despite the value of MIR decreasing from 42.7 in 1976 to 36.7 in 2017. At site 3 Rogaczewo, an improvement in the ecological status was noted in comparison with the data from 2003 and 2007, up to a good state, however macrophyte index was poorer than in 1976 (Table 3). In 2017, the MIR values recorded at allstudied sites were similar, which was not only a consequence of comparable species composition of water plants but also similar contributions of particular taxa in the total cover. At sites 1, 2 and 3 the number of indicatory taxons identified was 25, 26 and 28, respectively, at a similar total coverage at sites 2 and 3. At site 1 the cover with *Lemna minor* was greater, (cover coefficient $P = 7$), which at the indicative value $L = 2$ gave a lower value of MIR. Trophic conditions of Rów Wyskoć water evaluated in 2017 by the Mean Trophic Rank was similar at the three sites and showed increase of water trophy (Table 4).

In the group of plants mentioned in Table 2, that do not have indicatory MIR values, the majority represented species commonly seen in lowlands near watercourses or ponds, such as *Phragmites australis, Lycopus europaeus, Carex pseudocyperus, Malachium aquaticum* (Kłosowski S, Kłosowski G. 2001, Rutkowski 2006). For instance, reed is found in oligotrophic as well as eutrophic waters so it is difficult to assign to it an indicatory value.

Table 1. List of taxa present in studied sites of Rów Wyskoć channel in the year 2017 with cover (*P*), indication value (*L*) and weight coefficient (*W*)

	1	2	3	L	W
	P				
Algae					
Cladophora sp.	5	1		1	1
Chara sp.			1	6	2
Pteridophytes					
Equisetum fluviatile		1		6	2
Dicotyledons					
Berula erecta	4	3	4	4	2
Callitriche cophocarpa	2	1		5	2
Ceratophyllum demersum		3	2	2	3
Ceratophyllum submersum		1	2	2	3
Hydrocotyle vulgaris	1		2	5	1
Lysimachia vulgaris	1		1	4	1
Mentha aquatica	1	1	1	5	1
Myosotis palustris	2	1	1	4	1
Nuphar lutea			1	4	2
Polygonum amphibium	2	1	1	4	1
Ranunculus circinatus	1			5	2
Rorippa amphibia		1	1	3	1
Rumex hydrolapathum	1	1	1	4	1
Sium latifolium	1	1	1	7	1
Veronica anagalis-aquatica		1		4	2
Monocotyledons					
Acorus calamus	1		1	2	3
Alisma plantago-aquatica	3	2	1	4	2
Butomus umbelatus	1	1		5	2
Carex acutiformis	1	1	1	4	1
Carex riparia	3		2	4	2
Elodea canadensis	3	1	1	5	2
Glyceria fluitans			1	5	2
Glyceria maxima	4	1	5	3	1

Table 1. cont.

	1	2	3	L	W
	P				
Monocotyledons					
Glyceria plicata		1		5	1
Hydrocharis morsus-ranae	1		1	6	2
Iris pseudoacorus	1	2	1	6	2
Lemna minor	7	3		2	2
Lemna trisulca			3	4	2
Phalaris arundinacea	5			2	1
Potamogeton crispus		3		4	2
Potamogeton natans		1	1	4	1
Sagittaria sagittifolia		1	1	4	2
Sparganium emersum	2	3	3	4	2
Sparganium erectum	2	6	1	3	1
Typha latifolia	2		4	2	2

Table 2. List of identified taxa without MIR indication value

Site	Taxa identified also in years 1976-2007	Other species
1 Racot	No data	*Agrostis stolonifera, Eupatorium cannabinum, Lycopus europaeus, Lysimachia nummularia, Malachium aquaticum, Phragmites australis*
2 Wyskoć	*Bidens frondosa, Lycopus europaeus*	–
3 Rogaczewo	*Agrostis stolonifera, Bidens frondosa, Calystegia sepum, Carex pseudocyperus, Lysimachia nummularia, Phragmites australis*	*Urtica dioica*

Table 3. Ecological status of study sites at Rów Wyskoć in the year 2017 on the background of earlier studies (years 1976 and 2007: Gołdyn et al. 2009; year 2003: Szoszkiewicz et al. 2006)

Site	Macrophyte River Index				Ecological status			
	1976	2003	2007	2017	1976	2003	2007	2017
1 Racot	-	33.4	-	34.8	-	moderate	-	moderate
2 Wyskoć	42.7	40.3	38.0	36.7	good	good	good	good
3 Rogaczewo	44.1	32.2	32.3	36.1	good	moderate	moderate	good

Table 4. Values of MTR index, ecological status and water trophy at the study sites on Rów Wyskoć in the year 2017

Site	Mean Trophic Rank (MTR)	Ecological status	Trophic status
1 Racot	34.8	moderate	eutrophy
2 Wyskoć	36.7	good	eutrophy
3 Rogaczewo	36.1	good	eutrophy

Table 5. Concentrations of soluble reactive phosphates, total phosphorus and nitrates in surveyed sites of Rów Wyskoć in June 2017 and trophic status according to Chemical Index of trophy (CIT)

Site	Soluble reactive phosphates mg PO_4 dm^{-3}	Total phosphorus mg P dm^{-3}	Nitrate nitrogen mg N-NO_3 dm^{-3}	Trophic status CIT
1 Racot	0.87	0.39	0.80	Meso-eutrophy
2 Wyskoć	1.17	0.43	0.00	Meso-eutrophy
3 Rogaczewo	0.40	0.29	1.20	Eutrophy

On the basis of the data from three vegetation seasons for sites 2 and 3, it is possible to draw conclusions on some tendencies of changes in the macrophyte species composition. At site 2, the number of indicatory taxa increased from 9 in 1976, to 21 in 2007 and 26 in 2017, while at site 3 the analogous numbers were

26, 17 and 28 taxa. At site 3, in the year 2017 following species were not observed: *Hippurus vulgaris* (prefers water rich in calcium), *Ranunculus circinatus* (eutrophic water, sand-silt substrate) and *Eleocharis palustris* (eutrophic water, sandy substrate). The absence of these species may indicate increased shadowing of the sites and changes in the character of the river sediments. At site 2 in 2017, lackof *Lemna trisulca* was observed (although it is common in the entire country), whereas the appearance of *Ceratophyllum submersum* (scattered sites in Poland), *Polygonum amphibium* (sandy substrate, common in Poland) and *Potamogeton crispus* (eutrophic water, common species) was noted. At the three studied sites of Rów Wyskoć, five associations of water vegetation were identified, four from the class of *Phragimitetea* (*Glycerietum maximae*, *Phalaridetum arundinaceae, Sparganietum erecti, Typhetum latifoliae)* and one from the class of *Lemnetea* (*Lemno-Spirodeletum*).

The syngenetic units of water plants identified in the field studies:

<u>Site 1 (Racot)</u>

Phragmitetea (Tx. et Preisg. 1942)
Phragmitetalia (Koch 1926)
Phragmition (Koch 1926)
Glycerietum maximae (Nowiński 1928; Hueck 1931)
Magnocaricetalia (Pign. 1953)
Magnocaricion (Koch 1926)
Phalaridetum arundinaceae (Libb. 1931)
Lemnetea (Koch et Tx 1954)
Lemnetalia (Koch et Tx. 1954)
Lemnion minoris (Koch et Tx. 1954)
Lemno-Spirodeletum (Koch 1954)

<u>Site 2 (Wyskoć)</u>

Phragmitetea (Tx. et Preisg. 1942)
Phragmitetalia (Koch 1926)
Phragmition (Koch 1926)
Sparganietum erecti (Roll 1938)

<u>Site 3 (Rogaczewo)</u>

Phragmitetea (Tx. et Preisg. 1942)
Phragmitetalia (Koch 1926)
Phragmition (Koch 1926)
Glycerietum maximae (Nowiński 1928; Hueck 1931)
Typhetum latifoliae (Soó 1927).

The association of *Glycerietum maximae* is typical of eutrophic habitats and shows diverse composition of species (Podbielkowski and Tomaszewicz 1996). It is supposed to play a considerable role in overgrowing of lakes and old river beds. At sites 1 and 3 this association is accompanied with *Lemna minor* (1) and *Lemna trisulca* (3).

The association of *Phalaridetum arundinaceae* forms compact phytocenoses, characteristic of eutrophic waters (Podbielkowski and Tomaszewicz 1996). *Phalaris arundinaceae* can be used as a plant species protecting the banks of rivers and ditches against erosion by strengthening them with root system (Pawłat and Nazaruk 1991). In fast flowing waters, it can substitute reeds. Some patches observed at site 1 included the contributions of duckweed, reed sweet-grass and common frogbit.

The association of *Sparganietum erecti* forms the rush-bed of diverse species composition (Podbielkowski and Tomaszewicz 1996). It has anthropogenic character and can develop at sites exposed by macrophyte cutting (Matuszkiewicz 1981). This association occurs at site 2 (Wyskoć) with a contribution of *Sparganium emersum*.

The association of *Typhetum latifoliae* usually occupies eutrophic sites on organic or organic-mineral substrate. It often forms floristically rich communities of distinct bilayer structure, but at site 3 (Rogaczewo) the species composition was reduced to *Typha latifolia* with a small contribution of duckweed. This association is characteristic for mesotrophic and eutrophic habitats and plays a significant role in detrophication of waters (Rodwell 1995, Podbielkowski and Tomaszewicz 1996).

The association of *Lemno-Spirodeletum* occurs mainly in eutrophic and mesotrophic waters (Podbielkowski and Tomaszewicz 1996). In the studied sites the association covered small areas at site 1, accompanied with *Cladophora* sp. and lesser water-parsnip. The presence of *Cladophora* is a good indicator of eutrophication of surface waters and often correlated with the inflow of phosphates from anthropogenic sources (Parker and Maberly 2000).

Analysis of the physico-chemical state of Rów Wyskoć waters in the vegetation period of 2017 proved, that water was highly oxygenated only at the beginning of the vegetation season (10.6 mg $O_2 \cdot dm^{-3}$). The mean value of dissolved oxygen in the vegetation season 2017 was 6.6 mg $O_2 \cdot dm^{-3}$, which implies that the water quality was below good state. The pH value varied from 8.43 to 8.78, which also classified the water quality below good state. The level of loading with organic pollutants, whose presence contributed to the use of oxygen in the process of self-cleaning, was at a medium level. The value of BOD5 varied from 1.26 to 6.48 mg $O_2 \cdot dm^{-3}$ (the mean value was 3.34 mg $O_2 \cdot dm^{-3}$). The water conductivity varied from 655 to 792, with the mean value of 722 $\mu S \cdot cm^{-1}$. Also these two indicators caused that the water quality was below good state.

According to the level of biogenic substances, the water quality was also classified as below good. The content of phosphates varied from 0.05 to 0.26 mg $PO_4 \cdot dm^{-3}$ at the mean of 0.17 mg $PO_4 \cdot dm^{-3}$. The contents of nitrate nitrogen and nitrite nitrogen were 2.46 mg $\cdot$ dm^{-3} and 0.07 mg $\cdot$ dm^{-3} respectively.

5. Summary

Development of agriculture, in particular increased use of chemicals for different purposes, significantly contributed to the elevated level of mineral components in the water discharge from the fields. The consequence was excessive trophy of surface waters accelerating eutrophication. The main sources of pollution were intensification of agricultural production (including excessive fertilization with mineral and organic substances) in the drained areas with increasing amount of households, farmhouses and industrial wastes. Nitrogen compounds occurring in surface water can be of organic or inorganic origin. Almost each chemical form of nitrogen stimulates the process of eutrophication and leads to elevation of biological productivity of waters. The eutrophication of surface waters depends on high concentration of organic and inorganic phosphorus compounds, both soluble and insoluble in water. They originate mainly from the municipal sewage, waters from agriculture (fertilizers, pesticides) and soil erosion caused by landscape changes.

Analysis of the data from monitoring of river water permits evaluation of effectiveness of measures taken to restrict the inflow of pollutants from point and non-point sources of pollution. Results of such a monitoring also support rational management of water resources (Shrestha and Kazama 2007). Evaluation of changes in the ecological state of Rów Wyskoć waters performed on the basis of historical data and confronted with presented studies has shown, that despite a continuous decrease in the macrophyte indices (Table 3), the water at the three study sites was characterized by good or moderate ecological state. At site 1 in Racot, the trophy was the highest and the ecological state the lowest from among the three sites studied. At site 3 in 2017, the ecological state was still good although the values of macrophyte indices were lower than in 1976 (Table 3). The trophy of Rów Wyskoć water in 2017 determined by the MTR method corresponded to eutrophied waters.

Obtained results showed an increase of the number of taxa in comparison to the historical data however, particular species were no longer present. For instance, at site 3 in 2017, lack of *Hippurus vulgaris* (indicator of Ca level in water), *Ranunculus circinatus* (sand-muddy substrate) and *Eleocharis palustris* (sandy substrate) were found. Their absence can indicate increase of shadowing of the site, modification of water chemistry and changes in the physicochemical character of the river sediments. Certain changes in the species composition do not depend directly on the changes in water quality indicators, e.g. at site 2 in a commonly occurring plant *Lemna trisulca* was not found, but other species appeared, like *Ceratophyllum submersum,* which occupies scattered sites all over the country. Actual studies showed, that especially shadowing can play crucial role in limitation of the presence of aquatic taxa (Jusik and Staniszewski 2019).

At the study sites on Rów Wyskoć five associations of water plants were identified, including four from the class of *Phragimitetea* and one from the class of *Lemnetea*. These associations are characteristic of eutrophic waters, often have anthropogenic character and occur near the sites or areas that are the sources of pollutants (Rodwell 1995).

6. Conclusions

1. On the basis of values of macrophyte indices it can be concluded that the ecological state of water at the sites in Wyskoć and Rogaczewo was good, while the water at the site Racot was of moderate ecological state.
2. Analysis of macrophyte indices determined at the three sites of study indicated equalization of the ecological state and level of trophy in the water of Rów Wyskoć watercourse.
3. Analysis of physicochemical data characterizing the Rów Wyskoć water in the vegetation season of 2017 showed that the water quality was below good state.

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Abstract

Studies were were undertaken to evaluate the direction of changes in the ecological state and trophy of Rów Wyskoć on the basis of biological indices and selected indices describing the water quality parameters. The field study needed for determination of the macrophyte indices were carried out in June and July 2017. The indices used in paper were the Macrophyte River Index (MIR) used in Poland for evaluation of ecological status and Mean Trophic Rank (MTR) used in Great Britain and other countries (Poland, Ireland) for evaluation of trophy of flowing waters. In the field studies carried out along the section of 100 m at each study site, the coverage with particular taxa of vascular plants, ferns and macroscopic algae. Only the plants that have contact with water for over 90% of their vegetation period were taken into account. Each species was assigned with a specific degree of coverage.

In the sites covered with compact patches of water vegetation of areas greater than 10 m^2, the phytosociological releves were taken and the macrophyte associations were identified. The sites of studies were three control sites in villages Racot (1), Wyskoć (2) and Rogaczewo (3). The trophy of flowing water was evaluated on the basis of concentrations of total phosphorus, dissolved phosphates and nitrate nitrogen, using the Chemical Index of Trophy (CIT)

The catchment area of the Rów Wyskoć watercourse was determined on the basis of the Raster Map of Hydrographic Divisions in Poland (the abbreviation in Polish MPHP) in the scale 1:50000 (2010) supplied by the National Water Management Authority (KZGW). The physiographic characterization of the catchment was made on the basis of topographic maps in the scale of 1:10000 and the Digital Model of the Land (NMT) offered by Main Centre of Geodetic and Cartographic Documentation (CODGiK) The structure of the catchment area use was described on the basis of the Corine Land Cover Project realized by the General Inspectorate of Environmental Protection (GIOŚ).

The physicochemical state of water was characterized on the basis of a set of data comprising 8 parameters describing water quality: dissolved oxygen (O_2), BOD5, conductivity at 20°C ($\mu S \cdot cm^{-1}$), pH, ammonium nitrogen ($N\text{-}NH_4$), nitrate nitrogen ($N\text{-}NO_3$), nitrite nitrogen ($N\text{-}NO_2$) and phosphates (PO_4). The classes of surface water quality were assumed according to the Act of Law in the Journal of Laws of August 5th 2016 on the classification of the state of uniform areas of surface waters and environmental norms of quality for priority substances.

On the basis of values of macrophyte indices it can be concluded that the ecological state of water at the sites in Wyskoć and Rogaczewo was good, while the water at the site Racot was of moderate ecological state.

Analysis of macrophyte indices determined at selected sites of study indicated similarity of the ecological state and level of trophy in the water of Rów Wyskoć. Analysis of physicochemical data characterizing the Rów Wyskoć water in the vegetation season of 2017 showed that the water quality was below the good state.

Keywords:
water quality, biological indicators, macrophytes

Zmiany stanu ekologicznego i jakości wód Rowu Wyskoć

Streszczenie

Celem pracy było określenie kierunku zmian stanu ekologicznego oraz trofii Rowu Wyskoć. Wykorzystano również wskaźniki biologiczne oraz wyniki analiz wybranych wskaźników jakości wody. Prace terenowe niezbędne do określenia wartości wskaźników makrofitowych przeprowadzono w czerwcu i lipcu 2017 roku. Wykorzystano wskaźnik MIR (Makrofitowy Indeks Rzeczny) używany w Polsce do oceny stanu ekologicznego oraz MTR (Mean Trophic Rank) wykorzystywany w Wielkiej Brytanii i w innych krajach (Polska, Irlandia) w ocenie trofii wód płynących. Podczas prac terenowych prowadzonych na odcinku 100 metrów na każdym stanowisku, odnotowano pokrycie poszczególnych taksonów roślin naczyniowych, paprotników i glonów makroskopowych. Uwzględniono tylko rośliny mające kontakt z wodą przez ponad 90% okresu wegetacji. Każdemu gatunkowi przypisano stopień pokrycia powierzchni cieku. W miejscach, gdzie występowały zwarte płaty roślinności wodnej o powierzchni ponad 10 m^2 wykonano zdjęcia fitosocjologiczne i wyznaczono zespoły roślinne tworzone przez makrofity. Wybrano trzy punkty kontrolne, które znajdowały się w miejscowościach Racot (1), Wyskoć (2) i Rogaczewo (3).

Trofię wód płynących określono na podstawie stężeń fosforu ogólnego, fosforanów rozpuszczonych oraz azotu azotanowego z wykorzystaniem Chemicznego Indeksu Trofii CIT.

Zlewnię Rowu Wyskoć wyznaczono na podstawie Rastrowej Mapy Podziału Hydrograficznego Polski (MPHP) w skali 1:50000 (2010) udostępnionej przez Krajowy Zarząd Gospodarki Wodnej (KZGW). Charakterystykę fizjograficzną zlewni określono na podstawie map topograficznych w skali 1:10000 oraz Numerycznego Modelu Terenu (NMT) udostępnionego przez Centralny Ośrodek Dokumentacji Geodezyjnej i Kartograficznej (CODGiK). Strukturę użytkowania zlewni określono na podstawie projektu Corine Land Cover Głównego Inspektoratu Ochrony Środowiska (GIOŚ).

Stan fizykochemiczny wód scharakteryzowano na podstawie zbioru danych, który obejmował 8 parametrów jakości wody: tlen rozpuszczony (O_2), BZT_5, przewodność w 20°C ($\mu S \cdot cm^{-1}$), odczyn (pH), azot amonowy ($N\text{-}NH_4$), azot azotanowy (N-

NO_3), azot azotynowy (N-NO_2) oraz fosforany (PO_4). Klasy jakości wód powierzchniowych przyjęto zgodnie z Dziennikiem Ustaw z dnia 5 sierpnia 2016 roku w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych oraz środowiskowych norm jakości dla substancji priorytetowych.

Na podstawie wskaźników makrofitowych można stwierdzić, że odcinki zlokalizowane w miejscowościach Wyskoć i Rogaczewo mieściły się w dobrym stanie ekologicznym, jedynie odcinek w Racocie wykazywał umiarkowany stan ekologiczny. Wyniki uzyskane przy wykorzystaniu metod makrofitowych wskazują na postępujące wyrównywanie się stanu ekologicznego oraz poziomu trofii pomiędzy badanymi stanowiskami. Analiza stanu fizykochemicznego wód Rowu Wyskoć w okresie wegetacyjnym 2017 roku wykazała, że wszystkie analizowane wskaźniki klasyfikowały wodę tego cieku poniżej stanu dobrego.

Słowa kluczowe:
jakość wód, wskaźniki biologiczne, makrofity

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Depopulation in the Concept of Sustainable Development

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1. Introduction

The concept of sustainable development was first used in 1713 by H.C. von Carlowitz in his deliberations on the crisis in the mining industry and the idea of sustainable forest management (Najder-Stefaniak 2017, p. 191). In the public debate, it was used again in the 1970s as a response to the fuel crises and the perceived environmental consequences of economic development and resource constraints. Initially, sustainable development was defined as *development that meets the needs of the present without compromising the ability of future generations to meet their own needs. It* contains within it two key concepts:

a) *the concept of 'needs', in particular the essential needs of the world's poor, to which overriding priority should be given; and*
b) *the idea of limitations imposed by the state of technology and social organization on the environment's ability to meet present and future needs* (Our Common Future 1987).

The concept has not become normative, although it has been enshrined in numerous documents and acts of international and national law (Kenig-Witkowska 2018, p. 28-29). An example is Article 5 of the Constitution of the Republic of Poland, in which the legislator refers to an undefined concept of sustainable development as a principle to be followed by the Polish state in its actions.

In further considerations, sustainable development is understood *as a paradigm based on an over-egocentric system of values – the recognition of one's humanity as a compass for personal and social development and other complementarily connected aspects of development – economic and environmental.* (Borys 2019) The analysis of the concept expressed in relation to man, his place and role in the world, allows to indicate the process of evolution from an integrated approach to environmental, human, and development problems (Kenig-

Witkowska 2018, p. 29) to the search for opportunities to shape 'proper relations' between the human, natural, and economic capital. The foundations of the concept have also been laid for trends which, while declaring their use of the concept of sustainable development, express a clear hostility towards human existence (hereinafter referred to as depopulation trends). As a result of the activities of UN agencies, they are gaining more and more importance in the global dimension.

Depopulation trends are characterized by an approach that takes away human subjectivity and a special place and function, determined by the Creator that makes the Earth subject to themselves. Man perceived as a form of capital is contrasted with and equivalent to natural and economic capital. As a consequence, it is subject to shaping, management, assessment of its usefulness and effectiveness, as well as reduction. The development of depopulation trends is based on the desire of their supporters to build a new global economic and social order. In fact, these trends negate the essence of sustainable development, which by definition cannot assume the existence of phenomena such as depopulation, failure to respect the institution of the family, low remuneration, widespread use of abortion or euthanasia. These phenomena are evidence of unsustainable development.

The paper presents an attempt to characterize depopulation trends in the concept of sustainable development and analyze their impact on structural changes. As indicated by the authors of numerous publications, the problem of depopulation will be one of the main problems of the 21st century. Current research indicates the global, national, and regional dimension of the phenomenon. The consequences of depopulation processes are strongly felt in Europe, Japan, and China. Among the highly developed countries, the population is growing in Australasia (New Zealand and Australia) (Jackson 2014).

2. Roots of depopulation concepts

The concept of depopulation derives directly from eugenics, which was dynamically developing in the USA before World War II and was implemented and developed by Nazi Germany. Formally, depopulation efforts in the post-war period were initiated by the World Population Conference (WPC) in Bucharest, Romania, in August 1974 and the resulting World Population Plan of Action (WPPA 1974). The document indicates the risks to sustainable development arising from population growth. It calls for population policy to become an integral part of economic and social policy. Actions aimed at reducing the population must not contribute to limiting development activities. At the same time, the document defines reproductive rights to control and limit the population.

The document presenting the comprehensive concept of global depopulation together with the tools of its implementation is the *National Security Study Memorandum*, kept secret until the 1990s. *NSSM 200. Implications of Worldwide*

Population Growth for U.S. Security and Overseas Interests (The Kissinger Report) (Kissinger 1974). Population growth in underdeveloped but resource-rich countries is identified by The Kissinger Report as the most important threat to the political and economic security of the US and other developed countries (Kissinger 1974, p. 57). The proposed remedy to the identified risks is a global fertility reduction strategy (Kissinger 1974, p. 74), based on the promotion of lifestyles alternative to parenthood, the development of contraception (Kissinger 1974, p. 110) and the assurance and promotion of abortion as a basic human right (Kissinger 1974, p. 114-120).

A significant event in the development of depopulation trends was also the International Conference on Population and Development (ICPD) held in Cairo in 1994, which resulted in The Cairo consensus. As its supporters and promoters point out, the Cairo consensus is based on values such as gender equality, sexual and reproductive health, and reproductive rights. The importance of this consensus for the development of depopulation is demonstrated by the words of Thoraya Ahmed Obaid, Executive Director of UNFPA, the United Nations Population Fund: *Cairo was a landmark meeting at which 179 governments agreed on a comprehensive set of actions to ensure universal access to reproductive health information and services, uphold fundamental human rights, reduce poverty, secure gender equality, protect the environment, and strengthen the institutions of democracy* (Obaid 2004). Attempts to block key depopulation mechanisms contained in the Cairo consensus have been made by the Vatican.

Depopulation roots should also be sought in the ongoing economic processes. The basic barrier to realising the neoclassical paradigm of continuous economic growth and wealth creation is the scarcity of natural resources coexisting with a growing population. The scarcity of resources excludes the possibility of a continuous increase in production and material consumption, as well as a levelling of wealth among the existing global population.

In the pre-industrial period, similar to the natural phenomena, technological progress and an increase in production contributed to a proportional increase in the population. The availability of food and goods satisfying basic needs, the increase in the quality of life meant that more and more of the newborn children lived to the procreative age. As a result, the population grew, the wealth of the individual remained stable or increased slightly. The decline in population and wealth was caused by epidemics, wars, and natural disasters. Since the Industrial Revolution, the technical and technological progress has served primarily to increase the wealth of the individual. The improvement in the quality of life and wealth is not accompanied by a proportional increase in the number of births (Fig. 1).

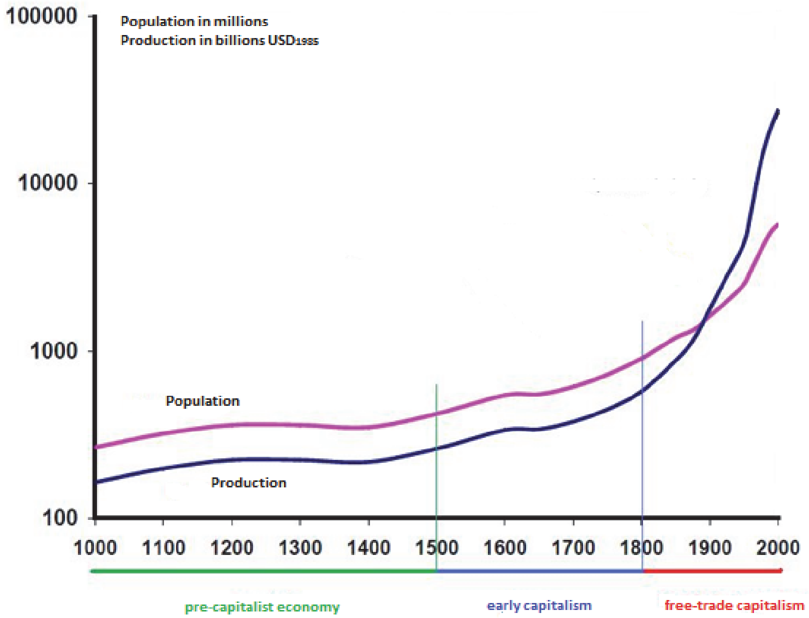


Fig. 1. Population and production in the world

Source: author's own work based on (Lucas 2010)

The globalisation process, the technological revolution, the ongoing changes in the functioning of the labour market constantly lead to the release of a growing part of the population from the labour market. The population consumes limited resources, contributes less to wealth creation, and needs to be managed. In the future, as indicated by U. Beck, workers' privileges acquired in the 20th century in rich countries will be rejected. A worker will have to work more and more for a lower wage and with worse social security coverage (Beck 2002, p. 26). To an increasing extent, the work performed by people is worthless and has the character of activities *that are supposed to bring only money to people – these are jobs that no one in the world would have to do, should not do or would not simply do if they were not paid for* (Lewis 2014, p. 91).

According to the theory of competitive advantage of M. Porter's nations, in modern conditions, the competitive advantage is determined by the resources of highly qualified employees with competences necessary for specific industries (Porter 1990). Human capital therefore constitutes a resource selected on the basis of criteria of productivity, creativity, and specialisation of individuals. The importance of highly qualified employees with the competences necessary for specific sectors is confirmed by the forecasts for the demand for specialists prepared for highly developed countries. For example, the German economy will lack 3 million skilled workers in 2030. In the perspective of 2040 this number will increase to 3.3 million people (Prognos AG 2015). At the same time, as a result of automation, automotive, transport, and financial services sectors will lose importance. People currently employed in these industries will become economically redundant. According to the projections presented by Pricewaterhouse-Coopers – by the early 2030s – the U.S. will lose 38 percent of existing jobs to automation. U.K. is expected to lose – 30%, Germany – 35% and Japan – 21% of jobs, respectively to machines within the same time frame (Pricewaterhouse-Coopers 2017).

3. The importance of population size for economic growth and development

Globally, there are two main approaches to perceiving population as a factor of economic growth and development: the approach of highly developed countries (depopulation approach) and the approach represented by the Middle Kingdom. The highly developed countries' approach is based on the principle of increasing marginal efficiency. According to this principle, each successive unit of resource should be used more efficiently than the previous one, each successive human being more productive, creative, and specialized.

The proponents of a population policy based on depopulation (among them: Ban Ki-Moon, former UN Secretary, Jeffrey Sachs, economist, Hans Joachim Schellnhuber, German atmospheric physicist, Bill Gates, founder of Microsoft, Ted Turner, CNN Chief Executive Officer, George Soros, David Rockefeller Junior, Oprah Winfrey), as a tool to eliminate the barrier of resource scarcity, propose to reduce the global population and maintain a stable, reduced population in the future. Depopulation is presented as a tool for the implementation of the principle of intergenerational equality enshrined in the 1987 Our Common Future, an expression of concern for the living conditions of future generations and the negative effects of overcrowding of the Earth (such as rapid degradation of the global natural environment, extreme poverty, famine and chronic malnutrition, illiteracy, drama of people with disabilities, military conflicts, the often tragic consequences of mass migration) and the creation of decent living conditions for people on the planet. At the same time, they reject calls for changes in existing patterns of production and consumption, including abandoning the strategy of increasing consumption through the ageing of products and continuous creation of new needs of the inhabitants of highly developed countries.

In economic terms, the reduction of population combined with increased resource efficiency and measures to decouple economic growth from natural resources should enable continuous and unrestricted economic growth. In the ecological dimension, depopulation is to be used to reduce environmental pressure, and in the social and political dimension, it is treated as a tool to eliminate conflicts between the rich and the poor (Fig. 2).

CityGroup pointed to the process of extreme economic stratification of societies and the resulting threats in 2005 by introducing the concept of *plutonomy* (Equity Strategy 2005). According to the data of Oxfam humanitarian organisation, in 2016 one percent of the richest people owned more wealth than the rest of humanity. The high rate of concentration of wealth in the hands of a small group of the richest people is noteworthy (Piontek 2015). These inequalities are contested in surveys that take into account the differences in population among countries (Woźniak 2006). The reduction of poverty is also indicated by United Nations' documents, according to which the number of people in the world living in extreme poverty has more than halved compared to the year 1990[1].

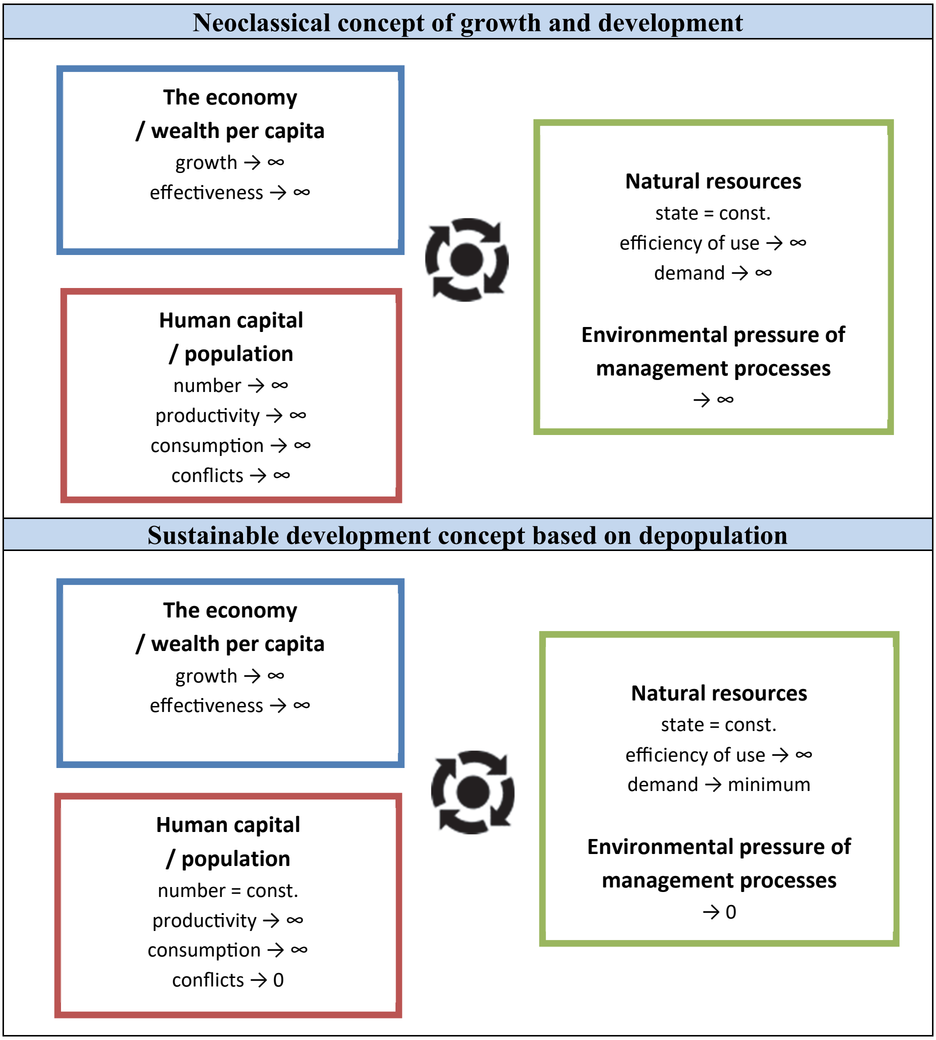
A different approach to the importance of human capital in quantitative terms is characteristic of China, which recognises the importance of the country's population for development and global expansion. During[2] the Meeting Marking the 30th Anniversary of Reform and Opening Up, Hu Jintao pointed out the following: *These efforts and achievements vividly demonstrate the power of the Party and the Chinese government, which are developing in tandem with the reform and opening policy, the power of China's 1.3 billion population as it advances, the power of reform and opening and the power of socialism with Chinese characteristics*. (Juntao 2008) In 2015 China ended its one-child policy conducted since 1979 by allowing the citizens to have two children (End of one-child policy 2018). In the wake of growing demographic problems, the government introduced incentive schemes for having a second child (cash incentives, tax breaks, extension of maternity leave). Works are underway to remove from the Civil Code all regulations concerning family planning in terms of children and legalization of surrogate parenting since 2020 (China One-child policy 2019).

At the same time, as part of its population policy, since 2014 China has been implementing a system of control and evaluation of citizens named the Social Credit System. In the system, citizens receive 'positive' points for behaviours desired by state authorities (for complying with the law, promoting ethical behaviour in society and 'good deeds,' e.g. donating blood or volunteering). Citizens committing violations of the law and established rules are subject to penalties in the form of deduction of points. Rewards and privileges are given to highly rated citizens (e.g. discounts on electricity and heating, cheaper public transport or priority in

[1] http://www.un.org.pl/cel1 (access on 5.03.2019).

[2] Secretary General of the Communist Party of China from 2002 to 2012, President of the People's Republic from 2003 to 2013, Chairman of the Central Military Commission from 2004 to 2012, https://en.wikipedia.org/wiki/Hu_Jintao (access on 10.03.2019).

hospital admissions). Penalties are imposed on people with low ratings, such as: denied access to prestigious places, loss of the right to travel abroad, slower Internet, limitation of the right to use public transport. Starting from 2020, the system will be extended to all residents of the Middle Kingdom (Szewerniak 2018).



Legend: „→” – heading towards

Fig. 2. Growth and development mechanism in the neoclassical concept of growth and development and the concept of sustainable development based on depopulation

Source: author’s own work

China's global expansion is driven, inter alia, by the 'One Belt, One Road' (OBOR) initiative of the Chinese government to connect China with the countries located along the ancient Silk Road and the new Maritime Silk Road. The preceding and accompanying action is the promotion of the internationalisation of the yuan by China since 2009 (Wang 2016). The OBOR Project is a strictly globalistic concept and in the long term serves the purpose of liquidating nation states. UN Secretary General Antonio Guterres assessed the project as consistent with the UN Agenda for Sustainable Development 2030. As he pointed out, *the initiatives are aimed at beneficial cooperation and the development of networks between countries and regions in terms of infrastructure, finance, trade, and people.* (PAP, IAR 2017) In 2008, Hu Jintao, quoted above, in a speech addressed to the highest authorities of China and the Central Military Commission, declared the following: *'We will use our open policy, seize the economic crisis in the West as a historical moment, and use effective measures to turn them into Socialist China's economic and cultural colonies. Our colonization of these countries is the historical process of communism's triumph over rotten capitalism. We Chinese communists must shoulder the great historical mission, and use socialism to defeat capitalism, eventually liberating the entire humanity with Communism.'* (Newman 2016). The cited quotation clearly indicates hostile motives of Chinese economic expansion. The analysis of the strategy of China's ongoing economic expansion in Africa shows that it is dictated by three reasons: the pursuit of the appropriation and exploitation of African natural resources, the possibility of finding work for Chinese citizens and the acquisition of new markets (demand) for the growing production potential. Currently, this expansion has a dimension of economic expansion declared as cooperation based on the win-win principle and expansion through settlement, which in the long term is to lead to the creation of a 'Chinese continent in Africa.' (French 2014).

4. Depopulation in international instruments

The concept of depopulation in the 1990s was implemented into the concept of sustainable development. It is currently included in most international programming, strategic, and religious documents. It occupies an important place in economic, social, and natural sciences.

The most orthodox supporters of the depopulation concept are calling for a reduction in the world population of at least 90%, so that it does not exceed 500 million. The material expression of their views is the granite monument (Fig. 3) set up in 1980 in Elbert County in State of Georgia (USA) containing a ten-point declaration written in eight contemporary and four ancient languages (Babylonian, ancient Greek, Sanskrit, and Egyptian hieroglyphics), including the following postulates: *Maintain humanity under 500,000,000 in perpetual balance with* *nature* (point 1), *Be not a cancer on the earth – Leave room for nature — Leave room for nature* (point 10)[3].

Fig. 3 The Georgia Guidestones – coordinates 34°13′55.40″N 82°53′39.80″W

Source: https://en.wikipedia.org/wiki/Georgia_Guidestones (access on 20.12.2018)

In view of the admissible volume of the paper, an extensive examination of the documents must be limited to selected documents, in particular the 2030 Agenda for Sustainable Development and the Paris Agreement. The first of these documents is an action plan for people, the planet, prosperity, and the strengthening of universal peace in conditions of greater freedom. The declarative statements characteristic of the Agenda (we are determined to eliminate, protect, ensure) and the pursuit of a deep global revolution in economic, political, and social life (including global equality, justice and the elimination of social classes) indicate the intentions of the authors of the document, which are to build a new global order drawing on the system of values contained in *The Communist Manifesto* (Marx, Engels 1848) whose authors were the Italian communists T*he Ventotene Manifesto* (Spinelli, Rossii, Colorni 1941).

In the context of the analysis of depopulation trends, among the objectives of the UN 2030 Agenda for Sustainable Development (A/RES/70/1), the following ones are noteworthy:

[3] The Georgia Guidestones, coordinates 34°13′55.40″N82°53′39.80″W.

a) Goal People – *We are determined to end poverty and hunger, in all their forms and dimensions, and to ensure that all human beings can fulfil their potential in dignity and equality and in a healthy environment*,
b) Goal Planet – *We are determined to protect the planet from degradation, including through sustainable consumption and production, sustainably managing its natural resources and taking urgent action on climate change, so that it can support the needs of the present and future generations*,
c) Goal Prosperity – *We are determined to ensure that all human beings can enjoy prosperous and fulfilling lives and that economic, social and technological progress occurs in harmony with nature*.

It is impossible to achieve these objectives in conditions of limited resources, acceptance of the neoclassical paradigm of continuous economic growth and growing global population. The state of global equity, sustainable consumption, and sustainable resource management can only be achieved through population reduction. A detailed analysis of the goals and targets of the 2030 Agenda for Sustainable Development allows us to formulate a thesis that its authors, in the process of achieving sustainable development, predict the rejection of market values expressed by classical and neoclassical economics, as well as democratic and libertarian values.

The Paris Agreement expresses the same values as Agenda 2030. (L 282/4) In accordance with Article 2(1), the Agreement aims to strengthen the global response to the threat of climate change in the context of sustainable development and poverty eradication efforts. The Parties to the Agreement, as indicated in the Preamble, shall, when taking action on climate change, respect, promote and take into account commitments relating to human rights, health rights, the rights of indigenous peoples, local communities, migrants, children, persons with disabilities and persons who are vulnerable, the right to development as well as gender equality, women's empowerment and inter-generational justice. Population reduction was thus directly included in the agreement, and abortion and euthanasia guarantee the fulfilment of the obligations of the states.

Undoubtedly, the acceptance and support of the concept by the Catholic Church, expressed, among other things, in the Encyclical of Pope Francis *Laudato Si*, is highly surprising (Laudato Si' 2015). The document includes both lament on the fate of the empowered 'Sister Earth,' who is suffering painfully from human activity[4], and the call for acceptance of the pressing challenge to protect

[4] *This sister now cries out to us because of the harm we have inflicted on her by our irresponsible use and abuse of the goods with which God has endowed her. We have come to see ourselves as her lords and masters, entitled to plunder her at will. The violence present in our hearts, wounded by sin, is also reflected in the symptoms of sickness evident*

our common home, which includes the concern to unite the whole human family in the pursuit of sustainable and integrated development (Laudato Si' 2015, point 13, p.12). In fact, the papal call for acceptance of sustainable development is a call for acceptance by Catholics of depopulation and the tools for its implementation. Speaking to members of Pontifical Academy of Social Sciences the Pope Francis calls for new 'supranational' authorities to enforce UN goals. He said: *When a supranational common good is clearly identified, there is need for a special legally constituted authority capable of facilitating its implementation ... groups of neighboring nations — as is already the case — can strengthen their cooperation by attributing the exercise of certain functions and services to intergovernmental institutions that manage their common interests* (Montagna 2019). Thus, he clearly indicated the objectives of the sustainable development concept, which are to build a new global socio-economic order in the name of the common good and to establish management institutions without democratic legitimacy.

5. Depopulation-related projections of the population

The implementation of depopulation concepts on a global scale is directly reflected in the projections of fertility, population changes, and the population. The UN projections entitled *World Population to 2300* (UN DESA 2004) predicts a lasting decline in the number of women in all continents to two children by 2050 (Fig. 4). At the same time, the average annual rate of population change projections for 2100 assume a constant decrease in population in all regions of the world, with the reservation that in Europe negative rates will be maintained throughout the century, in Asia and South America they will be reached from 2060 (Fig. 5). (UN DESA 2017) As a result of the actions taken, the total population should be kept stable at 9 billion people, as an average option. In the low – the most desirable – variant, the UN forecasts, in the 2300 perspective, that the population will decrease to 2.3 billion people (Fig. 6).

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in the soil, in the water, in the air and in all forms of life. This is why the earth herself, burdened and laid waste, is among the most abandoned and maltreated of our poor; she "groans in travail" (Rom 8:22)… (Laudato Si 2015, p.3). The dogmatic evaluation of considerations directly related to the pagan cult of 'Mother Gaia' goes beyond the subject of this article.

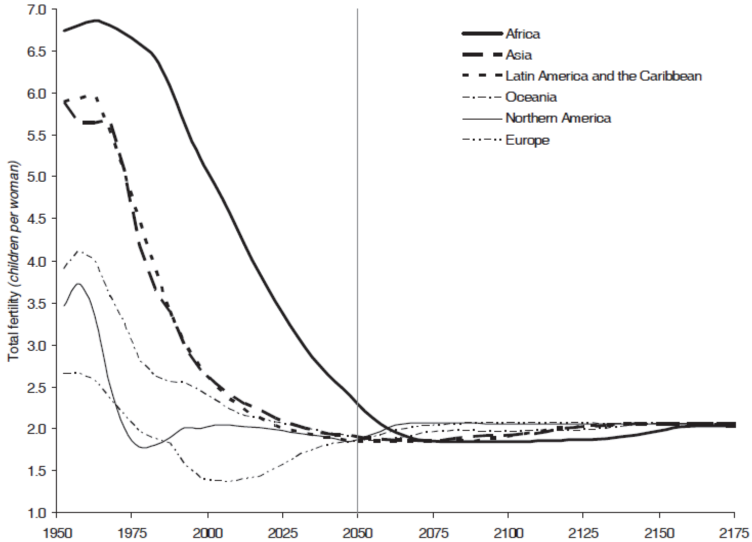

Fig. 4 Total fertility, major areas, estimates and medium scenario: 1950-2175

Source: UN DESA 2004

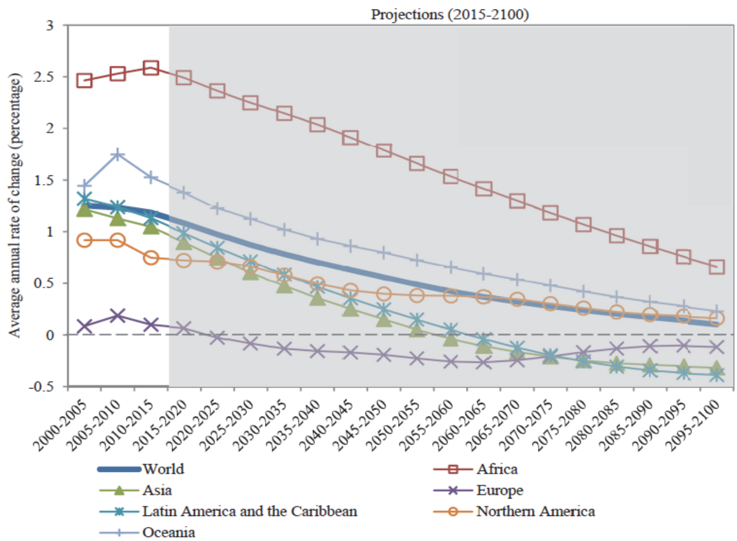

Fig. 5. Average annual rate of population change for the world and by region, estimates, 2000-2015, and medium-variant projection 2015-2100

Source: UN DESA 2017

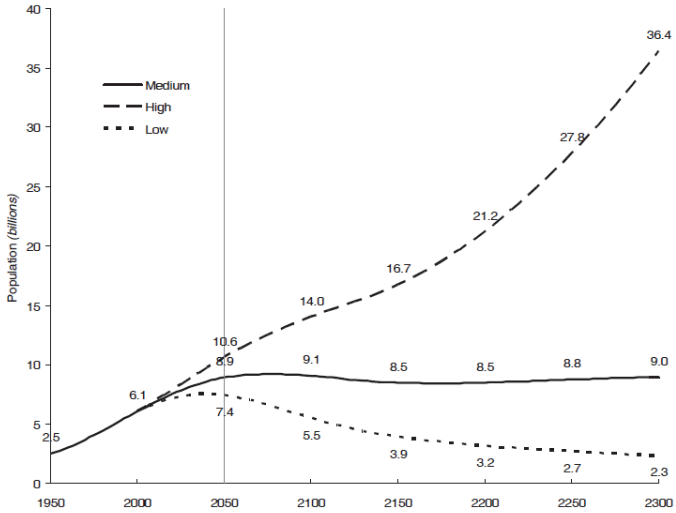

Fig. 6. Estimated world population: 1950-2000, and projections: 2000-2300

Source: UN DESA 2004

The depopulation process is also forecast for Poland. The UN DESA[5] population projections for Poland forecast a steady downward trend over the next eighty years. According to the projections, by 2030 the population will have decreased to 36.6 million, by 2050 to 32.4 million and by 2100 will have reached 21 million people (UN DESA 2017, p. 26). Total fertility (live births per woman) by 2050 will remain at a level not exceeding 1.4, 1.56 in 2050 and 1.76 in 2100 (UN DESA 2017, p. 35).

6. Mechanisms and tools for the implementation of depopulation

The problem of global overpopulation is widely discussed in the scientific literature. To a limited extent, due to the controversial nature of the issue, the tools used to implement depopulation are analysed. The depopulation tools used are differentiated according to the level of development and wealth of the region, or the country in which they are used. The aim of their application is to induce structural changes leading to ageing of societies and loss of natural growth. Mechanisms and instruments are of a legal, psychological and economic nature.

[5] Department of Economic and Social Affairs/Population Division.

Worldwide, since the 1970s, propaganda has been carried out to convince people of the global overpopulation and the global environmental dangers resulting from the population growth. It coexists with paradigms questioning humanity in the prenatal period or presenting the birth of man in the context of increasing greenhouse gas emissions and negative impact on the environment. An example of an approach is an article by S. Wynes and K. Nicholas, in which the authors identify four strong (low-emission) measures that contribute to systemic change and significantly reduce annual personal emissions: having one fewer child (58.6 tonnes CO_2-equivalent (tCO_2e) emission reductions per year), living car-free (2.4 tCO_2e saved per year), voiding airplane travel (1.6 tCO_2e saved per roundtrip transatlantic flight), eating a plant-based diet (0.8 tCO_2e saved per year). (Wynes, Nicholas 2017, p.1) It should be noted that most of the UN's catastrophic visions of overpopulation have not materialised (see State of the World 1984: A World-watch Institute Report on Progress toward a Sustainable Society. Edited by Lester R. Brown., New York: W.W. Norton, 1984).

Conscious parenthood and reproductive rights of women are promoted in both developed and developing countries, as expressed in the right to universal, unpaid and on-demand abortion and access to contraception. The promotion of reproductive rights is accompanied by the promotion of euthanasia of the elderly, the sick (including those suffering from mental illness, depression, alcoholism), as well as those who have problems with their daily duties. Reproductive rights are enforced by international bodies. For example, among the criteria used by the Council of Europe to assess Member States' respect for human rights is criterion 4.5 *Health and sexual and reproductive rights*, which includes access to sexual education, access to contraception, and access to safe and legal abortion (Muižnieks 2016). Contrary to the provisions of the European Convention on Human Rights and the judgements of the European Court of Human Rights, the Committee of Ministers of the Council of Europe calls on European states to facilitate access to abortion, citing famous judgments in such cases (ROP 2019). The effectiveness of actions to promote abortion as a tool of depopulation is evidenced by the fact that, according to available estimates, between 1990 and 2016 approximately 1.5 billion unborn children were killed, which is more than 20% of the current global population. On average, between 2010 and 2014, 25% of pregnancies in the world ended with abortion, including 30% in Europe (Guttmacher Institute 2018).

The supporters of depopulation in developed countries are opposed to any systemic measures promoting the family and encouraging an increase in fertility rate. Such actions are presented as a waste of public money. Hedonistic attitudes promoted among young people translate into unwillingness to marry and take responsibility for the family, as well as low fertility rates. People are encouraged to give up having children in the name of caring about the climate[6] or their future (Canadian action NO FUTURE, NO CHILDREN, in which participants declare: *I pledge not to have children until I am sure my government will ensure a safe future for them*[7]). Discrediting the role and value of the family is accompanied by the promotion of the substitution of intimate relations between humans and sex-robots and the promotion of love for animals as a substitute for motherhood and fatherhood. The process of subjectification and attribution of strictly human characteristics and needs to both robots (Słowik 2018) and animals is observed. Co-existence with robots, surrounding animals with love is to prevent the emergence of psychiatric and psychological problems of members of future societies deprived of natural human relations.

In countries building competitiveness based on cheap labour, remuneration is a depopulation factor. Low remuneration discourages people from having children whose parents are unable to provide the expected education, care, and start into adult life. They become a strong motive to seek work abroad. The strategy of offering cheap labour enables economic growth to be achieved in a short period of time. In the long run, it results in labour shortages, the need to open up to labour immigration, wage increases and, consequently, a loss of competitiveness to the benefit of poor countries. Contemporary economic migration – unlike migration in the past – is not compensated by natural increase, driven by high birth rates and low proportions at older ages (Jackson 2014, p. 4).

7. Conclusions

The concept of sustainable development through depopulation, which sees man as a form of capital equivalent to the natural environment and economic capital, is contrary to natural law, deprives future generations of the right to exist and is morally reprehensible in the light of the Judeo-Christian system of values. This concept should be seen as an attempt to reject civil liberties and the democratic system as such, which are constitutionally guaranteed by democratic states, in favour of a dictatorship exercised by organisations and individuals that care about the subjectively understood welfare of the planet.

In the economic dimension, the implementation of the concept of sustainable development through depopulation is an attempt to build a model of an economic system that rejects free market values, in which the type and amount of production and demand will be determined by the power that is currently difficult to

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[6] See: HRH The Duke of Sussex, *HRH The Duke of Sussex Interviews Dr Jane Goodall For The September Issue*, https://www.vogue.co.uk/article/prince-harry-jane-goodall-september-2019-issue (access on 21.09.2019).

[7] See: http://www.nofuturepledge.ca/# (access on 21.09.2019).

define. The reduction of the population, both globally and nationally, will potentially involve a number of negative phenomena, such as the collapse of domestic and, consequently, global financial system, the collapse of pension systems, as well as the insolvency of states. The course of these processes can be analysed using the example of Japan, a country experiencing dramatic change in the size, age structure, and spatial distribution of its population. The process of ageing and depopulation is felt in all areas of social, economic, cultural, and political life. Rural areas and medium-sized cities are characterised by a lack of any economic activity, abandonment of property, destruction and loss of value of property, lack of births, abandonment and deterioration of agricultural land and the encroachment of forests into urban areas. Due to similar patterns of socio-economic development, similar processes are expected in the near future in the rest of East and Southeast Asia (Matanle 2014).

In the light of the considerations carried out, the rejection of the depopulation concept should be postulated. Sustainable development should be a concept based on natural law, democratic values, sustainable consumption, and a fair distribution of resources and wealth. A factor in increasing wealth should be the desire to meet the needs of an increasing number of people, high quality and sustainable products. The economic mechanism must meet the criteria set out in the EU concept of a circular economy, in which the waste of resources is minimised and the category of waste does not exist. The realisation of such a concept of sustainable development requires the rejection by developed countries of the paradigm of the continuous increase in unjustified consumption.

It should also be noted that the continuation of depopulation activities by Western countries, in confrontation with China's global expansion, poses a real threat to the existence of these countries in the next 200 years. It should be predicted that the continuation of depopulation measures will lead to China gaining global dominance in both economic and population terms.

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Abstract

The aim of the paper is to characterize depopulation trends in the concept of sustainable development and to analyse their impact on structural changes in the population in the global perspective and the resulting economic consequences. The roots of depopulation trends were presented. Global approaches in the perception of population as a factor of economic growth and development were characterized. The problem of depopulation in selected international programming, strategic, and religious documents was analysed. To a limited extent, due to the controversial nature of the issue, tools implementing depopulation were presented. The economic and social consequences of the decrease in the population were indicated.

Keywords:
sustainable development, centrally planned economy, human capital, population policy, depopulation, world population projections

Depopulacja w koncepcji zrównoważonego rozwoju

Streszczenie

Celem artykułu jest charakterystyka nurtów depopulacyjnych w koncepcji zrównoważonego rozwoju oraz analiza ich wpływu na przemiany strukturalne ludności w ujęciu globalnym i wynikające z tego konsekwencje ekonomiczne. Przedstawione zostały korzenie trendów depopulacyjnych. Scharakteryzowano globalne podejścia w postrzeganiu liczby ludności jako czynnika wzrostu gospodarczego i rozwoju. Analizie poddany został problem depopulacji w wybranych międzynarodowych dokumentach programowych, strategicznych oraz religijnych. W ograniczonym zakresie – ze względu na kontrowersyjność zagadnienia – przedstawione zostały narzędzia urzeczywistniające depopulację. Wskazane zostały konsekwencje ekonomiczno-społeczne zmniejszania się liczby ludności.

Słowa kluczowe:
zrównoważony rozwój, ekonomia centralnie planowana, kapitał ludzki,
polityka ludnościowa, depopulacja, globalne prognozy ludności

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The Species Diversity of Grasslands in the Middle Wieprz Valley (PLH060005) Depending on Meadow Type and Mowing Frequency

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1. Introduction

Permanent grasslands cover about 21% of agricultural land in Poland (about 35% in Europe) and are the main sanctuary of biological diversity in agricultural areas. The sustainability of these grassland communities depends on their utilisation (cutting or grazing), i.e. the harvesting of biomass. However, according to the National Environmental Monitoring conducted in the years 2007-2012, the assessment of the conservation status of most natural habitats and many plant species occurring in agricultural areas yields unfavourable results. The predominant status of meadow, grassland and peat-bog habitats is unsatisfactory (U1) or bad (U2) (Program… 2015). The Middle Wieprz Valley (Dolina Środkowego Wieprza, PLH060005) comprises a mosaic of habitats with varying moisture levels, which is conducive to the occurrence of varied plant communities (Stamirowska-Krzaczek 2008, Warda et al. 2013). As many as 80% of the habitats in Poland undergo transformations due to natural processes such as plant succession or synanthropisation. The unfavourable changes in biological diversity result from natural biotic and abiotic processes caused by changes in land use (Czyż et al.

2013, Grzegorczyk et al. 1999, Kulik et al. 2017, Norderhaug 2000). The reduction or abandonment of use of meadows and pastures is a particularly negative influence. These changes lead to decreasing floristic diversity of meadow communities (Baryła & Urban 1999, Kryszak et al. 2010), manifested in the reduced numbers of species forming the particular communities (Kryszak et al. 2007, Kulik et al. 2016, Stypiński & Grobelna 2000) or disappearance of characteristic species of typical plant communities (Myśliwy & Bosiacka 2009) as well as increased presence of species that previously occurred sporadically (Kotańska et al. 2016, Ratyńska et al. 2007, Stamirowska-Krzaczek 2015, Warda et al. 2018).

The study objective was to assess the diversity of the species composition of selected grassland communities in different habitat conditions, depending on the frequency of mowing (0, 1 and 2).

2. Material and methods

2.1. The study area

The studies were conducted on grasslands in the middle Wieprz valley. The Wieprz river in its middle course is a natural, highly meandering river and is a right-hand tributary of the Vistula. Meadows are mainly associated with the floodplain of the Wieprz valley (Janiec & Rederowa 1992). The Wieprz Middle Valley is situated in the Nadwieprzański Landscape Park (Lublin Region). The meadow complex covers approximately 25% of the Park area (Stamirowska-Krzaczek 2008). A Natura 2000 area (PLH060005) was established in 2008 to protect the natural values of the meadows and slopes of the Wieprz valley within the Park.

2.2. Field study

Phytosociological investigations of grasslands in the middle Wieprz valley were carried out in 2017 (before the first cut: 3rd decade of May – 1st decade of June, and supplemented in July and August) using the Braun-Blanquet method (1964). Phytosociological relevés were made of an area of 25 m^2, representative of meadow phytocoenoses (Dzwonko 2007). The investigations focused on the vegetation of wet meadows *Molinietalia* order (mainly *Alopecuretum pratensis*, *Cirsietum rivularis*, *Deschampsia caespitosa* community), hay (fresh) meadows *Arrhenatheretalia* order (mainly *Arrhenatheretum elatioris*), meadows with communities of the *Molinio-Arrhenatheretea* class forming a mosaic, with species from both of the above-mentioned orders (e.g. *Poa pratensis-Festuca rubra* community), and rush meadows *Phragmitetea* class (mainly *Phalaridetum arundinaceae*, *Caricetum gracilis*, *Phragmitetum australis*). The types of meadows under study covered areas of varying size; hence the number of phytosociological relevés varied (respectively: 24, 44, 74 and 23). The adopted nomenclature of species was according to Mirek et al. (2002) while the taxonomy and nomenclature of communities according to Matuszkiewicz (2008). The 2-cut meadows were mowed after June 1 or 15 in the first cut and usually in August in the second cut. The 1-cut meadows were mowed usually after June 15 or July 1. The abandoned meadows were not mowed for a long time.

Apart the on-the-ground phytosociological investigations, an aerial studies with gyrocopter use before first regrowth and in September were carried out. The remote detection system is mounted on an ultralight gyrocopter flying at low altitudes, thanks to which it provides high-resolution images. Combined with data obtained from the gyrocopter, the on-the-ground data prepared in this study will enable a more precise assessment of the degradation of meadows in a spatial distribution in the Middle Wieprz Valley.

2.3. Data analysis

The floristic diversity of the grassland communities was determined based on two indices, namely the number of species (SN) and the Shannon-Wiener index H′ ($H' = \sum_{i=1}^{SN} p_i \ln{(p_i)}_i$, where p_i denotes cover-abundance by species i). In order to detect statistically significant differences between the obtained values of these indices for the particular grasslands (taking into account the research factors), a variance analysis was carried out, taking into account the Linear Model (LM) for the Shannon-Wiener index and a Generalised Linear Model (GLM) for the number of species on the assumption of the Poisson distribution of this variable. If significant differences were found in the values of the diversity indices due to one of the examined factors, Tukey's multiple comparison tests were carried out post hoc for non-equipotent groups. The aim of the tests was to indicate between which specific combinations (meadow type x utilisation frequency) statistically significant differences occur with regard to their species diversity.

In addition, a Multidimensional principal component analysis (PCA) (Jolliffe 2002) was carried out to detect the variation of the analysed dataset with regard to the values of the ecological indices (Ellenberg et al. 1992). Climatic conditions (L – light, T – temperature, K – continentality) and edaphic conditions (F – moisture, R – soil reaction, N – nitrogen content) were taken into account in the assessment. The method made it possible to identify the factors that differentiated the studied communities the most. Furthermore, it enabled the visualisation of these differences according to grassland community and mowing frequencies. Owing to the similar scale of the indices, the covariance matrix was used to estimate the components. The analyses were conducted using the R statistical software. The *vegan* library was used to compute the value of the Shannon-Wiener index, and the *rcompanion* library was used to analyse the multiple comparisons for counted observations.

3. Results and discussion

The number of plant species is the basic index of floristic diversity of grassland communities (Kostuch 1995). The results of the conducted (2017) phytosociological survey concern condition of the vegetation of the *Molinio-Arrhenatheretea* class, *Molinietalia* and *Arrhenatheretalia* order and *Phragmitetea* class. In the grassland under study, the value of this parameter varied depending on the type of meadow and mowing frequency (Table 1).

Table 1. Ranges of species number in the selected meadow communities

Cutting frequency	*Arrhenatheretalia*	*Molinietalia*	*Molinio-Arrhenatheretea*	*Phragmitetea*
0	18-23	14-31	15-23	3-25
1	22-34	13-27	15-32	4-21
2	25-37	26-37	15-29	1-19

Meadows with vegetation of the *Arrhenatheretalia* order had the greatest number of species. Furthermore, the number of species was found to increase with the growing frequency of use. The species composition of traditional hay meadows is the result of a complex combination of abiotic and biotic factors, management regimes, continuity of management and varying dispersal conditions (Norderhaug 2000). The least numerous communities occurred in rush meadows (*Phragmitetea* class). A more frequent use of the sward of these communities led to a decreased number of species. With reference to the research results discussed in an earlier study (Warda et al. 2018), the vegetation cover of rush meadows occurring in the Middle Wieprz Valley underwent small changes. In the other communities under study, no specific trends were observed with regard to changes in the number of species in the more frequently cut meadows.

As was the case with the number of species, the highest values of the Shannon-Wiener index were found in meadow communities representing the *Arrhenatheretalia* order, and the lowest values – communities of the *Phragmitetea* class. The scopes of the observed numbers of plant species and the obtained Shannon-Wiener index values are shown in box plots in Fig. 1 and 2.

The box plots take into account the types of meadows and cutting frequency as well as the combination of meadow type x cutting frequency. In general, both indices of floristic diversity have similar trends although certain differences occur between the specific groups of the analysed values.

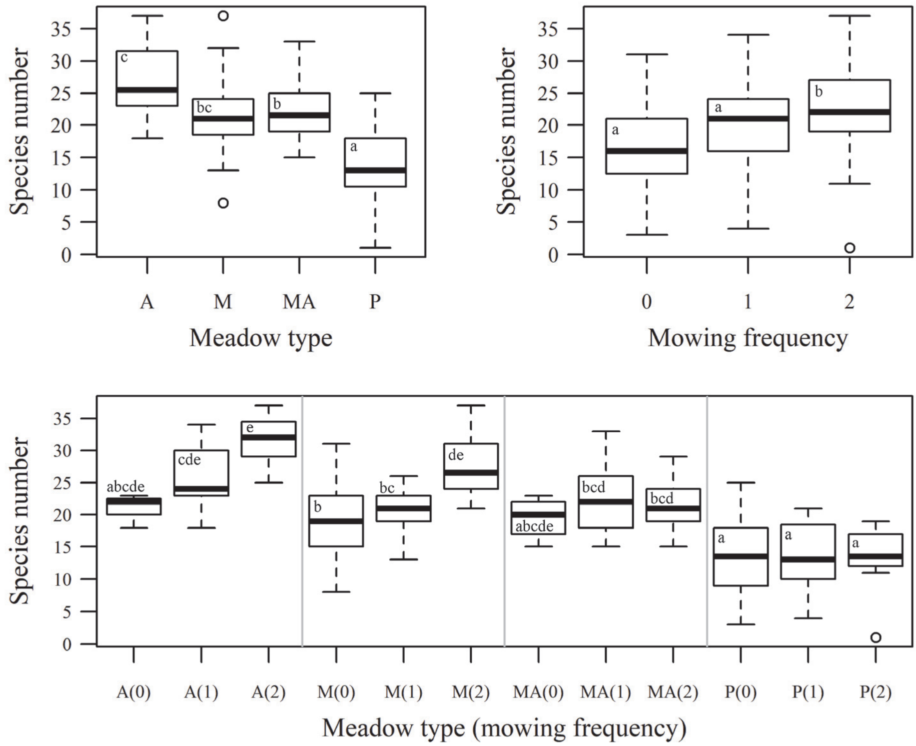

Fig. 1. Box plots for the number of species different letters indicate significant differences at $p < 0.05$; A - *Arrhenatheretalia*, M - *Molinietalia*, MA – *Molinio-Arrhenatheretea*, P - *Phragmitetea*

The investigation results concerning the number of species and Shannon-Wiener index values were processed statistically. A variance analysis was carried out; its results are presented in Table 2. They indicate a significant influence of both research factors (meadow type and cutting frequency) on the floristic diversity of the communities under study. The interaction between these factors was recognised as statistically significant in the case of species number, and insignificant in the case of the Shannon-Wiener index (even though it was close to being significant with $p = 0.07$).

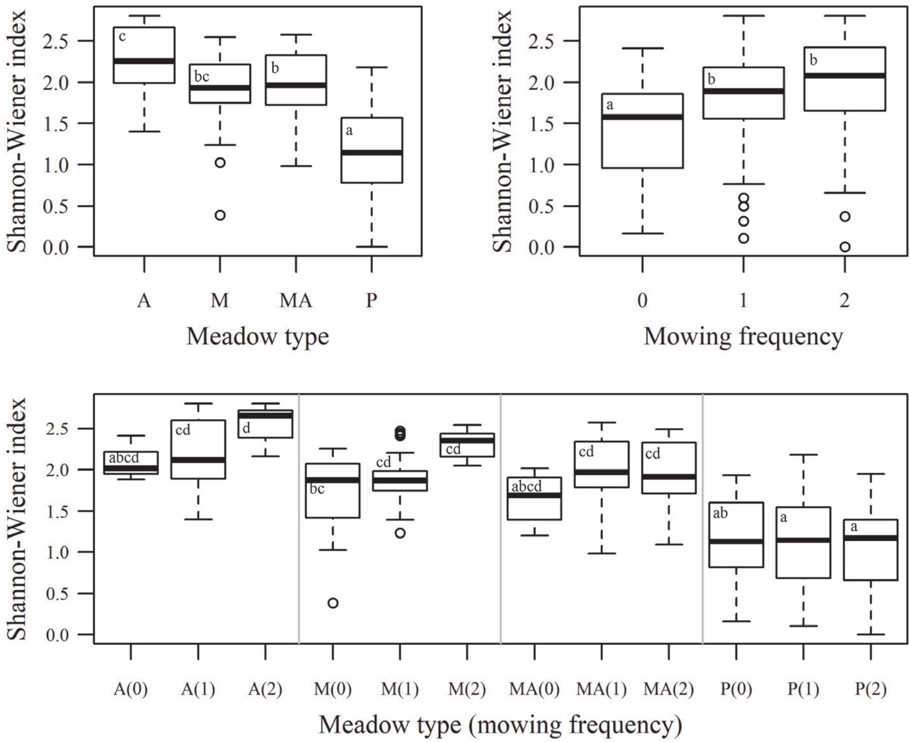

Fig. 2. Box-plots for values of the Shannon-Wiener index different letters indicate significant differences at $p < 0.05$; A - *Arrhenatheretalia*, M - *Molinietalia*, MA – *Molinio-Arrhenatheretea*, P - *Phragmitetea*

The statistical tests used in the species diversity assessment of the grassland communities under study confirmed the biggest significant differences between communities of the *Arrhenatheretalia* order and *Phragmitetea* class ($p <$ 0.0001 for both indices). In the case of cutting frequency, significant differences in diversity always occur between the vegetation of unused meadows (no cutting) and meadows cut twice ($p = 0.0031$ for the number of species, $p < 0.0001$ for the Shannon-Wiener index). The assessment results for meadows cut once was different, however. Based on the number of species, these meadows are in the same homogeneous group as uncut meadows, while based on the Shannon-Wiener index, they are in the same group as meadows cut once. Homogeneous groups, i.e. groups similar in terms of floristic diversity indices, were marked with letters on box plots 1 and 2. The analysis of homogeneous groups divided into communities (grassland) and cutting frequency (lower diagrams on Fig. 1 and 2) indicate that the biggest influence of cutting frequency on the increased species diversity occurred in meadows with communities of the *Arrhenatheretalia* and *Molinietalia* order, and the lack of influence was observed in meadows with communities of the *Phragmitetea* class. However, the multiple comparison tests confirm the correlation only in the case of communities of the *Molinietalia* order. This, however, can result from the fact that some subgroups (community x cutting frequency) are not numerous, which results in long confidence intervals and the groups being indistinguishable based on floristic diversity indices.

Table 2. Variation analysis for the number of species and values of the Shannon-Wiener index

Species number (GLM)					
Factor	Likelihood ratio	DF	Chi	*p*-value	
Type (T)	21.728	3	138.67	0.00007	**
Mowing frequency (MF)	10.403	2	13.65	0.00551	**
T * MF	19.700	6	19.70	0.00313	**
Shannon-Wiener index (LM)					
	SS	DF	MS	F	*p*-value	
Intercept	366.37	1	366.37	1935.13	<0.0001	**
Type (T)	24.80	3	8.26	43.66	<0.0001	**
Mowing frequency (MF)	1.59	2	0.79	4.19	0.0166	*
T *MF	2.24	6	0.37	1.97	0.0718	
Error	35.97	190	0.19			

** significant differences at level α=0.01 * significant differences at level α=0.05
T – meadow type (A, M, MA, P)

The deterioration of meadow communities is manifested in the reduced numbers, cover-abundance and, subsequently, disappearance of characteristic species (Warda et al. 2018). Unfavourable changes in the species composition of communities start with the primary syntaxon, i.e. a plant community, and progress in communities of a higher order in the phytosociological hierarchy if they are still affected by unfavourable factors. This leads to a change of the plant formation. The degenerative changes in meadow communities observed in the study area are have reached an advanced stage because the species characteristic of an order are already disappearing and the number of class indicator species is decreasing (Faliński 1991).

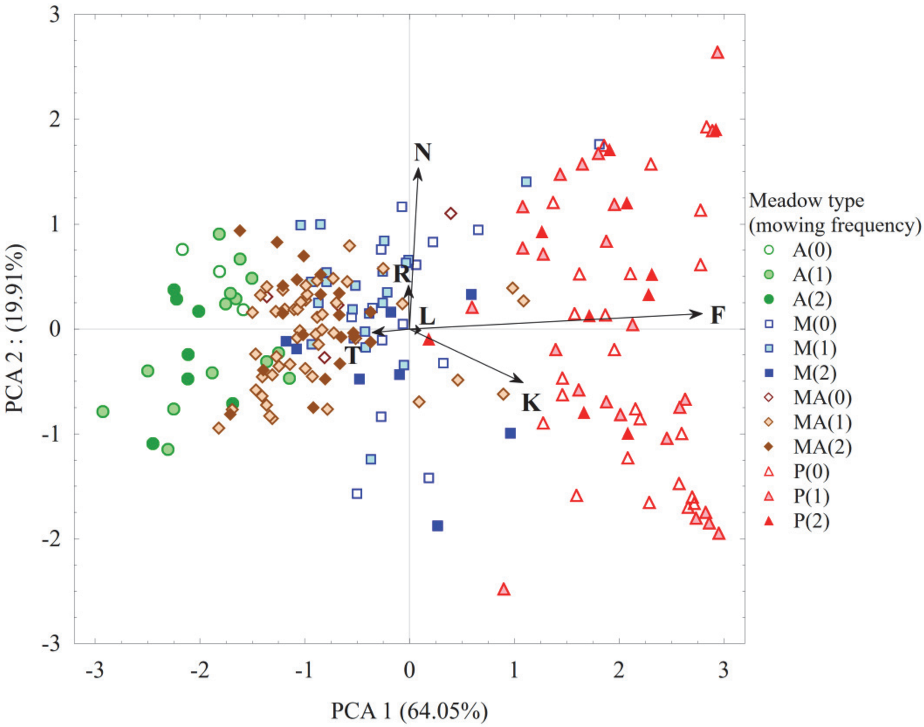

Fig. 3. PCA ordination graph for different types of communities based on Ellenberg's indices

In addition, a multidimensional principal component analysis (PCA) was carried out to detect the variation of the analysed dataset with regard to the conditions of occurrence of the studied grassland communities, described by values of the ecological indices. The PCA indicated that the first two principal components account for about 84% of the variation of the dataset (including, respectively, the first component, PCA1, accounts for 64%, and the second component, PCA2, accounts for 20%). The values of the first component are most closely linked with the values of the humidity index (F) and, to a smaller degree, the continentality index (K). Habitat humidity is the main factor determining the type of community and its species diversity. The values of the second component are most closely linked with the values of the soil nitrogen index (N). The ordination graph of the analysed communities, obtained by means of PCA, is presented in Fig. 3. An analysis of the data on the graph confirms that the communities are most distinguishable according to the values of the first component (linked with the values of the soil humidity index). The highest values of this component were obtained for communities of the *Phragmitetea* class, while the lowest – for communities of the *Arrhenatheretalia* order. Communities of the *Molinietalia* order are concentrated around the centre of the coordinate system determined by the principal components, while communities of the *Molinio-Arrhenatheretea* class share the characteristics of wet and fresh meadows. In addition, the ordination diagram indicates that the group of meadows of the *Phragmitetea* class is more diverse floristically due to the values of the second principal component (the differential of PCA2 values is twice as big). This is indicates the significance of soil nitrogen content for the diversity of the analysed group of communities. The results of the analysis do not confirm the influence of the manner of meadow utilisation on the values of the principal components. The points referring to the communities with different cutting frequencies cover similar areas of the graph within the individual meadow community types.

4. Conclusions

The phytosociological investigations were carried out in 2017 on the grasslands in the Middle Wieprz Valley. The floristic diversity of the grassland communities was determined based on two indices, namely the number of species (SN) and the Shannon-Wiener index H′. The investigations focused on the vegetation of wet meadows (*Molinietalia* order), hay (fresh) meadows (*Arrhenatheretalia* order), meadows with other communities of the *Molinio-Arrhenatheretea* class, and rush meadows (*Phragmitetea* class).

Similar trends were observed in the case of the number of species and the Shannon-Wiener index values. These indices varied depending on the type of meadow and mowing frequency.

Meadows with vegetation of the *Arrhenatheretalia* order had the greatest number of species. Furthermore, the number of species was found to increase with the growing frequency of use. The least numerous communities occurred in rush meadows (*Phragmitetea* class). A more frequent use of the sward of these communities led to a decreased number of species.

The results of a variance analysis indicate a significant influence of both research factors on the floristic diversity of the grasslands under study. The biggest significant differences were confirmed between meadow vegetation of the *Arrhenatheretalia* order and *Phragmitetea* class. The biggest influence of cutting frequency on the increased species diversity occurred in meadows with communities of the *Arrhenatheretalia* and *Molinietalia* order.

According to a multidimensional principal component analysis (PCA) indications, habitat humidity is the main factor determining the type of meadow community and its species diversity.

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Abstract

The studies were conducted on grasslands in the middle Wieprz valley in 2017. The aim of study was to assess the diversity of the species composition of selected grassland, depending on the frequency of mowing. The investigations focused on the meadow vegetation of *Molinietalia* order, *Arrhenatheretalia* order, the *Molinio-Arrhenatheretea* class and *Phragmitetea* class. The floristic diversity of the grassland communities was determined based on two indices, namely the number of species (SN) and the Shannon-Wiener index H′. In order to detect significant differences between the obtained values of these indexes for the particular grasslands (taking into account the research factors), a variance analysis was carried out, taking into account the Linear Model (LM) for the Shannon-Wiener index and a Generalised Linear Model (GLM) for the number of species on the assumption of the Poisson distribution of this variable. In addition, a Multidimensional principal component analysis (PCA) (Jolliffe 2002) was carried out to detect the variation of the analysed dataset with regard to the values of the ecological indices (Ellenberg et al. 1992). In the grassland under study, the number of species varied depending on the type of meadow and mowing frequency. Meadows with vegetation of the *Arrhenatheretalia* order had the greatest number of species. Furthermore, the number of species was found to increase with the growing frequency of use. The least numerous communities occurred in rush meadows (*Phragmitetea* class). A more frequent use of the sward of these communities led to a decreased number of species. Similar trends were observed in the case of the Shannon-Wiener index values. A variance analysis was carried out and its results indicate a significant influence of both research factors (meadow type and cutting frequency) on the floristic diversity of the communities under study. The biggest significant differences were confirmed between meadow vegetation of the *Arrhenatheretalia* order and *Phragmitetea* class. The biggest influence of cutting frequency on the increased species diversity occurred in meadows with communities of the *Arrhenatheretalia* and *Molinietalia* order. According to a multidimensional principal component analysis (PCA) indications, habitat humidity is the main factor determining the type of meadow community and its species diversity.

Keywords:
grassland, vegetation, floristic diversity, meadow type, mowing frequency, Middle Wieprz Valley

Różnorodność gatunkowa użytków zielonych w Dolinie Środkowego Wieprza (PLH060005) w zależności od typu łąki i częstotliwości koszenia

Streszczenie

Badania fitosocjologiczne przeprowadzono w 2017 roku na użytkach zielonych w dolinie środkowego Wieprza. Dolina Środkowego Wieprza (PHL060005) stanowi mozaikę siedlisk o zróżnicowanym uwilgotnieniu, co sprzyja występowaniu różnorodnych zespołów roślinnych. Celem badań była ocena zróżnicowania składu gatunkowego wybranych użytków zielonych, w zależności od częstotliwości koszenia. Przedmiotem badań była szata roślinna łąk rzędu *Molinietalia*, *Arrhenatheretalia*, klasy *Molinio-Arrhenatheretea* i *Phragmitetea*. Różnorodność florystyczną badanych zbiorowisk roślinnych oceniono za pomocą dwóch wskaźników, jakimi są liczba gatunków (SN) oraz indeks Shannona-Wienera H′. W celu wykrycia istotnych różnic między uzyskanymi wartościami tych wskaźników dla poszczególnych zbiorowisk (z uwzględnieniem czynników badań) wykonano analizę wariancji z uwzględnieniem modelu liniowego (LM) dla indeksu Shannona-Wienera oraz uogólnionego modelu liniowego (GLM) dla liczebności gatunków przy założeniu rozkładu Poissona tej cechy. Dodatkowo wykonano wielowymiarową analizę głównych składowych PCA (Jolliffe 2002) w celu wykrycia zmienności analizowanego zbioru danych, ze względu na wartości wskaźników ekologicznych (Ellenberg et al. 1992). Na badanych użytkach zielonych, wartość tego parametru wykazywała zróżnicowanie w zależności od typu łąki oraz częstotliwości koszenia. Łąki porośnięte roślinnością rzędu *Arrhenatheretalia* były najbardziej liczne gatunkowo. Stwierdzono ponadto zwiększanie się liczby gatunków w zbiorowisku wraz z rosnącą częstotliwością użytkowania. Najmniej liczne zbiorowiska występowały na łąkach z roślinnością klasy *Phragmitetea*. Częstsze użytkowanie runi tych zbiorowisk przyczyniało się do zmniejszenia liczby gatunków. Podobne trendy stwierdzono w przypadku wartości indeksu Shannona-Wienera. Wykonano analizę wariancji, której wyniki świadczą o istotnym wpływie obu uwzględnionych czynników (typ łąki oraz częstotliwość koszenia) na zróżnicowanie florystyczne badanych zbiorowisk. Największe istotne różnice potwierdzono między szatą roślinną rzędu *Arrhenatheretalia* i klasy *Phragmitetea*. Największy wpływ częstotliwości koszenia na wzrost różnorodności gatunkowej zaznaczył się na łąkach z roślinnością rzędu *Arrhenatheretalia* i *Molinietalia*. Wskazaniem wielowymiarowej analizy głównych składowych PCA jest, że wilgotność siedliska jest tu głównym czynnikiem decydującym o typie szaty roślinnej i jego zróżnicowaniu gatunkowym.

Słowa kluczowe:
użytki zielone, szata roślinna, różnorodność florystyczna, typ łąki,
częstotliwość koszenia, Dolina Środkowego Wieprza

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Municipal Sewage Sludge Processing Method Effect on the Content of Polycyclic Aromatic Hydrocarbons

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1. Introduction

According to the GUS "Environmental Protection 2016" study, in 2015, 951.5 thousand tons of sewage sludge dry matter was produced in Poland. At the end of the same year, the amount of sludge accumulated in the sewage treatment plant was 6,483.9 thousand tons. Nowadays, many wastewater treatment plants are struggling with a steadily increasing amount of sludge. Each of these objects selects the processing method and final disposal of sewage sludge on the basis of its own capabilities. Stabilized sewage sludge may be used for natural or energetic purposes. These capabilities are sometimes limited by the presence of pollutants which, when released, may have a negative impact on the environment and ultimately on humans. These include polycyclic aromatic hydrocarbons (PAHs) and heavy metals (Boruszko 2013, Boruszko et al. 2015). The natural use of the sewage sludge may cause that these pollutants accumulate in the soil, transfer to waters and plants intended for consumption or feed (Ociepa-Kubicka 2012). The Environment Minister Regulation from February 6th 2015 on municipal sewage sludge (Journal of Laws 2015, item 257) specifies the parameters that must be met by sewage sludge used naturally, including agricultural use. These are 10 indicators that do not include PAHs. These compounds show low degradability and are classified as persistent organic pollutants (POPs) according to Regulation (EC) No 850/2004 of the European Parliament and of the Council of 29 April 2004 (Banach-Szott et al. 2012). PAHs are compounds composed of benzene rings (from two to more than a dozen) and alkyl substituents. They have a strong affinity to particulate matter and are poorly soluble in water, so they easily adsorb on the surface of sewage sludge (Macherzyński et al. 2015). PAHs are deposited in sewage sludge as a result of accumulation and bioaccumulation from domestic and industrial wastewater. The concentration of individual hydrocarbons in industrial wastewater depends on the type of industry. The industry which supplies the largest quantities of these compounds in sewage includes power plants, coking plants, coal and crude oil processing (Janosz-Rajczyk et al. 2006). PAHs may be discharged into domestic sewage along with rainwater. They contain pollutants from, among other things, the atmosphere, asphalt and car tires. In sewage sludge, PAHs can also be formed spontaneously through the transformation of complex carbon compounds, e.g. during septic tanks (Janoska et al. 1993). Despite the persistence of these compounds, their decomposition in the environment is possible. The effectiveness of PAH decomposition depends on the number of benzene rings in their structure, the ability of existing microorganisms to degrade these compounds and environmental conditions, such as the presence of oxygen, temperature, UV radiation and water content (Włodarczyk-Makła 2014). The U.S. EPA recommends that 16 PAH compounds be determined in environmental samples: naphthalene, acenaphthene, acenaphthene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthr-axcene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene. The benzo(a)pyrene belonging to this group is considered to be the most important indicator of PAH presence in the environment (Kubiak 2013). According to the International Agency for Research on Cancer (IARC), it is the main human endangering carcinogen.

The aim of the study was to determine the content of PAHs and the share of particular groups of PAHs in municipal sewage sludge at particular stages of their production and processing in municipal sewage treatment plants.

2. Object and methods

The research was carried out on the basis of sludge samples taken from the wastewater treatment plant in Białystok. The mechanical-biological treatment plant in Bialystok was launched in 1994. The last modernization was completed in 2008. The operation of the plant is based on the technology of active sludge divided into three nodes: mechanical, biological and sludge processing. About 80% of the amount of inflowing sewage is domestic wastewater, 20% is industrial wastewater. Their source is the town of Białystok and the communes adjacent to the town. The treated wastewater is discharged to the Biała River. According to the KPOŚK (National Urban Wastewater Treatment Plan) report of 2015, the actual PE of the facility is approximately 360,000, of which 56,200 is for industry. The maximum capacity of the plant is 450,000 PE. The planned flow capacity of the plant is 100,000 m^3/d. The reduction of incoming pollutants is estimated at 95% BOD, 90% total nitrogen, 96.8% total phosphorus and 85% total suspended solids. Sewage sludge is thickened and then fermented in four separate fermenters. The process takes place for 25-30 days at 35-37°C. Ultimately, the sludge is dewatered, and part of it is thermally dried and converted into pellets. It is used for fertilization and soil reclamation. Every year, 6800 tons of dry sludge mass is produced at the plant.

Sludge samples were collected in three research cycles: autumn (November), winter (February) and spring (April) in 2017 and 2018. In each cycle the samples of preliminary sludge, excess sludge from the press, digestate and dewatered digestate sludge were analyzed. For each sludge, 3 samples were taken for further testing. The samples were analyzed for concentration of 16 PAHs (naphthalene, acenaphthene, acenaphthene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene), benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)-anthracene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene) at the Faculty Chemical Laboratory of the Bialystok University of Technology. For this purpose, gas chromatography combined with mass spectrometry using the GC/MS Agilent 7890B chromatograph was used. The results were given as single compounds of PAHs, which were then grouped according to the number of aromatic rings. The results of PAH content in individual groups were subjected to statistical calculations. The changes occurring in the set of variables were analyzed using the Fisher's least significant differences test. The qualitative factor in the analysis of variance was the series of studies (after extraction) and the type of sludge. All the variables used in the analysis were characterized by normal distribution according to the Saphiro-Wilk test and homogeneity of variance according to Bartlett's test.

3. Results and discussion

The sum of PAHs in the analyzed sludge samples depended more on the timing of sampling of individual samples than on the type of sludge (Tab. 1). The average summary content of these compounds was the highest in the preliminary sludge in comparison to other sludge samples. Research on unprocessed sewage sludge was conducted by researchers in Poland and in other countries.

Oleszczuk (2009) showed a content of 16 EPA PAHs in sludge in the range from 2.83 mg/kg d.m. to 9.95 mg/kg d.m. and Li and others (2008) showed a content at a very high level from 88.81 mg/kg d.m. to 100.74 mg/kg d.m., a lower content was found in studies of sludge samples from China which ranged from about 0.5 mg/kg d.m. to 3.6 mg/kg d.m. (Feng 2008, Liu 2013). In research conducted in Scandinavia, Paulsrud et al. (1997) found a very broad range of 16 PAHs in sewage sludge from 1.0 mg/kg d.m. to 30 mg/kg d.m. Different contents result from sewage quality flowing into the treatment plant. In excessive sludge and after the fermentation process, the content of total PAHs was similar and lower than in preliminary sludge. The least of these compounds occurred in the sludge after fermentation and dehydration. The preliminary and dehydrated sludge was dominated by four-ring hydrocarbons, while the excess and after fermentation were dominated by three- and four-ring hydrocarbons.

Table 1. The content of PAHs with a given number of rings in the analyzed sewage sludge in mg/kg d.m.

Sample No	Sludge type	Series	Number of rings					Sum
			2	3	4	5	6	
1	Preliminary sludge	I	0.10	0.72	0.84	0.49	0.00	2.16
		II	0.10	1.09	2.26	1.00	0.67	5.12
		III	0.21	0.61	1.28	0.77	0.52	3.39
		mean	0.14	0.81	1.46	0.76	0.40	3.77
2	Excess sludge after press	I	0.03	2.58	2.35	0.39	0.00	5.35
		II	0.05	0.35	0.43	0.29	0.08	1.20
		III	0.05	0.87	0.60	0.26	0.08	1.86
		mean	0.04	1.27	1.12	0.31	0.05	2.83
3	Sludge after fermentation	I	0.13	1.75	1.89	0.37	0.00	4.14
		II	0.10	0.44	0.59	0.35	0.22	1.69
		III	0.11	1.06	0.80	0.40	0.23	2.59
		mean	0.11	1.08	1.09	0.37	0.15	2.88
4	Sludge after fermentation and dehydration	I	0.04	0.55	1.62	0.67	0.70	3.59
		II	0.07	0.29	0.38	0.22	0.21	1.17
		III	0.04	0.33	0.25	0.23	0.11	0.96
		mean	0.05	0.39	0.75	0.37	0.34	1.94

Most of the six-ring hydrocarbons were in the sludge after dehydration. Only for some of the compounds, statistically proven relationships were found and they occurred between the content of the tested PAHs in the case of 2-ring compounds between the preliminary sludge and the excessive sludge and dehydrated fermented sludge, and between the excessive sludge and the preliminary sludge and dehydrated fermented sludge. Further statistically proven differences were observed in the case of 5-ring compounds and they occurred between the preliminary sludge and the other investigated types of sludge. No statistically significant differences were observed in the case of 3, 4 and 6-ring compounds. Changes in the content of PAHs in sewage sludge during their processing with biological methods are indicated by many authors (Stringfellow 1999, Lu et al. 2013, Palani-samii in 2012, Villar et al. 2006). Some authors point to the presence of organic solvents that cause an increase in PAHs content in sludge. PAHs may also form in sludge spontaneously, in example during rotting processes, as a result of varying composition organic matter biotransformation. Fermentation of the investigated sludge did not contribute to the increase of PAH content in comparison to excessive sludge.

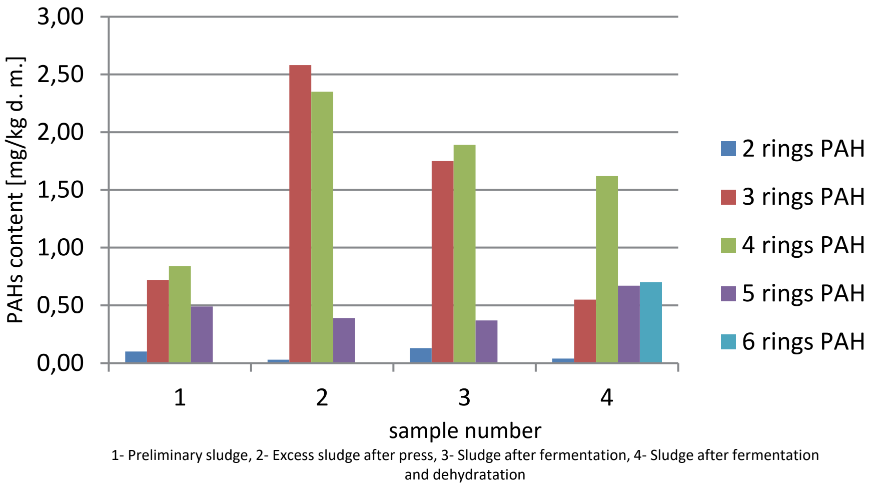


Fig. 1. PAH content in sewage sludge – autumn series

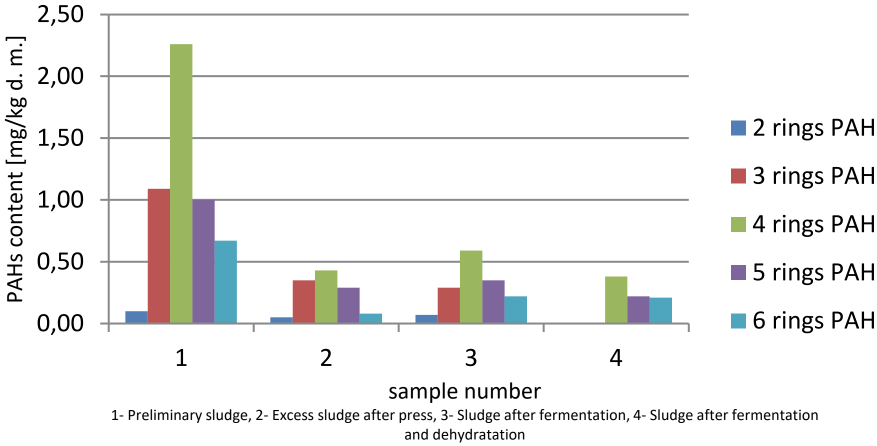
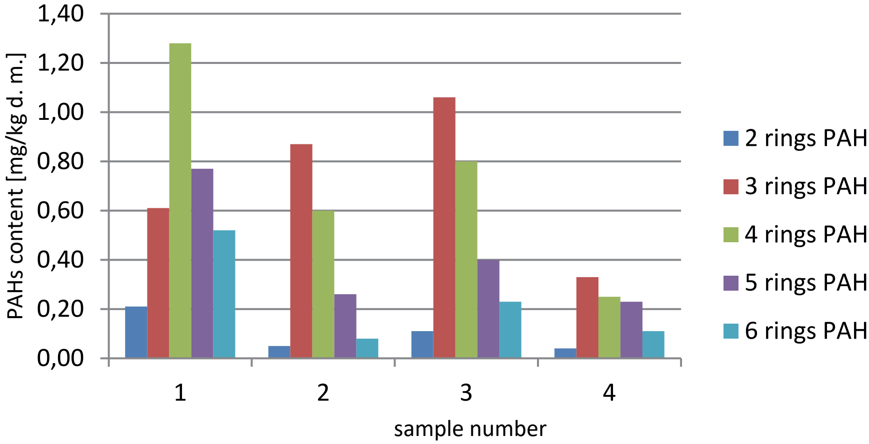


Fig. 2. PAH content in sewage sludge – winter series

The content of individual PAH groups in the investigated sludge was at a very different level depending on the series of studies, although no statistical differences between the terms (series) of sludge collection for individual PAH groups in the sludge were proved (Fig. 1, 2 and 3). Their highest amounts were recorded in series I (autumn). The content of 16 PAHs in this period was 5.4 mg/kg d. m. for excessive sludge, 4,1 mg/kg d. m. for digestate and 3,6 mg/kg d. m. for dehydrated sludge after fermentation. The exception was the preliminary sludge, in which the highest value of PAH was observed in winter (5.1 mg/kg d. m.). The highest share in the total content of PAH in the examined samples was found in three- and four-ring compounds (20.2- 44.9% and 38.7-39.8%, respectively). In the conducted studies, this correlation was observed for the winter and spring series (increase from 1.2 mg/kg d. m. in excessive sludge to 1.7 mg/kg d. m. in fermented sludge for the winter series and from 1.9 mg/kg d. m. to 2.6 mg/kg d. m. for the spring series). In the autumn series, the digested sludge contained slightly less PAH than the excessive sludge. For all series, the overall PAH content of the dehydrated digestate turned out to be lower than that of the excessive sludge.



1- Preliminary sludge, 2- Excess sludge after press, 3- Sludge after fermentation, 4- Sludge after fermentation and dehydratation

Fig. 3. PAH content in sewage sludge – spring series

In the autumn series the amount of PAH decreased by 33%, in the winter series only by 2.24% and in the spring series by 48.19%. This means that the content of PAHs in the analysed sludge decreased after processing. Similar results were obtained by Boruszko et al. (2015) and Włodarczyk-Makła (2010). According to the research carried out by the Institute of Environmental Protection for the treatment plant of Podlaskie Voivodeship in 1998-2000, the content of polycyclic aromatic hydrocarbons in sewage sludge in that period ranged from 2.6 to 17 mg/kg d.m. Comparing the results obtained (0.96-5.4 mg/kg d. m.) with those of previous years, it can be stated that the sum of PAHs in sewage sludge decreased.

Fluoranthene (8.65-17.92%), pyrene (7.54-16.30%) and phenanthrene (3.87-22.92%) were the dominating compounds. The advantage of fluoranthene, anthracene and pyrene over other PAHs in sewage sludge was found by Włodarczyk-Makuła et al. (2010). The content of benzo(a)pyrene, considered to be the most toxic aromatic hydrocarbon, was found in preliminary sludge. In the autumn series its content was 118 mg/kg d. m., and in the spring series 302 mg/kg d. m.. In the first series of studies, practically no six-ring PAHs were observed – only in the digested sludge after dehydration their value was 0.70 mg/kg d. m. It is assumed that a characteristic feature of PAHs is their increased release in the methane fermentation process (Włodarczyk-Makuła et al. 2010, Boruszko et al. 2015, Macherzyński et al. 2015). Studies on Oleszczuk and Baran (2004) show similar trends in the behaviour of PAHs in sludge. Authors found that the most mobile and at the same time the most susceptible to microorganisms, fungi and enzymes are hydrocarbons with the smallest number of aromatic rings in the particle. They show weaker hydrophobic properties than 5- and 6-ring PAHs and are less likely to bind to solid particles and therefore more bioavailable. On the other hand, PAHs with more rings and thus higher molecular weight are absorbed by the solids of the sludge and are characterised by low mobility (Marusenko et al. 2011). The authors claim that the fermentation process lowers the content of PAHs in the sludge, but the conducted studies do not confirm this relationship, the content of analyzed hydrocarbons in the digested sludge was similar to the content in the excess sludge.

In Poland, there are currently no provisions in place to limit the amount of PAHs in sewage sludge. The European Commission is planning to amend Directive 1986/278/EEC, which would set the required values for these pollutants to be met by sludge used in agricultural. It is proposed to establish the sum of 11 PAHs: acenaphthene, phenanthrene, fluorene, fluoranthene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, ben-zo(g,h,i)perylene and indeno(1,2,3-cd)pyrene. This value could not exceed 6 mg/kg d.m. of sludge. In case of the analyzed sludge, the highest total value of 16 PAHs was found in the excessive sludge during the autumn season (5.4 mg/kg d.m.). In terms of PAH content, the analyzed sludge can therefore be considered safe.

4. Conclusion

1. The 16 PAHs sum content depended on the type of sewage sludge and the highest was found in the preliminary sludge.
2. The process of fermentation, or rather dewatering of sludge after fermentation, lowered the content of 16 PAHs. Processing method affected the share of hydrocarbons in particular groups.

3. The share of individual PAH groups in terms of rings number depended on the season in which the sludge was collected for analysis.
4. The sludge samples were dominated by a group of three- and four-cyclic hydrocarbons, with the least amount of two- and six-cyclic hydrocarbons.
5. All investigated sludge samples did not exceed the normative content for the sum of 11 PAHs proposed by the European Commission for sludge used for agricultural purposes.

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Abstract

The aim of the study was to determine PAH content and the share of their individual groups in municipal sewage sludge at individual stages of their production and processing in a municipal wastewater treatment plant. Sludge samples were collected in three study cycles: autumn (November), winter (February) and spring (April) in 2017 and 2018. In each cycle the samples of initial sludge, excessive sludge after press, digestate sludge and digested dehydrated sludge were analyzed. Three samples were taken from each sludge for further analysis. The content of 16 PAH (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)-pyrene, dibenzo-(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-c, d)pyrene) was determined in the samples in the Faculty Chemical Laboratory at Białystok University of Technology. For this purpose, a gas chromatography method coupled to mass spectrometry using a GC/MS Agilent 7890B chromatograph was used. The results were given as single PAH compounds, which were then grouped by the number of aromatic rings. It was found that the total content of 16 PAHs depended on the type of sewage sludge and the highest one occurred in the initial sludge, and much lower in other sediments. The fermentation process, and more drainage of the fermentation sludge, reduced the content of 16 PAHs. The transformation processes had an influence on the hydrocarbon content in particular groups. The share of PAH groups depending on the number of rings in total 16 depended on the date of collection of studied sludges. In the studied sludges, a group of three and four-ring hydrocarbons dominated, and the least was two- and six-ring hydrocarbons. PAH content in all analyzed sludges did not exceed the norm for the total of 11 PAHs proposed by the European Commission for sludge used for agriculture.

Keywords:
PAH, sewage sludge, sludge disposal

Wpływ przeróbki osadów ścieków komunalnych na zawartość wielopierścieniowych węglowodorów aromatycznych

Streszczenie

Celem pracy było określenie zawartości WWA i udziału poszczególnych grup w komunalnych osadach ściekowych na poszczególnych etapach ich produkcji i przetwarzania w oczyszczalni ścieków komunalnych. Próbki osadów pobrano w trzech cyklach badań: jesienią (listopad), zimą (luty) i wiosną (kwiecień) w 2017 i 2018 roku. W każdym z cykli badano próbki osadu wstępnego, osadu nadmiernego po prasie, osadu przefermentowanego i osadu przefermentowanego poddanego dehydratacji. Z każdego osadu pobrano trzy próbki do dalszej analizy. Zawartość 16 WWA (naftalen, acenaften, acenaften, acenaften, fluoren, fenantren, antracen, fluoranten, piren, benzo(a)antracen, chryzen, benzo(b)fluoranten, benzo(k)fluoranten, benzo(a)piren, dibenzo(a,h)antracen, benzo-(g,h,i)perylen i indeno(1,2,3-c, d)piren) zostały zbadane w próbkach w Wydziałowym Laboratorium Chemicznym Politechniki Białostockiej. W tym celu zastosowano metodę chromatografii gazowej sprzężonej ze spektrometrią mas przy użyciu chromatografu GC/MS Agilent 7890B. Wyniki podano jako pojedyncze związki WWA, które następnie pogrupowano według liczby pierścieni aromatycznych. Stwierdzono, że łączna zawartość 16 WWA zależy od rodzaju osadu ściekowego, przy czym najwyższa z nich występuje w osadach wstępnych, a znacznie niższa w innych osadach. Proces fermentacji i dalsze odwadnianie osadu fermentacyjnego zmniejszyły zawartość 16 WWA. Procesy transformacji wpłynęły na zawartość węglowodorów w poszczególnych grupach. Udział grup WWA w zależności od liczby pierścieni w sumie 16 zależał od terminu poboru badanych osadów. W badanych osadach dominowała grupa węglowodorów trój- i czteropierścieniowych, a najmniej dwu- i sześciopierścieniowych. Zawartość WWA we wszystkich analizowanych osadach nie przekraczała normy dla 11 WWA zaproponowanej przez Komisję Europejską dla osadów wykorzystywanych w rolnictwie.

Słowa kluczowe:
WWA, osady ściekowe, unieszkodliwianie osadów

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Verification of the Methods for Calculating the Probable Maximum Flow in the Widawa River in the Aspect of Water Management in the Michalice Reservoir

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1. Introduction

From the point of view of water management, flows with a given probability of exceedance are important, especially in water reservoirs. By determining these flows, it is possible to design a reservoir adapted to local physiogeographical, hydrological or other conditions that will operate in line with its assumed function (Gunasekara & Cunnane 1991, Jayasiri et al. 2017, Laks et al. 2013, Mediero et al. 2010, Wiatkowski 2010)

The existing and planned reservoirs on the Widawa River perform a retention function, that is, they collect water during floods and play an important role during droughts. In the first case, excess water is kept in a reservoir and released from it as needed, while in the second case – it is used as a source of water for both agriculture and residents in periods of water deficit (water for consumption and for household purposes) (Dordevic & Dasic 2011, Melo et al. 2016).

Apart from the water storage function, reservoirs can also perform other functions such as water protection, water purification, water supply for industry and environment of biological life – aquatic ecosystems (Wiatkowski, Rosik-Dulewska, Tomczyk 2017, Suen & Eheart 2006).

This article focuses on the maximum flows that cause flood risk. Therefore, the most optimal method for their determination, which will be the closest to reality, is sought. Thanks to the use of accurate methods, adapted to the existing conditions, it is possible to manage water in a sustainable manner in accordance with the principles of sustainable development (George et al. 2017, Rong-Song & Chan-Ming 2017) in the conditions of high flows (these principles are defined, e.g. in instructions for managing water reservoirs). Such water management can provide adequate protection for people and property against potential losses resulting from floods and helps to preserve the natural values of a given place (Emami & Koch 2018, Krzanowski et al. 2014).

When determining maximum flows, the method accounts for a sufficiently long series of measurements (flood volume series at a given measurement point), based on which the designed flow values from the analysis of flood frequency can be determined. In this case, the main difficulty is in the selection of the probability distribution of flood size, which is related to the selection of procedures for determining the parameters. Probability distributions provide basic formulas for modelling flood quantiles with different probabilities of exceedance. After selecting an appropriate distribution, the next step is to estimate its parameters (Cunnane 1989, Młyński, Wałęga, Petroselli 2018). Various probability distributions are proposed and applied, depending, among others, on the climatic and geographic characteristics of the study region. In the USA, Pearson type III logarithmic distribution (LP3) is recommended as a distribution appropriate for defining annual maximum flood series, and the moment method is used to determine statistical parameters (USWRC 1981). The Generalised Logistic (GL) distribution is more suitable for flood data from the UK (Reed & Robson 1999). The L-Moment method is preferred for parameter estimation due to its strong properties in the presence of usually small or large values (outliers) and is recommended by many authors. However, this conventional flood rate analysis method mainly focuses on analyzing the annual maximum series of floods in natural conditions.

In the world, various methods, based on various assumptions, exist for determining probable maximum flows. In China, the Equivalent Frequency Regional Composition (EFRC) method is recommended, which assumes a perfect correlation between the flood peaks occurring in one sub-catchment and in the lower course of rivers, which means that in this method precipitation and surface hydrological processes are evenly distributed for all catchments. In reality, however, these correlations are different between catchments due to the spatial and temporal variability of precipitation and surface hydrological processes (Lu et al. 2012, Guo et al. 2004). In Mexico, the method of the Instituto de Ingenieria (IINGEN) was developed, which takes into account the maximum average annual flows for different durations. It assumes that these flows associated with different durations occur simultaneously. At the same time, it is based on the hypothesis that critical conditions for transfer are related to the duration unknown in advance, so that by taking into account all the durations, the method also accounts for the critical duration (Dominguez & Arganis 2012).

The biggest problems in the above-mentioned methods are as follows: (1) the differences in defining the most suitable watercourse section for the integration of probability distributions, (2) subjectivity in estimating flood duration (and, consequently, the maximum historical flood volumes) and (3) shape of the planned flood hydrographs (Genest et al. 2007, Rossi et al. 1984, Walder & O'Connor 1997).

In this study we determined the maximum possible flows using the Flood Frequency Analysis (FFA) method and the method of the Institute of Meteorology and Water Management in Poland (IMGW). In the first method one maximum flow value is selected for each year, while in the second one – one maximum value from the summer half-year period and one maximum value from the winter half-year period for each year (Condie & Lee 1982, Szulczewski & Jakubowski 2018). The FFA method is a classical method commonly known and used (Kidson and Richards 2005, Hirsch 2011), while the IMGW method is the Polish method recommended by the Institute of Meteorology and Water Management – National Research Institute (Szulczewski & Jakubowski 2018).

The aim of our article is to verify and evaluate the applicability of the FFA and IMGW methods for use in catchments of controlled rivers where a retention reservoir was built during the hydrological observation period. This problem is related to the necessity to update the probable maximum flows with a given probability of exceedance in the water management instruction, because since the construction of the reservoir the observational series has changed. This also applies to the design of new retention reservoirs.

The authors undertook to investigate whether the series of maximum flows prepared for the IMGW method allow one to recognize a change in the regime (caused by the construction of a retention reservoir) in the Zbytowa profile on the river Widawa, using the Mann-Kendall test.

2. Material and method

2.1. Characterization of the Widawa catchment area in the Zbytowa profile

The catchment area of the Widawa in the Zbytowa profile has an area of 738.80 km^2 (Fig.1). Other catchment parameters in this profile are as follows: asymmetry coefficient is 0.77 (which indicates asymmetry with a dominance of the left side) and the average catchment width (B) is 12.39 km. Administratively the catchment of the river Widawa in the Zbytowa profile is in the provinces: Lower Silesian, Opole and Greater Poland.

The length of the Widawa to the Zbytowa profile is 66.2 km. The average slope of the river channel is 1‰. The catchment area of the Widawa in the Zbytowa profile is of controlled type. The water gauging station on the Widawa is located at 42.77 km of the river's course (Fig.1) (KZGW 2012).

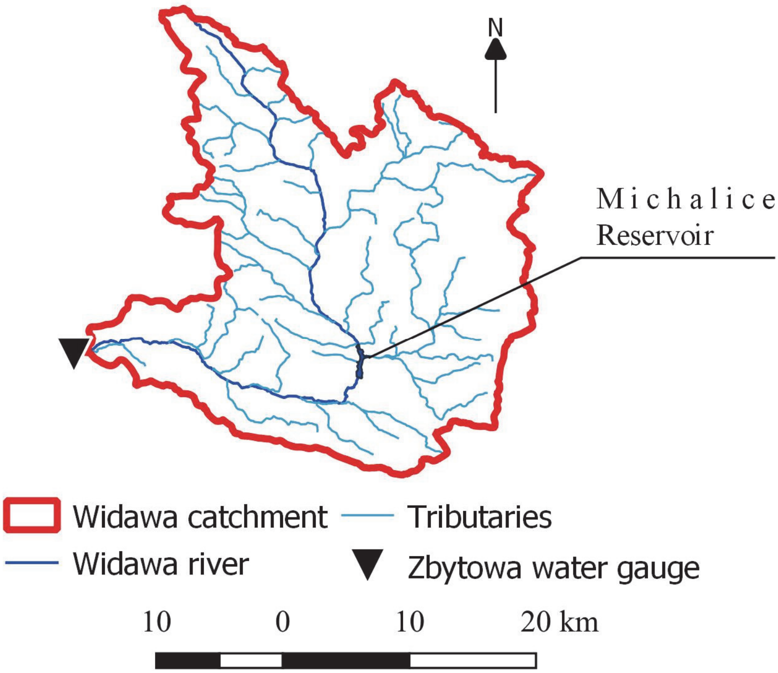

Fig. 1. The Widawa river catchment area

Over 70% of the catchment area consists of agricultural land and about 20% is covered by forests. The area is not heavily industrialized (Fig. 2b).

Over the years 1990-2018, the type of use of the Widawa river catchment area has slightly changed (Fig. 2, Tab. 1). The share of forests and seminatural areas increased from 19.4% in 1990 to 20.7% in 2018. The area of artificial surfaces rose by 2.6% and that of water bodies by 0.2%. Only the share of agricultural areas decreased from 77.3% to 73.2% (Tab. 1).

The Widawa river has its source near Drołtowice at 109.02 km of the river's course at an altitude of approx. 200 m a.s.l. and is the right tributary of the Odra (Włodek et al. 2016).

In 1971-2017, 47 water surges were recorded on the Widawa, out of which 25 in the summer half-year and 22 in winter.

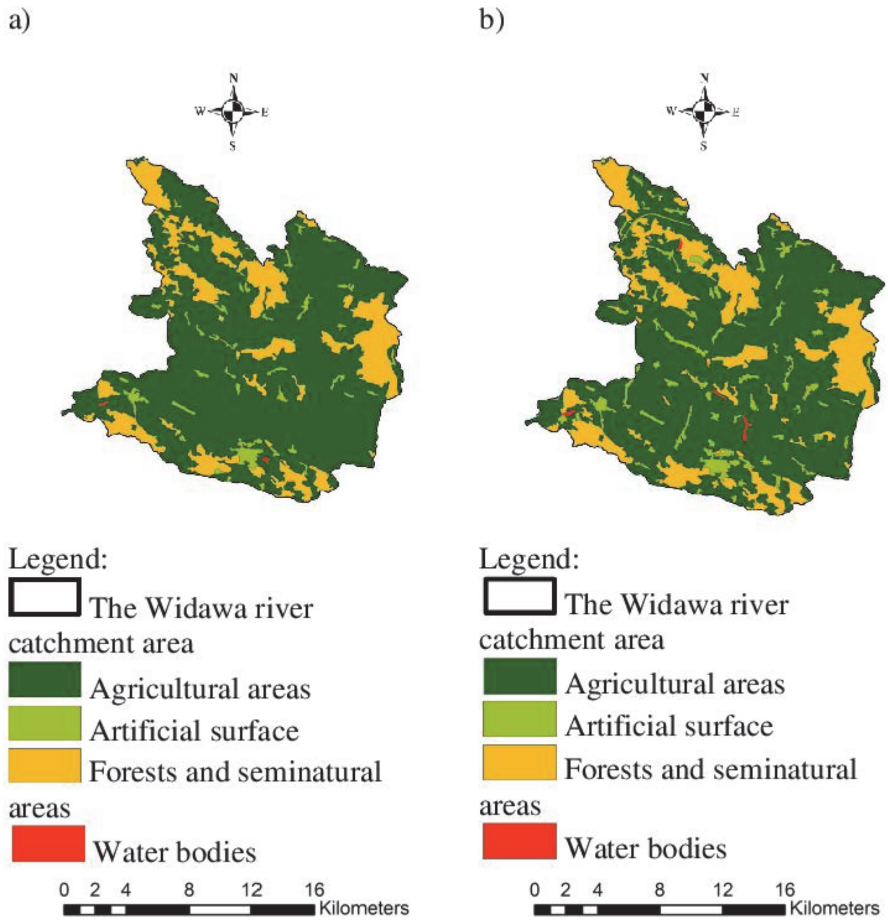

Fig. 2. The use of the Widawa catchment area, the Zbytowa profile in: a) 1990 b) 2018 (Source: GDOŚ 2019, own work)

Table 1. The change in use of the catchment area over time for years: 1990, 2000, 2006, 2012 and 2018 (Source GDOŚ 2019, own work)

Type/Year	1990	2000	2006	2012	2018
Forest and seminatural areas	19.4%	19.4%	19.9%	20.9%	20.7%
Agricultural areas	77.3%	77.2%	75.6%	73.3%	73.2%
Artificial surfaces	3.2%	3.2%	4.3%	5.5%	5.8%
Water bodies	0.1%	0.1%	0.3%	0.3%	0.3%

The hydrological regime of the river Widawa in the Zbytowa profile, classified according the criterion of Dynowska (1971,1997) is highly developed nival: the flow of the spring month exceeds 180% of the average annual flow (Fig. 3).

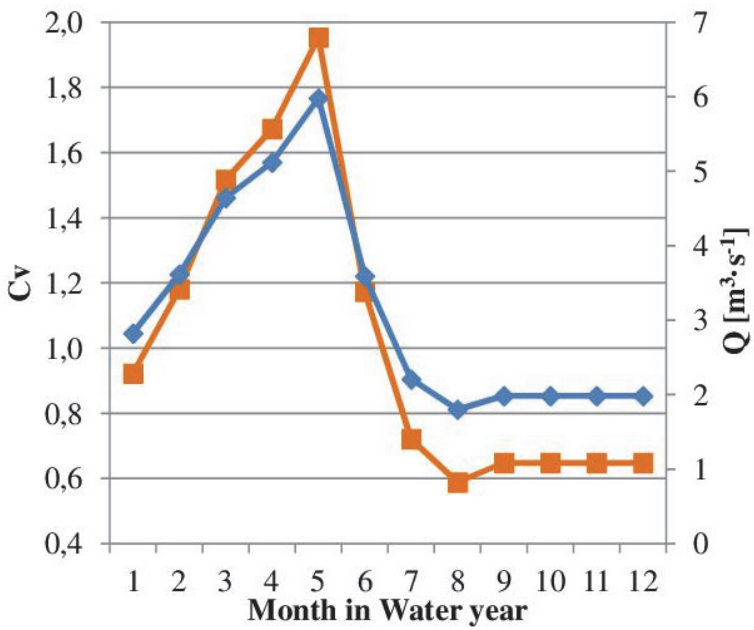

Fig. 3. Mean monthly discharges (Q) and coefficients of variation (Cv) of the Widawa measured at the Zbytowa gauging station for the period of 1971-2017

There are two reservoirs on the Widawa river: Michalice at 72.2 km of the river's course (Fig. 1) and Stradomia (at 97.0 km of the river's course).

2.2. Characteristics of the Michalice reservoir on the Widawa river

The water reservoir Michalice on the Widawa river was built in 1999-2000 and commissioned in 2001. This tank performs the following tasks: water supply for agriculture, generation of electricity, flood protection of areas located below the reservoir. The catchment in the dam profile is 509 km^2. The reservoir dam is a fourth – class facility and is located at 70.232 km of the Widawa river. The length of the dam is 455 m. The total capacity of the reservoir is: 1 748 195 m^3, flood capacity: 557 100 m^3, usable capacity: 1 191 095 m^3. Characteristic flows are: SSQ = 2.04 $m^3 \cdot s^{-1}$, SWQ = 10.9 $m^3 \cdot s^{-1}$ (Instruction 2006, Wiatkowski, Rosik-Dulewska, Tymiński 2010, Wiatkowski 2013).

2.3. Methodology for calculating the probable maximum flows used during the update of water management instructions and in the design of new retention reservoirs

Discharge data for the Widawa river, in the water gauge Zbytowa profile, covering the period of 1971-2017 were obtained from the Institute of Meteorology and Water Management – National Research Institute (Warsaw, Poland). This is a cross-section located 27.5 km downstream of Michalice. The advantage of the analyzed observational series from the Zbytowa profile is that this series is complete, i.e. no hydrological data are missing.
The flows were compiled in the hydrological year, which allowed for the inclusion of the entire water balance of the year (Null and Viers 2013).

The observational data from 1971-2017 were analyzed in three series: period 1971-2017 (full series), period 1971-2000 (series before the construction of the Michalice reservoir) and 2001-2017 (observational series after the Michalice reservoir began to operate).

A monotonic trend in the mean or median of a time series was detected by means of the Mann-Kendall test (MK test). (Blain 2015, Kendall & Stuart, 1968, Machiwal & Kumar Jha 2006, Folton et al. 2018). The critical value $u_{critical}(\alpha)$of the test statistic was assumed for the significance level of α=5%. The null hypothesis of the MK test assumes that the data come from independent, identically distributed variables (Blain 2015). For further calculations only the homogeneous series was selected.

The authors compared two methods for determining the maximum flows determining the probability of exceedance $Q_{max\ (i)}$, $p_{(i)}$ in rivers with controlled catchments based on observational series, i.e. the Flood Frequency Analysis method (FFA) (Condie & Lee 1982, Genest et al. 2007, Rossi et al. 1984, Szulczewski & Jakubowski 2018, Szulczewski, Jakubowski, Tokarczyk 2018) and the Institute of Meteorology and Water Management method (IMGW) (Szulczewski & Jakubowski 2018, Szulczewski, Jakubowski, Tokarczyk 2018).

In the FFA method, one maximum flow value was selected from each year. The IMGW method selected one maximum flow from the summer half-year and one from the winter half-year. The analyzes were conducted for each half-year separately (Szulczewski & Jakubowski 2018).

In both methods, for the multi-year observation probability distributions of maximum flows were estimated. The selected distributions allowed for Poland are: Pearson type III (PIII), log-normal (LN) and Weibull (W) (Condie & Lee 1982, Szulczewski, Jakubowski, Tokarczyk 2018, Szulczewski & Jakubowski 2018, Wdowikowski, Kaźmierczak, Ledvinka 2016). Additionally, in the IMGW method the distribution considered for the summer half-year is marked "-S" (from the word "Summer") and the distribution considered for the winter half-year is marked "-W" ("Winter").

An empirical distribution of maximum flows Q_{max} was created. The series of maximum flows $\{Q_{max\ 1}, Q_{max2},..., Q_{max\ N}\}$ was put in descending order: $\{Q_{max\ 1} \geq Q_{max\ 2} \geq ... \geq Q_{max\ N}\}$. For each value of $Q_{max,(i)}$, i = 1, 2, ..., N, the empirical probability of exceedance $p_{(i)}$ was calculated according to the formula (Cozzi et al. 2018, Młyński et al. 2019):

$$p_{(i)} = \frac{i}{N+1}, i = 1,2, \dots, N \tag{1}$$

where:
i – the number of the maximum flow $Q_{max\ (i)}$ from the range of terms in decreasing sequence $\{Q_{max\ 1}, Q_{max2},..., Q_{max\ N}\}$,
N – the number of terms in the range.

The maximum flows with a given probability of exceedance $Q_{max\ (i)}, p_{(i)}$ were calculated according to the formula based on the three-parameter Pearson type III distribution (Cozzi et al. 2018, Radecki-Pawlik et al. 2018):

$$f_{\Gamma}(x; \epsilon, \alpha, \lambda) = \frac{\alpha^{\lambda}}{\Gamma(\lambda)}(x-\epsilon)^{\lambda-1}e^{-\alpha(x-\epsilon)}, x > \epsilon, a, \lambda > 0 \tag{2}$$

where:
$\Gamma(\lambda)$ – Euler's gamma function,
$\in$ – the lower bound for this distribution, $m^3 \cdot s^{-1}$: $Q_{max} \geq \varepsilon$,
α – scale parameter, $m^3 \cdot s^{-1}$,
λ – shape parameter (dimensionless).

The value of $\in$ was estimated using the graphical method, the parameters α and λ were calculated using maximum likelihood estimation.

The obtained points ($Q_{max\ (i)}$, $p_{(i)}$) were placed on the graph. The X-axis has a logarithmic scale. The value of the lower bound for this distribution ∈ was read for probability p = 100%.

The probable maximum flow Qmax, $p_{(i)}$ in the three-parameter log-normal distribution was calculated using formula (3) (Młyński et al. 2019):

$$Q_{max,p} = \epsilon + \exp\,(\mu + \sigma \cdot u_p) \tag{3}$$

where:

∈ – the lower bound for this distribution of Qmax: Qmax ≥ ∈; the value determined by the method of moments,

μ – distribution parameter calculated by the maximum likelihood estimation,

σ – distribution parameter (standard deviation of variable ln(Qmax - ∈)), calculated using the maximum likelihood estimation.

The maximum flows determining the probability of exceedance $Q_{max\ (i)}$, $p_{(i)}$ in the three-parameter Weibull distribution was calculated using formula (4) (Bartkut & Sakalauskas 2008):

$$Q_{max,p} = \epsilon + \frac{1}{a}[-\ln(p)]^{1/8} \tag{4}$$

where:

∈ – the lower bound for this distribution of Qmax: Qmax ≥ ∈; the value read from the graph,

β – shape parameter of the distribution, β > 0; calculated using maximum likelihood estimation,

α – distribution scale parameter, α>0; calculated by the Maximum likelihood estimation.

The empirical distribution function was compared with the cumulative distribution function of the reference distribution using the Kolomogorov test (Zeng, Wang, Wu 2015) and Chi-square test (χ2) (McHugh 2013).

The critical value of the Kolmogorov distribution for α = 0.05 is $\lambda_{critical}$=1.32. In addition, one of the most reliable distribution functions was selected according to the minimum value of the Akaike information criterion (AIC) (Akaike 1974).

The Wilcoxon test verified whether there are significant differences in the results obtained by two methods in each observation period (Le 2013, van Vliet & Zwolsman 2008, Hajdukiewicz et al. 2018). For this purpose, the values of the most advantageous distributions (not discontinued by the tests: Kolomogorov, Chi-squared and AIC) were selected.

The analyzes of the minimum value of the AIC and the Wilcoxon test were carried out in the SAS software (University Edition).

3. Results and discussion

The homogeneity of the time series of maximum annual flows and maximum flows from the summer and winter half-year from three periods: 1971-2000, 2001-2017, 1971-2017 was verified with the MK test. In the FFA method, the series from all the three periods did not show a monotone trend. In the IMGW method only the series from the period 1971-2000, the summer and winter half-year did not show a monotone trend. It was the period before the construction of the Michalice reservoir. In turn, in the periods from 2001 to 2017 and from 1971 to 2017, only the series from the winter half-year did not show a monotone trend. This is due to the fact that the flows in the winter half-year are definitely lower than those in the summer half-year, as shown in the data from the Zbytów profile (Fig. 3). Moreover, the river regime in the winter half-year does not require as many flow-control measures as in the summer half-year. In the first half of summer, water management in the flood period (when the inflow to the reservoir exceeds 3 $m^3 \cdot s^{-1}$) requires filling of the usable capacity and then flood capacity (forced and flood forced) and controlling the operation of discharge devices (Instruction 2006). Other literature items hint at similar experiences and emphasize the homogeneity of results obtained using FFA (Kidson & Richards 2005, Hirsch 2011, Ullah et al. 2012).

During the analysis of the PIII, LN and W distribution graphs, it was found that in the FFA method, in all the three research series, the LN distribution fits the empirical data of Q_{max} (Fig. 4). This is confirmed by the Kolomogorov's test. The test shows that the empirical distribution function is a log-normal distribution in all the three test periods (Tab. 2). Additionally, the P III distribution in two periods: 2001-2017 and 1971-2017 was confirmed using the Kolmogorov test. However, the Chi-square test showed that only the LN distribution in three periods and W distribution in 2001-2017 have been fitted to the empirical distribution function (Tab. 2).

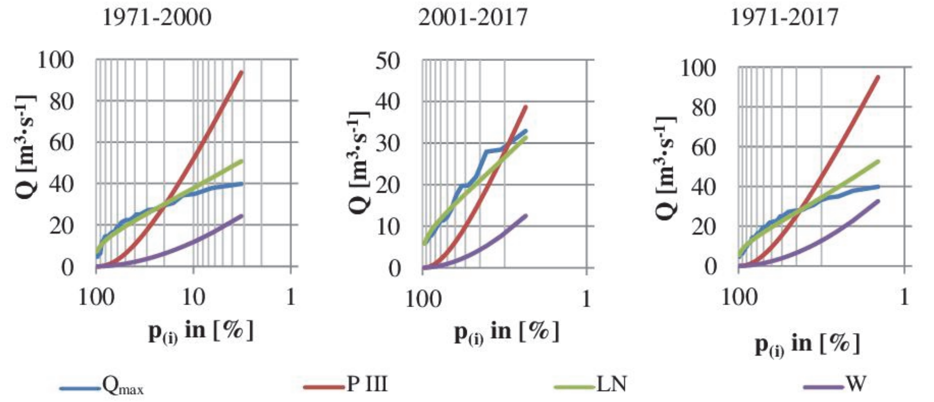

Fig. 4. Empirical curve Q_{max} and PIII, LN, W distributions according to the FFA method

Various authors have demonstrated the validity of using the method to determine the maximum flood flows in the aspect of rational management of reservoirs (e.g. Deduru Oya reservoir on the Deduru river, Sri Lanka) and dams (e.g. Malpaso dam in Mexico, Xiaodae dam in China) (Dominguez & Arganis 2012, Jayasiri et al 2017, Hassanli & Beecham 2013, Sordo-Ward et al 2017).

The Akaike information criterion showed that in the periods of 1971-2017 and 2001-2017 the best fitting distribution was the LN, while in 1971-2000 the best fitting distribution was the W distribution (Tab. 2).

In the IMGW method only in the summer half-year of the period 1971-2000, the PIII distribution was fitted to the empirical distribution of the Q_{max}.

However, the W distribution in four periods differed from the empirical distribution. Both in the IMGW method and in the FFA method in all the four study periods, the LN distribution turned out to be the most similar to the distribution of Qmax (Fig. 5). This was confirmed by the Kolomogorov test (Tab. 3). The Kolomogorov test also confirmed the P III-S distribution in the period 1971-2000 (Tab. 3). However, the Chi-square test showed that only the LN distribution in the four test periods and the W-S distribution in 1971-2000 and W-W in 2001-2017 have been fitted to the empirical distribution function (Tab. 3).

Table 2. Results of testing the agreement between the empirical (sample) distribution and the theoretical distributions in the FFA method

Period	Distribution	Kolmogorov test	χ2 test	AIC
1	2	3	4	5
1971-2000	LN	Dmax=0.06 λkol = 0.41	χ2=5.5 $\alpha_{test5\%}$=42.5	7.4
2001-2017	LN	Dmax=0.05 λkol = 0.22	χ2=1.4 $\alpha_{test5\%}$=26.3	63.7
1971-2017	LN	Dmax=0.06 λkol = 0.41	χ2=6.12 $\alpha_{test5\%}$=62.8	222.2
1971-2000	P III	Dmax=0.29 λkol = 1.59	χ2=202.9 $\alpha_{test5\%}$=42.5	9.8
2001-2017	P III	Dmax=0.22 λkol = 0.91	χ2=41.5 $\alpha_{test5\%}$=26.3	85.5
1971-2017	P III	Dmax=0.02 λkol = 0.14	χ2=256,2 $\alpha_{test5\%}$=62.8	282.7
1971-2000	W	Dmax=0.59 λkol = 3.23	χ2=76,7 $\alpha_{test5\%}$=42.5	3.4
2001-2017	W	Dmax=0.44 λkol = 1.81	χ2=18.4 $\alpha_{test5\%}$=26.3	89.5
1971-2017	W	Dmax=0.29 λkol = 1.99	χ2=123.8 $\alpha_{test5\%}$=62.9	292.1

Akaike information criterion showed that in the periods 1971-2017 and 2001-2017 the distribution of LN-W was fitted to the empirical distribution of the Q_{max}, while in the period: 1971-2000, the W-W distribution (Tab. 3).

In both methods, the best-fit distribution of Q_{max} is the log-normal distribution. A similar result was obtained by Szulczewski & Jakubowski (2018) for a series consisting of 44 years for the Widawa river in the Zbytów profile, who compiled p – values from the Goodness-of-fit of the χ2 test for Pearson type III, log-normal distributions, GEV and MIX. The LN distribution had the lowest p – value.

In the Wilcoxon test, the LN distribution values were compared for both calculation methods separately for three time intervals (1971-2000, 2001-2017, 1971-2017).

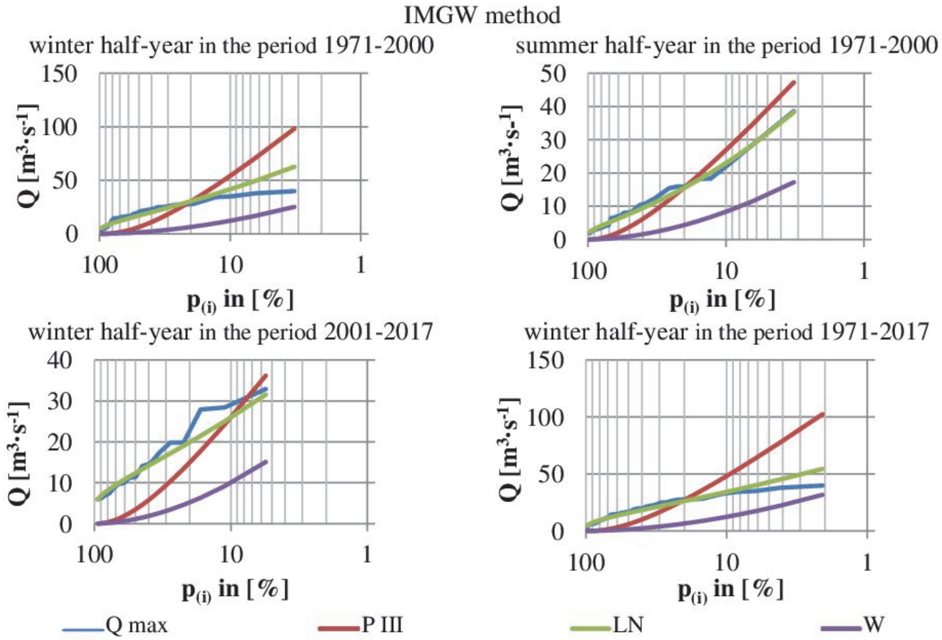

Fig. 5. Empirical curve of Q_{max} and PIII, LN, W distributions according to the IMGW method

The LN distributions from both calculation methods were compared using the Wilcoxon test for a 50% probability, taking values from three time intervals (in total six data samples – three from the IMGW method and three from the FFA method). The test showed no differences between the analyzed calculation methods.

Table 3. Results of testing the agreement between the empirical (sample) distribution and the theoretical distributions in the IMGW method

Period	Distribution	Kolmogorov test	χ2 test	AIC
1	2	3	4	5
1971-2000	LN-W	Dmax=0.07 λkol = 0.38	χ2=13.7 αtest5%=42.6	5.5
1971-2000	LN-S	Dmax=0.06 λkol = 0.32	χ2=1.2 αtest5%=42.6	88.3

Table 3. cont.

Period	Distribution	Kolmogorov test	χ2 test	AIC
1	2	3	4	5
2001-2017	LN-W	Dmax=0.06 λkol = 0.25	χ2=1.3 $\alpha_{test5\%}$=26.3	163.6
1971-2017	LN-W	Dmax=0.04 λkol = 0.27	χ2=6.6 $\alpha_{test5\%}$=62.8	224.8
1971-2000	P III-W	Dmax=0.42 λkol = 2.30	χ2=187.8 $\alpha_{test5\%}$=42.6	6.6
1971-2000	P III-S	Dmax=0.23 λkol = 1.26	χ2=41.0 $\alpha_{test5\%}$=42.6	117.0
2001-2017	P III-W	Dmax=0.40 λkol = 1.65	χ2=37.1 $\alpha_{test5\%}$=26.3	186.3
1971-2017	P III-W	Dmax=0.37 λkol = 2.53	χ2=246.2 $\alpha_{test5\%}$=62.8	280.9
1971-2000	W-W	Dmax=0.52 λkol = 2.85	χ2=70.8 $\alpha_{test5\%}$=42.6	3.4
1971-2000	W-S	Dmax=0.26 λkol = 1.42	χ2=21.0 $\alpha_{test5\%}$=42.6	130.8
2001-2017	W-W	Dmax=0.33 λkol = 1.36	χ2=20.1 $\alpha_{test5\%}$=26.3	188.5
1971-2017	W-W	Dmax=0.27 λkol = 1.85	χ2=110.4 $\alpha_{test5\%}$=62.9	290.9

4. Summary and conclusions

The comparative analysis of the values of maximum flows determining the probability of exceedance $Q_{max\ (i)}$, $p_{(i)}$, obtained using the FFA and IMGW methods as well as PIII, LN and W distributions, allows one to draw the following conclusions:

1. Observational series (from 1971-2017 and 2001-2017) prepared based on the maximum flows of water from the Widawa River (Zbytowa profile) for the FFA method were tested with the Mann-Kendall test. The test showed their homogeneity, despite the fact that a reservoir was built on the river and the water management in the catchment of this watercourse changed. However, observational series prepared for the needs of the IMGW method were homogeneous only before the construction of the reservoir (period 1971-2000). After the construction, observational series (1971-2017 and 2001-

2017) were only homogeneous in the winter half-year. This is due to the fact that the flows in the winter half-year are definitely lower than those in the summer half-year.

2. The calculation series prepared according to the IMGW methodology enabled the Mann-Kandall test to exclude homogeneous series resulting from the change in the regime following the construction and operation of the Michalice retention reservoir located on the Widawa river in the Zbytowa profile.
3. At the Zbytów profile of the Widawa, in both the FFA and IMGW method, for a series of flows from the multi-period 1971-2000 (the period before the reservoir construction) the AIC criterion indicated a different distribution (W distribution) than the Kolomogorov and Chi-square tests.
4. When analyzing the results of the Kolomogorov and Chi-square tests it appeared that if one of them indicated that the real distribution of the variable Q_{max} for the river Widawa (Zbytowa profile) were two distributions, the other indicated only one of them. It allowed us to choose one of three distributions.
5. The Wilcoxon test showed no significant differences between the analyzed methods used to determine the maximum flows determining the probability of exceedance $Q_{max\,(i),}\,p_{(i)}$ on the Widawa river (Zbytowa profile). Therefore, as a method for calculating the $Q_{max\,(i),}\,p_{(i)}$ in the Zbytowa profile of the Widawa in the context of managing the Michalice retention reservoir, one can recommend either of the methods: both FFA and IMGW.
6. The best-fitting distribution of the empirical distribution function Qmax for the Widawa River (the Zbytowa profile) in the three analyzed series is the LN distribution. It can be used to calculate the maximum flows determining the probability of exceedance $Q_{max\,(i),}\,p_{(i)}$ on the Widawa river (Zbytowa profile) needed to update the reservoir's water management instructions.

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Abstract

Flows with a given probability of exceedance are important from the point of view of water management, especially in water reservoirs. By determining these flows, it is possible to design a reservoir adapted to local conditions that will operate in line with the assumed function. Various methods exist in the world for determining the probable maximum flows; these methods are based on various assumptions. The aim of the article is to verify and assess the applicability of the Flood Frequency Analysis (FFA) and the IMGW method for use in catchments of controlled rivers where a retention reservoir was built during the hydrological observation period. This is important in updating the water management instructions and in designing new retention reservoirs. The authors undertook to investigate whether a series of maximum flows prepared for the IMGW method allows one to recognize the regime change, caused by the construction of the retention reservoir, in the water gauge Zbytowa profile on the Widawa River, using the Mann-Kendall test. The following distributions were used in the study: Pearson type III, log-normal and Weibull.

The Mann-Kendall test showed homogeneity of three observational series: 1971-2000, 2001-2017 and 1971-2017 prepared for the FFA method despite the fact that in 2001 the Michalice retention reservoir was commissioned on the Widawa river and the water management in the basin changed this watercourse. However, the observational series prepared for the IMGW method were homogenous only prior to the construction of the reservoir (1971-2000). The observational series prepared in this way enabled the Mann-Kandall test to exclude the homogeneous series caused by the regime change as a result of the construction and operation of the Michalice retention reservoir. Only after the construction of the retention reservoir the observational series from the winter half-year were homogeneous. This is due to the fact that the flows in the winter half-year are definitely lower than those in the summer half-year. The best-fitting distribution for the empirical distribution for the Widawa (the Zbytowa profile) in the analyzed series is a log-normal distribution that can be used to calculate the probable maximum flows needed to update the reservoir's water management instructions. The Wilcoxon test showed no difference between the calculation methods analyzed and used to estimate the probable maximum flows in the Zbytowa profile on the Widawa river. Therefore, as a method for calculating the probable maximum flows for the Widawa river (the Zbytowa profile) in the aspect of managing the Michalice reservoir or some other river with controlled catchment and parameters similar to those of the Widawa (in the Zbytowa profile), one can recommend either of the two analyzed methods: both FFA and IMGW.

Keywords:
water reservoirs, log-normal distribution, Pearson type III distribution,
Weibull distribution, maximum flow estimation, Flood Frequency Analysis,
IMGW method

Weryfikacja metod obliczania przepływów maksymalnych prawdopodobnych w rzece Widawie w aspekcie gospodarki wodnej zbiornika Michalice

Streszczenie

Przepływy o zadanym prawdopodobieństwie przewyższenia są istotne z punktu widzenia gospodarowania wodami na zbiornikach wodnych. Dzięki wyznaczeniu tych przepływów możliwe jest zaprojektowanie zbiornika dostosowanego do lokalnych warunków, który będzie funkcjonował zgodnie z założoną funkcją. Na świecie obowiązują różne metody wyznaczania przepływów maksymalnych prawdopodobnych, które bazują na odmiennych założeniach. Celem artykułu jest weryfikacja i ocena możliwości zastosowania metody Flood Frequency Analysis (FFA) i metody IMGW do zastosowania w zlewniach rzek kontrolowanych, na których w okresie obserwacji hydrologicznej wybudowano zbiornik retencyjny. Ma to znaczenie w aktualizacji instrukcji gospodarowania wodą oraz w projektowaniu nowych zbiorników retencyjnych. Autorzy podjęli się zbadania czy serie przepływów maksymalnych przygotowane dla metody IMGW pozwalają na rozpoznanie zmiany reżimu, w rzece Widawie w przekroju Zbytowa, przy pomocy testu Manna-Kendalla, spowodowanej wybudowaniem zbiornika retencyjnego. W pracy wykorzystano następujące rozkłady: Pearsona typ III, logarytmiczno-normalnego oraz rozkład Weibulla.

Test Manna-Kendalla wykazał jednorodności trzech serii obserwacyjnych: 1971-2000, 2001-2017 i 1971-2017 przygotowanych dla metody FFA pomimo, że na rzece Widawie w 2001 roku został oddany do eksploatacji zbiornik retencyjny Michalice i zmieniło się gospodarowanie wodą w zlewni tego cieku. Natomiast serie obserwacyjne sporządzone dla metody IMGW były jednorodne jedynie przed budową zbiornika (okres 1971-2000). Tak przygotowana seria obserwacyjna umożliwiła testowi Manna-Kandalla wykluczyć serie jednorodne spowodowane zmianą reżimu na skutek wybudowania i pracy zbiornika retencyjnego Michalice. Jedynie po budowie zbiornika retencyjnego serie obserwacyjne z półrocza zimowego były jednorodne. Jest to spowodowane tym, że przepływy w półroczu zimowym są zdecydowanie niższe niż przepływy w półroczu letnim. Najbardziej dopasowanym rozkładem zmiennej Q_{max} dla rzeki Widawy (profil Zbytowa) w analizowanych seriach jest rozkład logarytmiczno-normalny, który może zostać wykorzystany do obliczeń przepływów maksymalnych prawdopodobnych potrzebnych do aktualizacji instrukcji gospodarki wodnej zbiornika. Test Wilcoxona wykazał, brak różnic pomiędzy analizowanymi metodami obliczeniowymi użytymi do obliczeń maksymalnych przepływów o określonym prawdopodobieństwie przewyższenia rzeki Widawy (profil Zbytowa), dlatego też jako metodę do obliczania przepływów maksymalnych prawdopodobnych w zlewni rzeki Widawy w profilu Zbytowa w aspekcie gospodarowania wodami zbiornika retencyjnego Michalice lub innej rzeki o zlewni kontrolowanej o podobnych parametrach zlewni co zlewnia rzeki Widawa (profil Zbytowa), można wskazać obie analizowane metody: FFA i IMGW.

Słowa kluczowe:
zbiorniki wodne, rozkład logarytmiczno-normalny, rozkład Pearsona III typu,
rozkład Weibulla, wyznaczanie przepływów maksymalnych, Flood frequency analysis,
metoda IMGW

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Glycerine as an External Source of Carbon Supporting Denitrification Process

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1. Introduction

Supplementation of wastewater under treatment with carbon from external sources often becomes essential to achieve high wastewater treatment plant efficiency as such plants must comply with very strict requirements regarding limitation of nitrogen concentration. Use of conventional carbon sources is associated with wastewater treatment plant high operating costs. The costs of external carbon source, and waste management, make in total more than 50% of all costs of wastewater treatment (Fernández-Nava et al. 2010, Ignatowicz et al. 2011). Furthermore, a period of macrobial adaptation is often required after the introduction of a given carbon source into the wastewater treatment plant system (Elefsiniotis and Li 2006; Min at al. 2002). This became a premise for seeking of other alternative sources of organic carbon.

A waste product, showing high potential as an external source of carbon, is glycerine fraction being a by-product of biodiesel production. There are many reports on application of glycerine as a proper source of carbon for wastewater treatment (Bodik et al. 2009, Akunna et al. 1993, Torà et al. 2011) as well as about application of glycerine to reduce biomass generation (Kulikowska and Bernat 2015). Today, in many countries diesel oil is supplemented with biodiesel causing successive increase of its production, therefore, generation of some amount of glycerine fraction (Kulikowska and Bernat 2015, da Silva et al. 2009). Production of circa 10 litres of biodiesel generates 1 litre of glycerine (Johnson and Taconi 2007, Guerrero et al. 2012). The glycerine phase contains, apart from glycerol (propane-1,2,3-triol – 50-60%) also other substances such as methanol, mono-diacylglycerols, free fatty acids as well as soaps. Glycerol originating from biodiesel production contains many contaminants, therefore, with increase of its production, glycerine prices decreased. Consequently, glycerol became waste, which should be rendered harmless and price of this product is more attractive compared to other substrates used as external sources of carbon in denitrification and dephosphatation processes (Yazdani and Gonzales 2007, Janczukowicz and Rodziewicz 2013).

The research work performed was aimed at demonstration that application of glycerine as external source of carbon in wastewater treatment process has positive impact on effectiveness of elimination of nitrogen forms from wastewater and may replace other alternative sources of carbon.

2. Methodology of research

Tests were performed during municipal wastewater treatment process performed in two independent reactors (R1 and R2) with SBR-type activated sludge. Their active volume was 10 dm^3, whereof 6.5 dm^3 was occupied by activated sludge, whereas the remaining volume was occupied by mechanically treated raw wastewater delivered from Białystok wastewater treatment plant.

Table 1. Work parameters of SBR reactors

Pos.	Indicator	Value	Unit of measure
1	Activate sludge concentration	3.5	kg/m^3
2	Sludge index	120-150	cm^3/g
3	Chamber hydraulic load	1.4	m^3/m^3·d
4	Load of organic compounds	0.2-0.3	kg COD/m^3·d
5	Decantation coefficient	0.3	–

A single reactor operating cycle lasted 6 hours and comprised the following stages: wastewater supply (2 min.), anaerobic mixing (60 minute), aeration (3.5 h), sedimentation (1 h) and decantation (0.5 h). During the stage of aeration performed via a diffuser located at reactor bottom, compressed air was supplied, depending on the operation stage, in amount from 0.1 up to 3.0 mg O_2/dm^3; activated sludge concentration was 3.5 kg/m^3, sludge index fluctuated from 120 to 150 cm^3/g, chamber hydraulic load was 1.4 m^3/m^3·d and load of organic compounds was 0.2 kg COD/m^3·d. Glycerine, as a source of easily assimilable organic compounds, in amount of 100 mg to 1 dm^3 of wastewater was being added to one of the chambers (R2) in each cycle, after twenty minutes from wastewater filling. Table 1 shows operating parameters of SBR reactors.

Wastewater samples were filtrated, in each the following parameters were being determined, each time, in accordance with the applicable methodology:

- COD – dichromate method as per PN-74/C-04578.03 standard,
- BOD_5 – manometric method based on OxiTop standard,
- $N\text{-}NH_4$ – spectrophotometric method as per PN-ISO 7150-1:2002 standard,
- $N\text{-}NO_3$ – spectrophotometric method as per PN-82/C-04576/08 standard,
- N_{tot} – spectrophotometric method as per PN-EN ISO 6878:2006 standard,
- P_{tot} – spectrophotometric method as per PN-C-04576-00:1973P standard.

COD fractions: S_S (dissolved easily biodegradable), S_I (dissolved non-degradable biologically), X_S (organic suspension slowly degradable), X_I (organic suspension non-degradable biologically) were determined based on ATV-A 131 guidelines. Nitrates elimination velocity r_v, during SBR reactor process stages, was calculated from formula (1):

$$r_v=(C_0-C_e)\cdot t^{-1}\ \left[\text{mg N}\cdot\text{dm}^3/\text{h}\right] \tag{1}$$

where:
C_0 – nitrates concentration at the beginning of the process stage [mg N/dm^3],
C_e – nitrates concentration at the end of the process stage [mg N/dm^3],
t – process stage time [h].

3. Test results and interpretation

The results of wastewater tests performed without supplementation with carbon from an external source (R1 reactor) and with glycerine added as carbon from external source (R2 reactor) are presented in Table 2.

Figure 1 shows a listing of COD proportion to total nitrogen at particular check points. According to ATV, Henze, Szpindor, Łomotowski, Janczukowicz, Akunna, denitrification proceeds uninterruptedly if COD/N_{tot} proportion varies from 4 to 10. COD to N_{tot} proportion in wastewater in both SBR reactors was insufficient for denitrification process course and was below the recommended range. Supplementation of the reactor with glycerine improved this relationship and COD/N_{tot} proportion reached the recommended level.

In research work presented by Bernat et al. [12] on application of glycerine as an external source of carbon for elimination of nitrogen forms in SBR-type chambers, it was found that the optimal COD/N_{tot} proportion should be 3.0, as in such case, both elimination of nitrogen compounds proceeds in the best way and biomass generation in SBR-chambers is at the lowest level. COD/N_{tot} proportion in the tested raw wastewater was close to that recommended by the authors as it was 4.49, whereas just before supplementation with glycerine as the carbon source, COD/N_{tot} proportion was 3.11.

Table 2. Summary of wastewater results

	Reactor	COD	BOD_5	N_{tot}	NO_3^-	NO_4^+	P_{tot}
		[mg O_2/dm^3]	[mg O_2/dm^3]	[mg N/dm^3]	[mg N/dm^3]	[mg N/dm^3]	[mg P/dm^3]
Raw wastewater	R1	530	230	118	2.6	51.1	18.5
	R2	530	230	118	2.6	51.1	18.7
Wastewater after filling (20 min) **after 20 min**	R1	268	125	84.0	3.9	58.2	15.2
	R2	262	125	84.1	4.8	42.2	15.0
Denitrification process (20 min) **after 40 min**	R1	262	120	68.7	2.4	55.3	18.0
	R2	322	150	72.0	2.2	49.0	16.9
Denitrification process (20 min) **after 60 min**	R1	259	120	55.2	3.6	41.6	12.8
	R2	331	145	69.0	2.6	45.2	15.0
Nitrification process (1.5 h) **after 2.5 h**	R1	254	115	48.1	4.6	33.5	1.5
	R2	279	120	61.2	6.6	24.4	1.2
Nitrification process (2 h) **after 4.5 h**	R1	243	98	24.3	8.6	9.7	1.1
	R2	234	98	6.5	3.6	2.9	0.8
Decantation (0.5h) **after 6 h**	R1	35	6	14.4	8.6	1.8	0.8
	R2	28	2	5.6	3.2	0.6	0.5

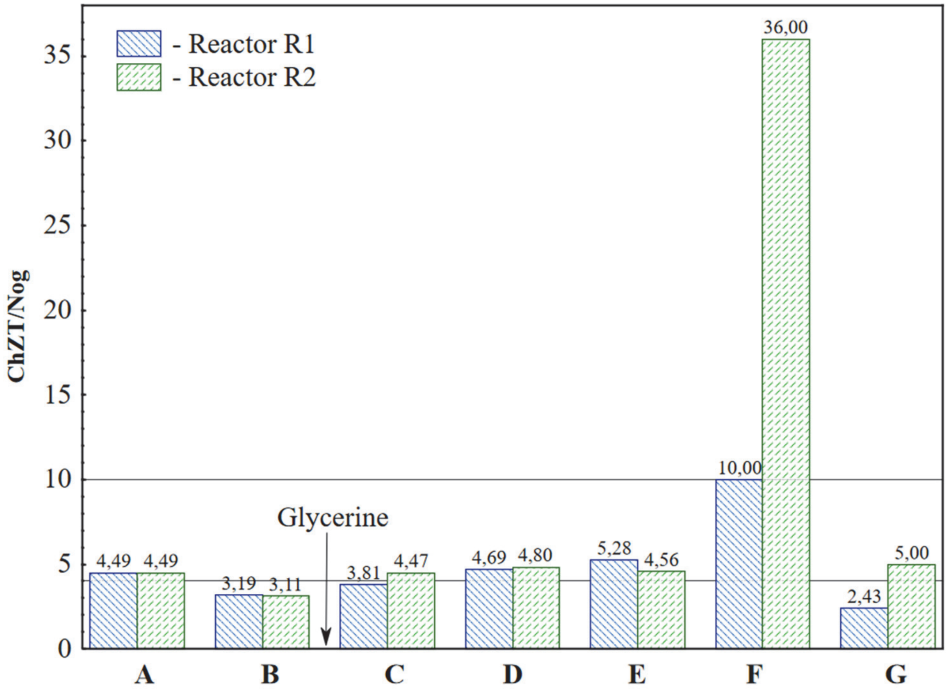

Fig. 1. Comparison of COD to total nitrogen at individual control points (A – raw wastewater; B – wastewater after filling (20 min); C – denitrification process (20 min); D – denitrification process (20 min); E – nitrification process (90 min); F – nitrification process (120 min); G – decantation (30 min))

Value of COD in raw wastewater was 530 mg O_2/dm^3, whereas BOD_5 – 230 mg O_2/dm^3. Total nitrogen concentration in raw wastewater was 118 mg N/dm^3, ammonium nitrogen – 51.5 mg N/dm^3, nitrates 2.6 mg N/dm^3 and total phosphorus – 18.5 mg P/ dm^3.

After twenty minutes as of reactors filling, assimilable carbon was consumed by denitrification bacteria resulting in reduction of COD (by approximately 50%) and BOD_5 (by approximately 46%). COD value amounted to 268 mg O_2/dm^3 (in R1 reactor) and 262 mg O_2/dm^3 (in R2 reactor), whereas BOD_5 value amounted to 125 mg O_2/dm^3 (both in R1 and R2 reactors). Total nitrogen concentration in both reactors decreased to approximately 84 mg N/dm^3. Concentration of nitrates increased up to 3.9 mg N/dm^3 in R1 reactor, and up to 4.8 mg N/dm^3 in R2 reactor. Ammonium nitrogen concentration increase was noted for R1 reactor up to 58.2 mg N/dm^3, whereas in R2 reactor ammonia nitrogen concentration decreased down to 42.2 mg N/dm^3.

Then, glycerine was added to R2 reactor as carbon external source, and after twenty minutes of anaerobic denitrification process, subsequent samples were taken. Glycerine supply to R2 reactor resulted in increase of COD up to 322 mg O_2/dm^3, and BOD_5 – up to 150 mg O_2/dm^3. However, in R1 reactor , to which no glycerine was supplied, further insignificant decrease of COD to 262 mg O_2/dm^3 and BOD_5 to 120 mg O_2/dm^3 was noted. The denitrification process resulted also in reduction of total nitrogen concentration in both reactors – in R1 down to 68.7 mg N/dm^3, whereas in R2 – down to 72 mg N/dm^3. Similar decreasing trend was noted for nitrates – in R1 reactor the concentration was 2.4 mg N/dm^3, and in R2 reactor – 2.2 mg N/dm^3. Ammonium nitrogen concentration decreased insignificantly in R1 reactor down to 55.3 mg N/dm^3, whereas in R2 reactor a reverse situation was noted, i.e. ammonium nitrogen concentration increased up to 49 mg N/dm^3, but this concentration was still lower than in R1 reactor.

After subsequent twenty minutes of anaerobic wastewater treatment in R1 reactor, further slight decrease of COD down to 259 mg O_2/dm^3 was noted, whereas BOD_5 value remained unchanged – 120 mg O_2/dm^3. In R2 reactor with glycerine added, a reverse situation occurred, i.e. further increase of COD up to 331 mg O_2/dm^3 was noted. BOD_5 decreased down to 145 mg O_2/dm^3, but those values were higher than in the reactor without supplementation with carbon source. Total nitrogen concentration continued to decrease and in R1 reactor was 55.2 mg N/dm^3. In the case of R2 reactor, total nitrogen concentration was higher than in R1 reactor and amounted to 69 mg N/dm^3. In both reactors increase of nitrates concentrations up to 3.6 mg N/dm^3 in R1 reactor and 2.6 mg N/dm^3 in R2 reactor was noted. Ammonium nitrogen concentration decreased in R1 reactor down to 41.6 mg N/dm^3, whereas in R2 reactor – down to 45.2 mg N/dm^3. The difference of ammonium nitrogen concentration at this check point between reactor without carbon source (R1) and reactor with glycerine (R2) was 3.6 mg N/dm^3.

Subsequent samples were taken after 1.5 h of wastewater aeration. COD value in R1 reactor was 254 mg O_2/dm^3, whereas BOD_5 was 115 mg O_2/dm^3. In reactor R2, despite reduction of COD value by 52 mg O_2/dm^3 (15.7%) down to 279 mg O_2/dm^3 and BOD_5 value by 25 mg O_2/dm^3 down to 120 mg O_2/dm^3, those values were higher than in R1 reactor without glycerine added. Also total nitrogen concentration in reactor without carbon source added was lower and amounted to 48.1 mg N/dm^3. In the case of R2 reactor, concentration of total nitrogen was 61.2 mg N/dm^3. The difference of total nitrogen concentrations between R1 and R2 reactors was 13.1 mg N/dm^3. Due to oxygen supply to the reactors, retardation of the denitrification process had happened, therefore, concentration of nitrates in R1 reactor increased up to 4.6 mg N/dm^3. In R2 reactor increase of nitrates concentration up to 6.6 mg N/dm^3 was also noted. Ammonium nitrogen concentration decreased in R1 reactor down to 33.5 mg N/dm^3, whereas in R2 reactor – down to 24.4 mg N/dm^3. The difference in ammonium nitrogen concentrations at this check point between R1 reactor without carbon source and R2 reactor containing glycerine was 9.1 mg N/dm^3.

Due to further wastewater aeration (2 h), COD value in R1 reactor was 243 mg O_2/dm^3. In glycerine containing reactor, further consumption of assimilable organic compounds proceeded, which resulted in lower COD value being approximately 234 mg O_2/dm^3. BOD_5 value decreased in both reactors down to 98 mg O_2/dm^3. Total nitrogen concentration in R1 reactor was 24.3 mg N/dm^3, whereas in R2 reactor it was lower by 17.8 mg N/dm^3 and amounted to 6.5 mg N/dm^3. Nitrates concentration in R1 reactor continued to increase up to 8.6 mg N/dm^3, whereas in R2 reactor it decreased down to 3.6 mg N/dm^3. Long wastewater aeration time caused considerable decrease of ammonium nitrogen concentration in both reactors compared to the previous check point. In R1 reactor, concentration of this nitrogen form was 9.7 mg N/dm^3, whereas in R2 reactor – 2.9 mg N/dm^3. The difference in ammonium nitrogen concentrations between R1 reactor without carbon source and R2 reactor containing glycerine was 6.8 mg N/dm^3.

COD value in treated wastewater from R1 reactor decreased, after decantation process, down to 35 mg O_2/dm^3, whereas BOD_5 value decreased down to 6 mg O_2/dm^3. Despite addition of carbon from external source, COD in treated wastewater with added glycerine amounted to 28 mg O_2/dm^3, and BOD_5 – 2 mg O_2/dm^3. These are lower values with relation to R1 reactor where no additional source of carbon was used. Total nitrogen concentration in treated wastewater from R1 reactor decreased down to 14.4 mg N/dm^3, ammonium nitrogen decreased down to 1.8 mg N/dm^3, but the decantation process had no impact on nitrates concentration, value of which amounted to 8.6 mg N/dm^3. Wastewater treatment in R1 reactor caused elimination of total nitrogen in 87.8%, as well as ammonium nitrogen, in 96.5%. In the case of the glycerine containing reactor, total nitrogen concentration in treated wastewater was reduced to 5.6 mg N/dm^3, ammonium nitrogen concentration was reduced down to 0.6 mg N/dm^3 and nitrates concentration was reduced down to 3.2 mg N/dm^3. Wastewater treatment in R2 reactor caused elimination of total nitrogen in 95.3% and ammonium nitrogen – in 98.8%. Application of glycerine in R2 reactor had impact on higher efficiency of the wastewater treatment process than in R1 reactor, where no supplementation with carbon from external source was applied. Despite increase of nitrates concentration in treated wastewater, nitrates concentration in the reactor in which external source of carbon was applied, was lower by as much as 5.4 mg N/dm^3. Concentration of total phosphorus in treated wastewater decreased down to 0.8 mg P/dm^3.

Just like in the paper of Bodik et al. (2009), where test results in laboratory and technical scale on use of glycerine fraction in denitrification process performed in SBR chambers were presented, no increased values of COD concentrations were noted in the outflow, which proves correctly selected glycerine dose and its application in the denitrification process.

COD fractions in wastewater were determined in order to establish their quantitative share and percentage. Determination of COD fractions allows for evaluation of wastewater susceptibility to biological treatment, additionally indicating hardly decomposable contaminants reducing effectiveness of wastewater biological treatment. Easily biodegradable, hardly (slowly) biodegradable and non-biodegradable (undecomposable) compounds are distinguished.

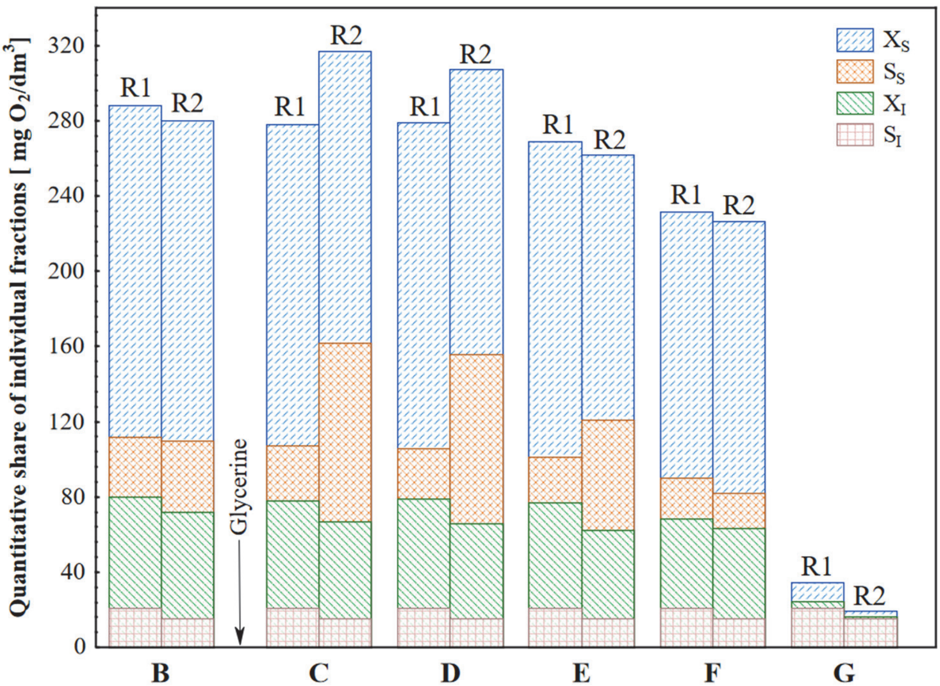

Fig. 2. Quantitative share of individual fractions in a reactor without addition of a carbon source (R1) and a reactor with the addition of glycerine (R2) (B – wastewater after filling (20 min); C – denitrification process (20 min); D – denitrification process (20 min); E – nitrification process (90 min); F – nitrification process (120 min); G – decantation (30 min))

Fraction of dissolved organic substances that are easily biodegradable S_S as well as fraction of insoluble slowly biodegradable organic substances X_S are counted to the biodegradable fraction. To non-biodegradable fraction, fractions of dissolved non-biodegradable substances S_I are counted, likewise, insoluble organic non-biodegradable substances X_I (Sadecka et al. 2011, Myszograj 2017).

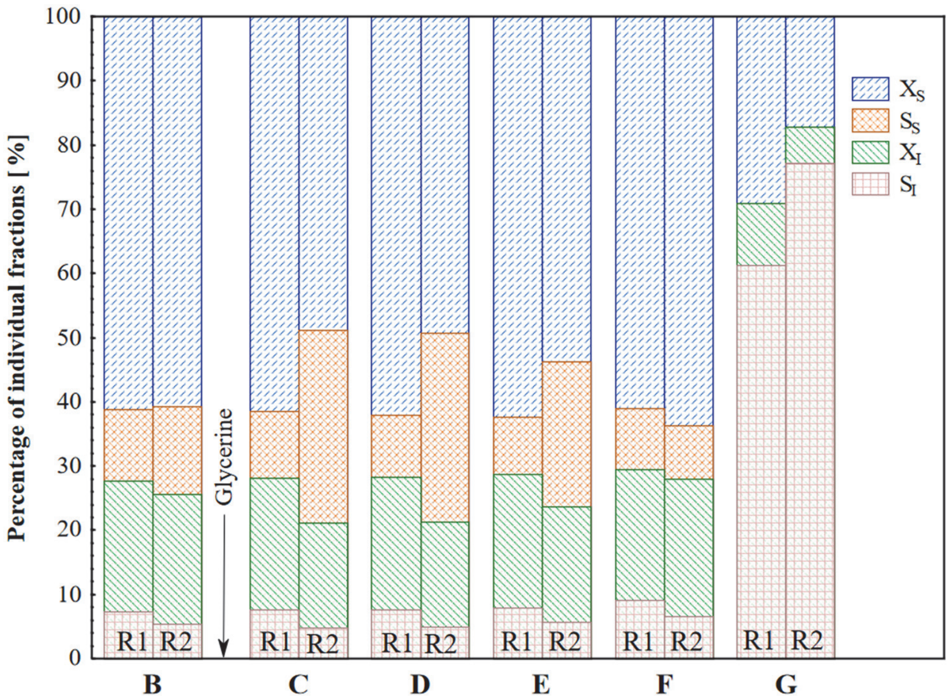

Fig. 3. Percentage of individual fractions in a reactor without addition of a carbon source (R1) and a reactor with the addition of glycerine (R2) (B – wastewater after filling (20 min); C – denitrification process (20 min); D – denitrification process (20 min); E – nitrification process (90 min); F – nitrification process (120 min); G – decantation (30 min))

Figure 2 shows quantitative share, whereas Figure 3 qualitative share of particular fractions in R1 reactor to which no carbon source was added and R2 reactor with glycerine supplied. Introduction of carbon from external source in form of glycerine to municipal wastewater caused increase of S_S fraction by 57 mg O_2/dm^3 thus increasing the percentage of easily biodegradable dissolved organic compounds from 10% to 30%.

Increased volume of easily assimilable carbon compounds contributed to increase of denitrification velocity. Figure 4 shows velocity of denitrification after twenty minutes from supply of carbon source and the average denitrification velocity.

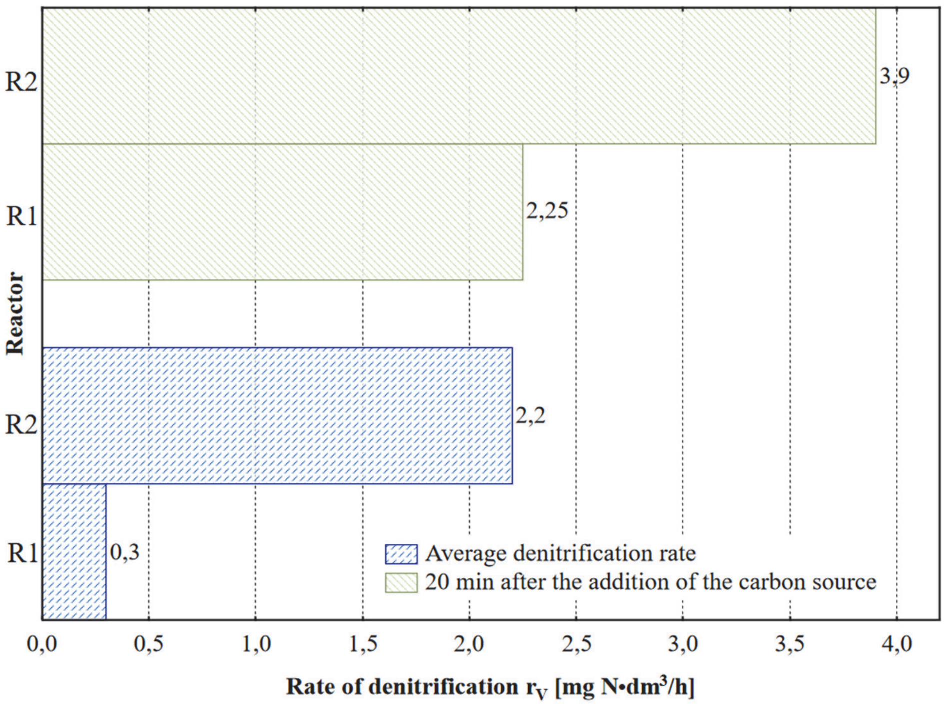

Fig. 4. Rate of denitrification 20 min after the addition of the carbon source and average denitrification rate

In the initial stage of denitrification, with addition of external carbon source i.e. glycerine, acceleration of nitrogen compounds elimination by 1.65 mg N·dm^3/h compared to R1 control reactor, was noted. In the case of the average denitrification velocity in the reactor without carbon source added, the velocity was much lower and it was only 0.3 mg N·dm^3/h, whereas the difference in velocity between both reactors was 1.9 mg N·dm^3/h.

3. Conclusions

1. Application of glycerine as an external source of carbon during wastewater treatment resulted in higher efficiency of nitrogen forms elimination compared to that reactor in which no carbon from an external source was used, with simultaneously achieved low level of COD values in treated wastewater.
2. Application of glycerine to municipal wastewater treatment caused decrease of nitrates concentration in treated wastewater by 3.2 mg N/dm^3 compared to that reactor in which no carbon from external source was used.
3. The addition of glycerine to municipal wastewater caused increase of volume of easily biodegradable dissolved organic compounds defined as S_S fraction in R2 reactor by 57 mg O_2/dm^3 (from 10% to 30%).
4. Glycerine, which is a waste product, can successfully be used as an external source of carbon in the denitrification process.

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Abstract

Supplying external carbon sources to treated wastewater is often necessary to achieve high efficiency by wastewater treatment plants that must meet very strict requirements for reducing the nitrogen concentration. The use of conventional carbon sources brings high operating costs for wastewater treatment. It became a reason to look for other, alternative sources of organic carbon.

The paper presents the effectiveness of nitrogen removal from wastewater with the use of glycerol as an external carbon source. The research was carried out during the municipal wastewater treatment process in two independent SBR-type activated sludge chambers on a laboratory scale. A single cycle of the reactor operation lasted 6 hours and included the following phases: sewage supply (2 min), mixing (anaerobic) (60 min), aeration (3.5 hours), sedimentation (1 hour) and decantation (0.5h). To one of the chambers in each cycle, after twenty minutes of the sewage supply, glycerol was added as a source of easily available organic compounds. Tests have shown that the use of glycerol as an external carbon source during wastewater treatment resulted in higher nitrogen removal efficiency than in the reactor where no external carbon source support was applied with a low level of COD value in treated wastewater. Wastewater treatment in the reactor without the addition of a carbon source resulted in the total nitrogen removal in 87.8% and ammonium nitrogen in 96.5%, whereas wastewater treatment in the reactor with the addition of glycerol resulted in the removal of total nitrogen in 93.6% and ammonium nitrogen in 98.8%. Despite the increase in the final nitrate concentration in both reactors, the nitrate concentration in the reactor using an external carbon source was lower by as much as 3.4 mg N/dm^3.

The COD fractions and their changes in wastewater were determined in order to find out their quantitative and percentage share. Determination of COD fraction allows to assess the susceptibility of wastewater to biological treatment, additionally indicating impurities that are difficult to decompose, which reduce the effectiveness of biological wastewater treatment. Introduction of an external carbon source in the form of glycerol to municipal sewage caused an increase in the S_S fraction by 57 mg O_2/dm^3, thus increasing the percentage of readily biodegradable dissolved organic compounds from 10% to 30%. The increased amount of easily available carbon compounds has contributed to the increase of denitrification rate. In the initial phase of denitrification with the addition of an external carbon source in the form of glycerol, an acceleration in the removal of nitrogen compounds by 1.9 mg N·dm^3/h compared to the control reactor, was observed.

Keywords:
SBR reactor, external carbon source, denitrification, glycerine, wastewater treatment

Gliceryna jako zewnętrzne źródło węgla wspomagające proces denitryfikacji

Streszczenie

Dostarczanie do oczyszczanych ścieków zewnętrznych źródeł węgla często staje się niezbędne do osiągnięcia wysokiej efektywności oczyszczania ścieków, które muszą spełniać bardzo surowe wymagania dotyczące ograniczenia stężenia azotu. Zastosowanie konwencjonalnych źródeł węgla niesie za sobą wysokie koszty eksploatacyjne oczyszczali ścieków. Stało się to przesłanką do poszukiwań innych, alternatywnych źródeł węgla organicznego.

W artykule przedstawiono skuteczność usuwania azotu ze ścieków z wykorzystaniem gliceryny jako zewnętrznego źródła węgla. Badania prowadzono podczas procesu oczyszczania ścieków komunalnych w dwóch niezależnych komorach osadu czynnego typu SBR w skali laboratoryjnej. Pojedynczy cykl pracy reaktora trwał 6 godzin i obejmował takie fazy jak: doprowadzenie ścieków (2 min), mieszanie (beztlenowa) (60 min), napowietrzanie (3,5 h), sedymentację (1 h) i dekantację (0,5 h). Do jednej z komór w każdym cyklu po dwudziestu minutach od napełnienia ścieków dodawano glicerynę jako źródło łatwo przyswajalnych związków organicznych. Przeprowadzone badania wykazały, że zastosowanie gliceryny jako zewnętrzne źródło węgla podczas oczyszczania ścieków spowodowało wyższą skuteczność usuwania azotu niż w reaktorze, gdzie nie zostało zastosowane wspomaganie zewnętrznym źródłem węgla przy jednocześnie uzyskanym niskim poziomie wartości ChZT w ściekach oczyszczonych. W reaktorze bez dodatku źródła węgla usunięcie azotu ogólnego wynosiło 87,8% oraz azotu amonowego w 96,5%. Oczyszczanie ścieków

w reaktorze z dodatkiem gliceryny spowodowało usunięcie azotu ogólnego w 93,6% oraz azotu amonowego w 98,8%. Pomimo wzrostu końcowego stężenia azotanów w obu reaktorach, w reaktorze z zastosowaniem zewnętrznego źródła węgla stężenie azotanów było niższe aż o 3,4 mg N/dm^3.

Wyznaczono frakcje ChZT i ich zmiany w ściekach w celu ustalenia udziału ilościowego i procentowego. Wyznaczenie frakcji ChZT pozwala na ocenę podatności ścieków na oczyszczanie biologiczne, wskazując dodatkowo zanieczyszczenia trudno rozkładalne, zmniejszające efektywność biologicznego oczyszczania ścieków. Wprowadzenie zewnętrznego źródła węgla w formie gliceryny do ścieków komunalnych spowodowało wzrost frakcji S_S o 57 mg O_2/dm^3, zwiększając tym samym procentową zawartość związków organicznych rozpuszczonych łatwo biodegradowalnych z 10 do 30%. Zwiększona ilość łatwo przyswajalnych związków węgla przyczyniła się do zwiększenia szybkości denitryfikacji. W początkowej fazie denitryfikacji z dodatkiem zewnętrznego źródła węgla w postaci gliceryny zauważono przyśpieszenie usuwania związków azotu o 1.9 mg N·dm^3/h w porównaniu do reaktora kontrolnego.

Słowa kluczowe:
reaktor SBR, zewnętrzne źródło węgla, denitryfikacja, gliceryna, oczyszczanie ścieków

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Identification and Analysis of Noise Sources in a Plate Girder Railway Bridge with Orthotropic Deck

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1. Introduction

Moving railway transport vehicles are sources of noise and determine the acoustic climate around railway lines. When they pass over steel bridges, the transverse vibrations of structural sheets can emit aerial sounds that are an environmental nuisance (Costley et al. 2015, Li et al. 2016, Li & Wu 2014, Zvolenský et al. 2017, Janas 2018). This problem is mainly observed in the vicinity of steel structures but also nearby steel-concrete bridges (Oostdijk et al. 2015, Saito et al. 2015), concrete bridges (Li & Wu 2012, Song & Li 2018) and on high–speed railway bridges (Kozuma & Nagakura 2012, Liu et al. 2014). A comparison of noise surrounded by different types of bridges was presented in (Thomspon 2009). Steel provides low internal attenuation and structures made of steel can easily be subject to poorly damped free vibrations and/or a resonance of high amplitudes. In particular, in structures with large-surfaced elements, the induced transverse vibrations can lead to large emissions of aerial sound that are received by the human ear as noise. The unpleasant buzzing characteristics of this noise make it particularly vexing to the human ear, both outside and inside residential dwellings. The problem of bridge noise is mentioned in the Eurocode [EN 1993-2, 2010], some rules for designing quiet bridges are presented in International Union of Railways recommendations (UIC Code 717R, 2010).

This article presents the results of noise and vibration testing on a plate girder railway bridge. The main purpose of the research was to determine the causes of noise increase in the surroundings of such a bridge.

2. Characteristics of the tested object

The tested bridge was a free supported, plate girder structure with a steel platform and a track located on the ballast (Figure 1). It was a kind of structure that is nowadays often designed and built. The span length of the tested bridge was 31.68 m, the height of girders amounted 2.47 m. The ballast was laid on the deck made of an orthotropic metal plate. The thickness of the ballast layer under the concrete sleepers was at least 0.35 m. There was no vibroisolation under the ballast. The object was in a very good technical condition, was opened to operation just a few months before the test.

a) b)

Fig. 1. The tested bridge: a) side view, b) bottom view

3. Study of acoustic phenomena

In order to determine the bridge impact on noise, synchronized measurements were carried out at three measuring points (m.p.):

- M1 – the microphone beside the track, 50 m beyond the bridge, at the distance of 7.5 m from the track axis and 1.5 m above the rail level (reference point),
- M2 – the microphone next to the bridge, at the distance of 7.5 m from the track axis and 1.5 m above the rail level,
- M3 – the microphone under the bridge, 1.5 m above the ground level.

Arrangement of measurement points is shown in Figure 2.

The multi-field B&K 4961 microphones were used, with frequency range of 5 Hz – 20 kHz and dynamic range 20-130 dB. The measurements were taken at air temperature +20°C, with relative humidity of 50-70% and weak wind strength (<3 m/s). The microphones were covered by B&K UA-0237 windscreens and set up on a tripod and special masts. Signals were recorded by means of 6-channel B&K LAN-XI 3050-A-060 measuring modules (cassette). The analysis was performed using the B&K PULSE Reflex program. Before testing, the measuring system was checked with the B&K 4231 sound calibrator.

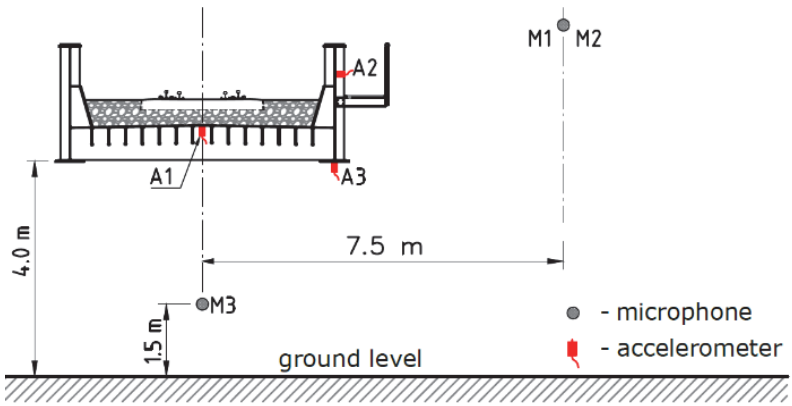

Fig. 2. Cross-section of the tested bridge and measuring points

The acoustic effects were registered during the passage of passenger trains, including long-distance trains, railbuses, regional trains and cargo trains - results of the research are presented in the article (Janas 2019). The total noise under the bridge (m.p. M3) was higher from 4.0 to 7.8 dB than the noise beside the track, beyond the bridge (m.p. M1). The noise beside the bridge (m.p. M2) does not differ significantly from the noise beside the track beyond the bridge (m.p. M1).

In order to precisely determine the reasons for the increase in noise, in this article the acoustic phenomena surrounding the bridge were analyzed in detail. The signals recorded during the train passage were divided into parts, for which harmonics were calculated using the FFT method. Amplitudes are spectrogram values, whereas frequency and time are arguments.

Figure 3a shows the background spectrogram. The spectrograms obtained during the passage of a cargo train at the speed of 40 km/h are shown in Figure 3b, c, d.

The sound pressure level next to the track, beyond the bridge in comparison to the background level increases in the entire analyzed range of the frequencies (Figure 3b). The sound pressure level next to the bridge (Figure 3c) is larger in the low frequency range (up to approx. 250 Hz) than the level next to the track, beyond the bridge. The sound pressure level under the bridge (Figure 3d) is much larger in the low frequency range (up to approx. 400 Hz) than the level next to the track, beyond the bridge.

For a detailed analysis of the sound, the amplitude-frequency characteristics averaged during the passage, in the third octave bands, are shown in Figure 4. The total level of noise is also shown in this figure.

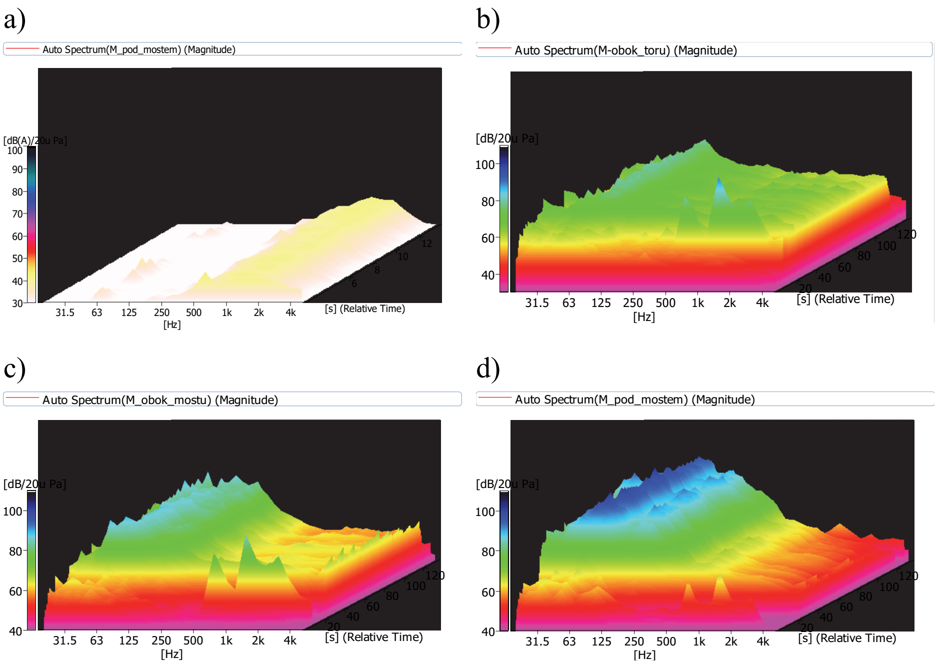

Fig. 3. Spectrogram of a background sound pressure (a) and spectrograms recorded during the passage of a cargo train: b) beside the track beyond the bridge (m.p. M1), c) next to the bridge (m.p. M2), d) under the bridge (m.p. M3)

In the standards, the permissible noise level in the vicinity of a bridge when traveling on individual trains is not defined. But, it can be noticed that during the analyzed passage (cargo train, 40 km/h) the total noise under the bridge was 7.2 dB higher than the noise next to the track, beyond the bridge. Such an increase in noise is perceived by people as about a twofold increase in nuisance. The highest sound level values are in the range of 50-125 Hz. The total noise beside the bridge was only 0.6 dB higher than the noise next to the track, beyond the bridge.

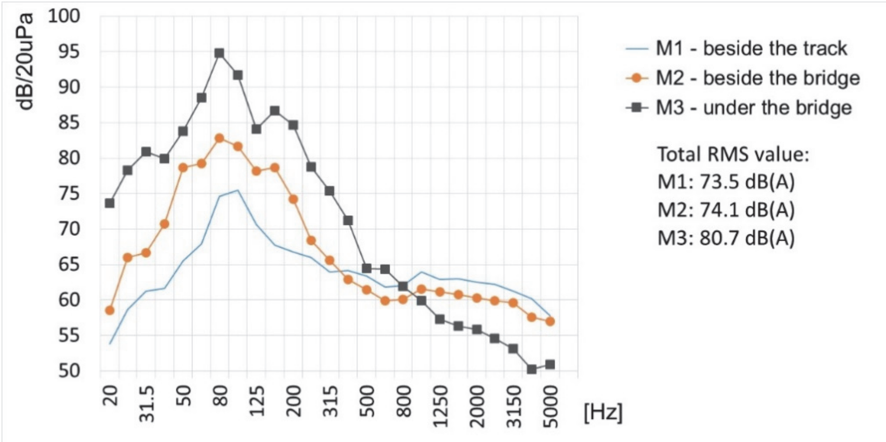

Fig. 4. Levels of the acoustic pressure versus frequency bands during the passage of a cargo train at the speed of 40 km/h

In order to extract the frequency bands for which the largest changes in sound pressure levels occur, the differences between measuring points in individual frequency bands were calculated – the results are shown in Figure 5.

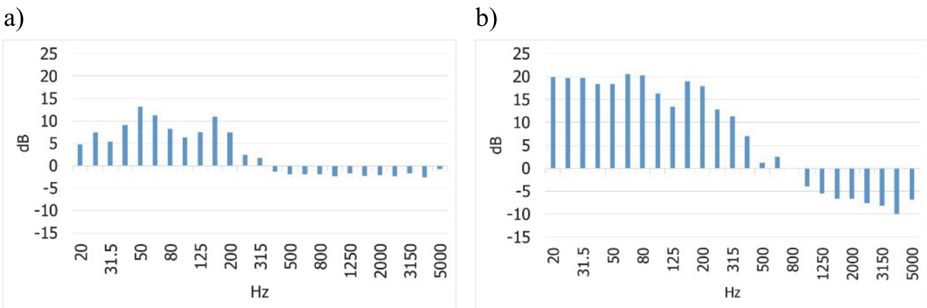

Fig. 5. Differences in the sound pressure levels: a) between point M1 and point M2, b) between point M1 and point M3

The sound pressure level next to the bridge (m.p. M2) is slightly larger in the range of 20-200 Hz than the level at the reference point (m.p. M1). For higher frequencies, the pressure level is almost equal or slightly lower – the differences do not exceed 2.5 dB.

The sound pressure level under the bridge (m.p. M3) is in the range of 20-400 Hz and much larger than the noise at the reference point – the differences reach 20 dB. For higher frequencies, above 1000 Hz, the sound level is lower even by 5 to 10 dB.

4. Study of acoustic and vibration phenomena

Acoustic vibration tests were carried out in order to determine the effect of bridge elements on sound emissions to the environment. The following elements were subjected to tests (Figure 2): the deck in vertical direction (m.p. A1), the girder web in horizontal direction (m.p. A2) and the girder in vertical direction (m.p. A3). For vibration measurements B&K 4507B-006 accelerometers were used with sensitivity of 50 mV/ms^{-2}, frequency range of 0.2 Hz – 6.0 kHz and measuring range of 140 m/s^2 (±peak). The accelerometers were mounted with special magnet holders. The measuring system was checked by the B&K 4294 calibration exciter.

Along with the vibration measurements of structure elements, the level of acoustic pressure next to the bridge (m.p. M2) and under the bridge (m.p. M3) was measured.

A coherence function was applied to identify the main sources of noise in the bridge structure. Subjecting the measured signals to the Fourier transform allowed an analysis of the signals in the frequency domain, where the square of the standardized function of mutual correlation corresponded to the value of the standardised coherence function. A comparison of the coherence function values for various elements of the bridge and directions allowed the main sources of acoustic energy radiation to be determined. The value of the coherence function can be reduced (lowered) as a consequence of the interfering noise. In the current study, the coherence function was determined using the formula (1):

$$\gamma_{xy}^2(f) = \frac{\left|\bar{G}_{xy}(f)\right|^2}{\bar{G}_{xx}(f)\cdot\bar{G}_{yy}(f)} \tag{1}$$

where:
$G_{xy}(f)$ – the cross-spectral density between signals x and y,
$G_{xx}(f)$, $G_{yy}(f)$ – the auto spectral density of x and y, respectively.

This method (i.e. determining the coherence functions of the ‘material’ vibration and acoustic vibration type) can be utilized for studying the effect of individual vibration sources on the acoustic pressure at a specific point of an acoustic field. Selected results of this analysis are presented in Figure 6 and Figure 7.

The coherence function has real values and describes the relationships between signals in the frequency domain. If there is a linear relationship between vibration and acoustic signals, and if the signals are not distorted by an interfering noise, the coherence function is equal to 1. If a linear relationship does not occur, the function is equal to 0.

The above-mentioned functions revealed that relationships existed between the vibration phenomena of structural elements and the acoustic phenomena. The coherence function has the highest values between the deck vertical vibrations and noise (Fig. 7a). Therefore, it can be assumed that the main source of the noise under the bridge (m.p. M3) is the platform plate (m.p. A1). The coherence between the horizontal vibrations of the girder web is definitely smaller (Fig. 7b). There was no coherence between the vertical girder vibrations and noise under the bridge (Fig. 7c).

a) b) c)

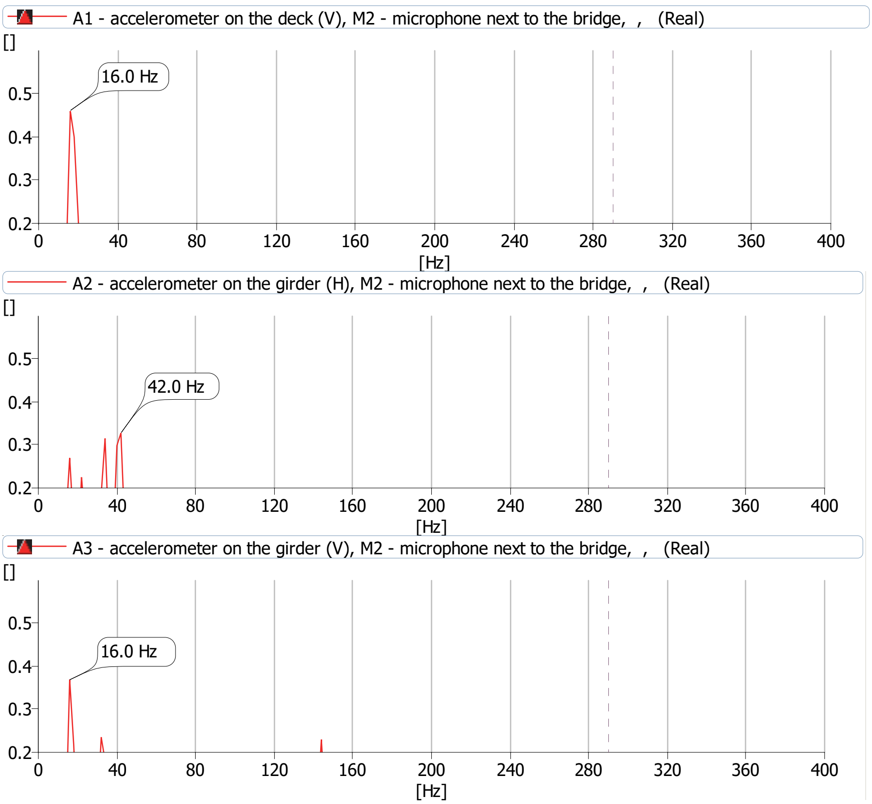

Fig. 6. Coherence function between acoustic pressure at point M2 and: a) vibrations at point A1, b) vibrations at point A2, c) vibrations at point A3

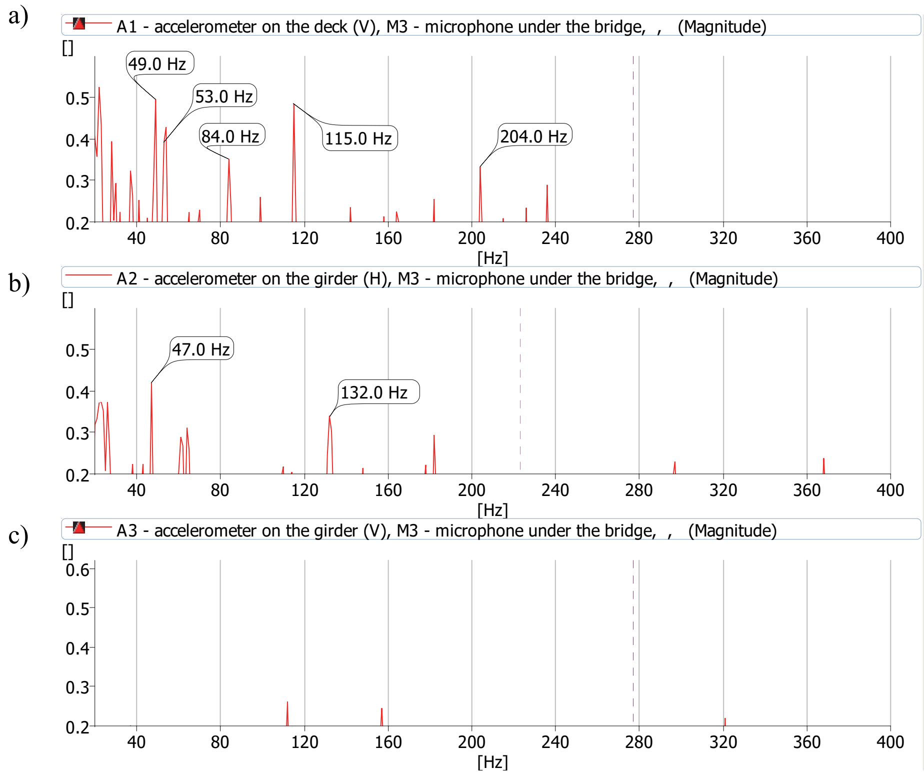

Fig. 7. Coherence function between acoustic pressure at point M3 and: a) vibrations at point A1, b) vibrations at point A2, c) vibrations at point A3

The measurements and analyses were performed several times at the same measuring points, but with different railway cargo vehicles passing. The coherence functions were invariably similar to each other. Therefore, it can be concluded that acoustic phenomena determined during a normal operation of the bridge result primarily from the type of structure (geometric properties, materials, equipment elements) and, to a small extent, from the type of load. This was confirmed by the constancy of the characteristic lines related to the resonance frequencies of the structural elements.

5. Conclusions

Steel plate girder bridges with an orthotropic deck and tracks laid on the ballast may pose a threat to environment. In the analysed case, the sound pressure level under the bridge was more than 7 dB higher than the noise next to the railway line, beyond the bridge. Such a large increase in noise was also observed in the vicinity of other bridges of similar construction, e.g. (Thomspon 2019). The increase is observed in the range of low and medium frequencies, up to 400 Hz.

This phenomenon was caused by vibrations of bridge structural elements. The passage of a train excited vibrations in large-surface elements - in this case orthotropic deck. The analysis in narrow frequency bands allowed to confirm the high compatibility of platform vibrations (deck) and sounds under the bridge. A small agreement or no agreement exists between vibrations of the girder and acoustic pressure under the bridge.

The noise next to the tested structure did not differ significantly from the noise next to the track, beyond the bridge. The sounds emitted by trains were partially damped by the bridge girders - they were a kind of acoustic screen.

Because the analysed object was located low over the ground, sounds were damped by the ground and did not disseminate. However, it must be noted that this type of structure used on populated areas on high supports may be inconvenient for the environment.

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Abstract

The paper presents the results of a noise and vibration analysis of a steel railway plate girder bridge with an orthotropic deck and ballast. This kind of bridges may pose a threat to environment. In order to precisely determine the reasons for the increase in noise, in this article the acoustic phenomena surrounding the bridge were analyzed in detail.

Sound characteristics were determined in three points – next to the railway line outside the bridge, next to, and under the bridge. The sound characteristics are presented in one-third octave bands and narrow frequency bands. The analysis was based on comparing the levels of acoustic pressure and determining the summary levels. The narrow frequency bands analysis included an identification of the frequency composition of the generated sounds. A significant increase in noise under the bridge was found.

The sound pressure level next to the track, beyond the bridge in comparison to the background level increases in the entire analyzed range of the frequencies. The sound pressure level next to the bridge was only 0.6 dB higher than the noise next to the track, beyond the bridge The sound pressure level under the bridge is much larger in the low frequency range (up to approx. 400 Hz) than the level next to the track, beyond the bridge. It can be noticed that in analysed case the total noise under the bridge was 7.2 dB higher than the noise next to the track, beyond the bridge. The highest sound level values are in the range of 50-125 Hz.

This phenomenon was caused by vibrations of bridge structural elements. The passage of a train excited vibrations in large-surface elements - in this case orthotropic deck. The analysis in narrow frequency bands allowed to confirm the high compatibility of platform vibrations (deck) and sounds under the bridge. A small agreement or no agreement exists between vibrations of the girder and acoustic pressure under and next to the bridge. The analysed type of structure can be a nuisance to the environment if it is located on high supports in urbanized areas.

Keywords:
noise, vibrations, steel railway bridge, coherence

Identyfikacja i analiza źródeł hałasu w kolejowym moście blachownicowym z pomostem ortotropowym

Streszczenie

W artykule przedstawiono rezultaty analizy hałasu i drgań mostu stalowego blachownicowego, z pomostem ortotropowym i torem ułożonym na podsypce. Tego rodzaju obiekty mogą stanowić zagrożenie dla środowiska. W pierwszej kolejności szczegółowo przeanalizowano zjawiska akustyczne w otoczeniu mostu. Ciśnienie akustyczne mierzono w trzech punktach – obok linii kolejowej poza mostem, obok mostu i pod mostem. Charakterystyki dźwięku porównano w wąskich pasmach częstotliwości i w pasmach tercjowych. Określono również poziomy sumaryczne i stwierdzono znaczny wzrost hałasu pod obiektem.

Poziom ciśnienia akustycznego obok toru poza mostem, w porównaniu do poziomu tła, wzrasta w całym analizowanym zakresie częstotliwości. Poziom ciśnienia akustycznego obok mostu jest porównywalny do poziomu obok toru poza mostem – różnica wynosi jedynie 0.6 dB. Sumaryczny hałas pod mostem był o 7,2 dB wyższy niż hałas przy torze, poza mostem. Poziom ciśnienia akustycznego był wyższy w zakresie niskich częstotliwości – do ok. 400 Hz. Najwyższe wartości poziomu dźwięku mieściły się w zakresie 50-125 Hz.

Do identyfikacji źródeł dźwięku zastosowano metodę funkcji koherencji. Wykazano, że wzrost hałasu pod obiektem jest spowodowany wibracjami elementów konstrukcji. Przejazd pociągu wzbudzał drgania elementów wielkopowierzchniowych (w tym przypadku pomostu ortotropowego), które przyczyniły się do emisji hałasu. Analiza w wąskich pasmach częstotliwości pozwoliła na potwierdzenie koherencji drgań pomostu i dźwięków pod mostem. Nie stwierdzono występowania zgodności między charakterystyką drgań dźwigara blachownicowego i ciśnieniem akustycznym obok mostu.

Przeprowadzone analizy pozwalają stwierdzić, że analizowany typ konstrukcji może być uciążliwy dla środowiska, szczególnie wtedy, gdy będzie zlokalizowany na obszarze zurbanizowanym, np. na wysokich podporach.

Słowa kluczowe:
hałas, drgania, most stalowy kolejowy, koherencja

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The Effect of Meteorological Conditions on PM_{10} and $PM_{2.5}$ Pollution of the Air

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1. Introduction and work's aim

Air pollutants include solid, liquid or gaseous substances of foreign origin, or naturally occurring in the atmosphere when their level exceeds the limit value. Pollutants entering the atmosphere may be generated during production processes, combustion, transport or the municipal sector and households (Nadziakiewicz 2005). The sources release into the atmosphere mainly nitrogen oxides, carbon oxides, particulate matter, sulphur dioxide and carbon dioxide (Juda-Rezler 2006). Other pollution sources which change the natural composition of the air include landfill sites and dumps which release into the air particulates as well as poisonous gasses, particularly ammonia (Czarnecka & Kalbarczyk 2008). Typical air pollutants include particulate matter whose particles have different size, origin and form in which they occur. The term 'particulate matter' (PM) is applied when referring to the dispersed aerosol phase, and it denotes a mixture of solid and liquid particles dispersed in the air (WHO 2006, EEA, 2014). There are two major categories of particular matter whose measurement is part of air quality monitoring in the urban environment both in Poland and Europe: PM_{10} and $PM_{2.5}$. PM10 includes fine particles whose aerodynamic diameter does not exceed 10 μm. $PM_{2.5}$ is made up of very fine particles with the diameter of no more than 2.5 μm. The particles consist of e.g.: sulphur, heavy metals, toxic dioxins and polycyclic hydrocarbons as well as aromatic hydrocarbons and allergens (Malec & Borowski 2016). As particles are capable of remaining in the atmosphere over a time, they may negatively influence human health, the biosphere or other environment elements (Malec & Borowski 2016, Sówka et al. 2016). PM_{10} has a substantial adsorbing surface which holds back harmful substances causing respiratory diseases. Particles of $PM_{2.5}$ are more harmful because they penetrate the deepest located, smallest bronchioles which are a component of the non-ciliated part of the respiratory tract, and directly enter the bloodstream. (Cembrzyńska et al. 2012). Many studies have confirmed a correlation between particulate matter concentration and morbidity and mortality rate (Power et al. 2011, Weuve et al. 2012, Wilker et al. 2015, Gruszecka-Kosowska 2018). PM harmfulness is not so much associated with their abrupt emission as the prevalence of conditions which favour dispersal of the particles (Drzeniecka-Osiadacz & Netzel 2010), the following meteorological conditions being decisive: air temperature, wind speed and direction, air humidity and solar radiation intensity (Gioda et al., 2013, Kim et al. 2015, Oleniacz et al. 2016 a, b). Accordingly, EU directives (in particular Directive 2008/50/WE) detail the permissible levels of particular matter in the air, and encourage the development of a PM monitoring system and of action plans. It is important to get to know the mechanisms leading to pollutant accumulation and dispersal, also at a local scale. A stage of such analyses may include determination of the effect of selected meteorological elements on the concentration of particulate matter in the air. Thus, it was attempted to determine the influence of air temperature, wind speed and direction, as well as air humidity on the concentration of PM_{10} and $PM_{2.5}$ in Siedlce.

2. Materials and methods

24-hour results of measurements of PM_{10} and $PM_{2.5}$ and of meteorological observations in Siedlce ($\varphi°=52°10'03''N$; $\lambda°=22°17'24''E$; H_sm a.s.l.=150 m) taken in 2012-2016 were analysed.The data, collected by an automated measurement station situated in Konarskiego Street, Siedlce, (Fig. 1) was sourced from the website of the Environmental Protection Inspectorate (www.gios. gov.pl). Siedlce is located in the east of Poland, in the central part of the Mesoregion Wysoczyna Siedlecka, Mazovian Voivodeship. The urban landscape of Siedlce includes residential and commercial areas. The residential areas are built to blocks of flats as well as single-family housing, and are intermingled with service-related spots. Areas developed with production and commercial facilities are located at the outskirts of the town. Despite lack of formal administrative division of the town's area, Siedlce can be divided into structural units. There are seven residential districts characterised by a certain degree of individuality: Nowe Siedlce (located in the north-east, with predominantly single-family houses), Piaski Zamiejskie (western part of the town, with single-family single-storey houses), Roskosz (southern part of the town, with both single-family houses and blocks of flats), Sekuła (southern part of the town with residential buildings), Stara Wieś (eastern part of the town with mixed types of housing), Śródmieście (the town's centre where there are many shops and shopping centres, measurement point in Konarskiego Street), Taradajki (south-eastern part of the town dominated by single-family houses), and two industrial districts: Północna Dzielnica

Przemysłowa (Northern Industrial District) and Południowa Dzielnica Przemysłowa (Southern Industrial District).

Fig. 1. Measurement point location (www.siedlce.pl)

The first stage included calculation of the number of days with a certain index of air quality based on 24-h concentrations of particulate matter. According to guidelines of the Chief Inspectorate for Environmental Protection, the Index of Air Quality includes six classes (http://powietrze.gios.gov.pl/ pjp/archives) (Table 1).

Table 1. Air quality index

	Very good	Good	Moderate	Satisfactory	Poor	Very poor
PM_{10} [μg/m^3]	0-21	21-61	61-101	101-141	141-201	> 201
$PM_{2.5}$ [μg/m^3]	0-13	13-37	37-61	61-85	85-121	> 121

The next step included analysis of excessive 24-h concentrations of PM_{10} and $PM_{2.5}$. The standard value, as set by WHO, was the 24-h concentration of 50 μg/m^3 for PM_{10} and 25 μg/m^3 for $PM_{2.5}$. Also, there was determined the number of days in individual months of the 5-year period when the concentration of particular matter exceeded the standard, in addition to minimum and maximum values of the concentration as well as the coefficient of variation.

Analysis of correlation and path analysis developed by Wright (1923) were used in order to analyse the effect of the following meteorological factors: air temperature, wind speed and direction, and air humidity on above-standard concentration of PM_{10} and $PM_{2.5}$.

Path analysis rests on a stepwise linear analysis of regression of standardised variables, which makes it possible to compare the extent of direct influence of individual causative variables on a casual (dependent) variable. Moreover, it allows assessment of the direct effect of causative variables resulting from their interrelations. The causative variables were as follows: X_1 – air temperature, X_2 – wind direction, X_3 – wind speed, X_4 – air humidity. The dependent variables (Y) included excessive concentration of PM_{10} and $PM_{2.5}$. For the sake of calculations, wind direction was expressed on an angular scale.

The first step of the analysis involved calculation of correlation matrix between variables, and multiple stepwise regression for variables standardised according to the equation:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \varepsilon_i \tag{1}$$

where:
Y, X_1, X_2, X_3, X_4 – standardised variables.

Standardisation was carried out based on the following formulae:

$$Y = \frac{Y_i - \bar{Y}}{S_y};\ X_{1,2,3,4} = \frac{X_i - \bar{X}}{S_x} \tag{2}$$

where:
Y_i – 24-h value of excessive concentration of PM_{10} or $PM_{2.5}$,
$\bar{y}$ – average 24-h concentration of particulate matter,
S_y – standard deviation of the concentration of particulate matter,
X_i – values of meteorological components,
$\bar{x}$ – average values of meteorological components,
S_x – standard deviation of meteorological components.

Partial coefficients of regression β_i are path coefficients which express the direct effect of each causative variable on the dependent variable. The relationship between the path coefficient p_i and regression coefficient is as follows: $p_j = \beta_i$. Indirect effects of each causative variable on variation in the concentration of particulate matter through the remaining independent variables were calculated as a sum of the products of correlation coefficients between the variables and relevant values of path coefficient, as shown below:

$$\sum p_j \cdot r_{ij} \tag{3}$$

where:
p_i – path coefficient,
r_{ij} – correlation coefficient.

The sum of the direct effect and indirect effect for each element of the equation is equal to the Pearson's coefficient of linear correlation, that is the overall effect of a given variable:

$$r_{yj} = p_j + \sum p_j \cdot r_{ij} \tag{4}$$

For explanations see formula (3).

3. Results

Table 2 presents the number of days with individual air quality indices for PM_{10} and $PM_{2.5}$. In the study years, the highest was the number of days with good air quality, in terms of both PM_{10} and $PM_{2.5}$. Over 32 and 21% of days were characterised by very good air quality, respectively for PM10 and $PM_{2.5}$. It should be noted that, as far as PM_{10} was concerned, the greatest was the number of days with very good air quality in the last two study years, that is 129 days in 2015 and 140 days in 2016. Poor and very poor air quality, due to the concentration of PM_{10} of over 141 μg/m^3, and of $PM_{2.5}$ of over 85 μg/m^3, was only occasional (in 2012 only).

Table 2. Annual number of days with individual types of air quality index for PM_{10} and $PM_{2.5}$ in the years 2012-2016

Year	Air quality index					
	very good	good	moderate	satisfactory	poor	very poor
	PM_{10}					
2012	91	233	27	10	3	2
2013	114	218	30	3		
2014	117	218	27	3		
2015	129	203	28	5		
2016	140	208	16	2		
Total	591	1080	128	23	3	2

Table 2. cont.

Year	Air quality index					
	very good	good	moderate	satisfactory	poor	very poor
	$PM_{2.5}$					
2012	59	226	50	18	10	3
2013	68	214	61	18	4	
2014	84	191	72	13	4	
2015	104	183	57	19	1	1
2016	80	211	54	15	7	
Total	395	1025	294	83	26	4

Over the five-year period, in all the study months the greatest were the numbers of days with good and very good air quality, in terms of PM_{10}. Moderate and satisfactory air quality was observed in the autumn and winter months (from October to April), it being poor or very poor in February only. The concentration of $PM_{2.5}$ present in the air was low enough to classify the majority of days (in each month) as characterised by good or very good air quality. Poor quality was observed during the winter period, from November to March, it being very poor in February only (Table 3).

Table 3. Monthly number of days with individual types of air quality index for PM_{10} and $PM_{2.5}$ in the years 2012-2016

Month	Air quality index					
	very good	good	moderate	satisfactory	poor	very poor
	PM_{10}					
January	30	102	15	4		
February	17	84	30	7	3	2
March	29	91	28	7		
April	40	105	4	1		
May	73	83				
June	103	48				
July	73	82				
August	73	83				
September	59	91				
October	30	108	18			
November	25	105	16	3		
December	39	98	17	1		

Table 3. cont.

Month	Air quality index					
	very good	good	moderate	satisfactory	poor	very poor
	$PM_{2.5}$					
January	13	82	36	13	6	
February	9	64	40	21	6	3
March	13	83	42	12	5	
April	20	113	18	1		
May	54	101				
June	95	55				
July	86	69				
August	50	104	1			
September	31	114	6			
October	9	82	48	9		
November	7	68	44	13	3	1
December	8	90	59	14	6	

An above-standard PM_{10} concentration (>50 µg/m^3) in the study period was observed from January to March and from October to December (heating season). The greatest number of days with exceedences was found in February (10% of days) and March (33% days). Also, PM_{10} content in these months had the highest variation, the respective values being 47.4 and 29.1% (Table 4).

Table 4. Minimum (µg/m^3), maximum (µg/m^3) values and the coefficient of variation (%) of exceedence for PM_{10} in individual months in the years 2012-2016

Month	Min.	Max.	Coefficient of variation	Number of days when standards were exceeded	Percentage of number of days in the study period when exceedences were observed
January	50.8	125.7	28.2	31	20
February	50.9	252.1	47.4	56	40
March	50.3	139.1	29.1	51	33
October	50.5	83.9	16.0	34	22
November	50.5	129.3	27.1	35	23
December	50.2	111.6	21.5	27	17

Correlation analysis revealed that the concentration of PM_{10} was significantly related to air temperature in February and March, wind speed in February and December, air humidity in February, and wind direction in November (Table 5). Path analysis indicated that an above-standard concentration of PM_{10} in January was affected by wind direction and wind speed although the effect was statistically insignificant. In February, the highest significant direct effect on PM_{10} content was associated with air temperature and wind speed. The value of the direct effect of temperature is indicative of the fact that as air temperature increased by 1 degree Celsius, PM_{10} content declined by an average of 0.466 μg/m^3 whereas a 1 m/s increase in wind speed was followed by a decline in PM10 content of 0.257 μg/m^3, on average. The remaining parameters, that is wind direction and air humidity had only a slight effect on the examined parameter. The greatest indirect effect causing an increase in PM_{10} content was associated with air humanity (-0.148), the effect being primarily due to a direct influence of air temperature (-0.222).

Table 5. Correlation coefficients as well as direct and indirect effects of the influence of meteorological elements on PM_{10} content

Causative variable	Direct effect	Indirect effect	Correlation coefficient
January			
Wind direction(X_2)	0.218		-0.066
Indirect effect through X_3		0.0071	
Wind speed (X_3)	-0.247		-0.253
Indirect effect through X_2		-0.0063	
February			
Air temperature(X_1) –	-0.466*		-0.541*
Indirect effect through X_2		0.022	
Indirect effect through X_3		-0.024	
Indirect effect through X_4		-0.073	
Wind direction (X_2)	0.125	-0.035	0.091
Indirect effect through X_1		-0.080	
Indirect effect through X_3		0.0715	
Indirect effect through X_4		-0.0263	
Wind speed (X_3)	-0.257*	-0.047	-0.305*
Indirect effect through X_1		-0.043	
Indirect effect through X_2		-0.035	
Indirect effect through X_4		0.031	

Table 5. cont.

Causative variable	Direct effect	Indirect effect	Correlation coefficient
February			
Air humidity (X_4)	-0.153	-0.148	-0.301*
Indirect effect through X_1		-0.222	
Indirect effect through X_2		0.022	
Indirect effect through X_3		0.052	
March			
Air temperature (X_1)	0.139		-0.459*
Indirect effect through X_3		-0.0636	
Wind speed (X_3)	-0.447*		
Indirect effect through X_1		0.0185	
October			
Air temperature (X_1)	-0.595*		-0.476*
Indirect effect through X_2		0.119	
Wind direction (X_2)	-0.447*		0.073
Indirect effect through X_1		0.0185	
November			
Air temperature (X_1) –	0.195		-0.176
Indirect effect through X_2		0.0285	
Indirect effect through X_3		-0.010	
Wind direction (X_2)	0.349*		-0.343*
Indirect effect through X_1		0.016	
Indirect effect through X_3		-0.009	
Wind speed (X_3)	-0.215		-0.239
Indirect effect through X_1		-0.0094	
Indirect effect through X_2		-0.015	
December			
Wind speed	-0.481*		-0.481*

A similar small indirect impact on PM_{10} content was determined for air temperature, wind direction and wind speed. An increased concentration of PM_{10} in March was also directly related to wind speed and air temperature. A 1 m/s increase in wind speed was followed by a 0.447 μg/m^3 decline in PM_{10} content. Indirectly, a higher influence on PM_{10} was exerted by air temperature than wind speed. PM_{10} content in October was directly and significantly influenced by air temperature and wind direction. A 1 degree increase in temperature was followed by a 0.595 μg/m^3 decline in PM_{10} concentration whereas a 1 degree change in wind direction contributed to a 0.447 μg/m^3 decline in the concentration of PM_{10}. Indirectly, the effect of temperature was greater compared with wind direction. In November, there was observed a direct effect of air temperature, wind direction and wind speed resulting in an excessive concentration of PM_{10}, it being significant for wind direction only. The greatest indirect influence was associated with air temperature, it being the result of the effect of wind direction. In December, there was observed only direct effect of wind speed on above-standard PM_{10} content in the air. A 1 m/s increase in wind speed was followed by a 0.481 μg/m^3 decline in the concentration of PM_{10} (Table 5).

An excessive concentration of $PM_{2.5}$ in the five-year period was observed in January, February, March, September, October, November and December. The greatest number of days with above-standard $PM_{2.5}$ contents was recorded in February (as much as 76% days), October (68%), January (63%) and March (61%), the smaller number of such days being in September (Table 6). Correlation analysis demonstrated a significant relationship of above-standard $PM_{2.5}$ content with air temperature in January, February, October and November, wind speed in February, March, September, October, November and December, and a air humidity in February and March. Wind direction had a significant effect on an excessive concentration of $PM_{2.5}$ in September only (Table 7).

Table 6. Minimum (μg/m^3), maximum (μg/m^3) values and the coefficient of variation (%) of exceedence for $PM_{2,5}$ in individual months in the years 2012-2016

Month	Min.	Max.	Coefficient of variation	Number of days with above-standard concentration	Percentage of days when exceedence was recorded in the study period
January	25.2	117.4	42	98	63
February	25.5	151.1	49	107	76
March	25.2	95.6	38	94	61
September	25.3	53.3	20	35	23
October	25.1	78.1	29	105	68
November	25.2	144.1	42	113	75
December	25.2	102.7	37	120	77

Path analysis demonstrated that $PM_{2.5}$ content in January was directly affected by wind speed and air temperature but only the effect of wind speed was significant. A 1 m/s increase in wind speed was followed by a decline in $PM_{2.5}$ concentration of about 0.5 μg/m^3. Air temperature had a more pronounced indirect effect on the discussed parameter than wind speed (Table 7). In February, an above-standard $PM_{2.5}$ concentration was directly influenced by air temperature, wind speed and air humidity. An increase in temperature and a decline in wind speed were followed by a significant decline in the concentration of $PM_{2.5}$. Air humidity had the greatest indirect influence on the examined parameter, the effect being affected by air temperature. Wind speed and air humidity negatively and significantly influenced the variation in $PM_{2.5}$ concentration in March whereas in April the variation of over 25 µg/m^3 was directly and negatively affected by air temperature, the relationship being statistically insignificant. The variation in the concentration of $PM_{2.5}$ in September was directly affected by air temperature, wind direction, wind speed and air humidity. The effect was negative, which means that an increase in the value of these parameters was followed by a decline in $PM_{2.5}$ content in the air. The greatest indirect influence was associated with air temperature (totalling 0.376). The effect was predominantly due to an indirect impact through air humidity and temperature. The overall indirect effect of wind speed was 0.215 and it followed mainly from an indirect influence through wind direction. In October and November, the variation in $PM_{2.5}$ content was directly and negatively affected by air temperature, wind speed and air humidity, the impact of only wind speed being statistically significant. The greatest indirect impact was due to air temperature in October and air humidity in November. The impact in October was related to air humidity and in November to wind speed. Similarly to PM10, variation in $PM_{2.5}$ content in December was directly influenced by wind speed only, the influence being significant. A 1 m/s increase in wind speed was followed by a 0.486 µg/m^3 decline in the concentration of $PM_{2.5}$ (Table 7).

Table 7. Correlation coefficients as well as direct and indirect effects of the influence of meteorological elements on $PM_{2.5}$ content

Causative variable	Direct effect	Indirect effect	Correlation coefficient
January			
Air temperature(X1) –	-0.146		-0.252*
Indirect effect through X_3		-0.106	
Wind speed (X3)	-0.520*		-0.550*
Indirect effect through X_3		-0.0298	
February			
Air temperature (X_1) –	-0.366*		-0.518*
Indirect effect through X_3		-0.102	
Indirect effect through X_4		-0.049	

Table 7. cont.

Causative variable	Direct effect	Indirect effect	Correlation coefficient
February			
Wind speed (X_3)	0.390*		-0.477*
Indirect effect through X_1		-0.096	
Indirect effect through X_4		0.0089	
Air humidity (X_4)	-0.114		-0.242*
Indirect effect through X_1		-0.158	
Indirect effect through X_3		0.030	
March			
Wind direction (X2)	0.097		0.085
Indirect effect through X_3		-0.0219	
Indirect effect through X_4		0.0099	
Wind speed (X_3)	-0.492*		-0.488*
Indirect effect through X_2		0.0043	
Indirect effect through X_4		-0.0009	
Air humidity (X4)	-0.237*		-0.243*
Indirect effect through X_2		-0.0041	
Indirect effect through X_3		-0.0019	
September			
Air temperature (X1)	-0.338*		-0.282
Indirect effect through X_2		0.110	
Indirect effect through X_3		0.093	
Indirect effect through X_4		0.173	
Wind direction (X2)	-0.697*		-0.348*
Indirect effect through X_1		-0.053	
Indirect effect through X_3		0.129	
Indirect effect through X_4		-0.106	
Wind speed (X_3)	-0.500*		-0.010*
Indirect effect through X_1		0.063	
Indirect effect through X_2		0.180	
Indirect effect through X_4		-0.0280	
Air humidity (X4)	-0.277*		-0.167
Indirect effect through X_1		0.210	
Indirect effect through X_2		-0.268	
Indirect effect through X_3		0.050	

Table 7. cont.

Causative variable	Direct effect	Indirect effect	Correlation coefficient
October			
Air temperature (X_1)	-0.170		-0.227*
Indirect effect through X_3		-0.0193	
Indirect effect through X_4		-0.0378	
Wind speed (X_3)	-0.361*		-0.339*
Indirect effect through X_1		-0.0193	
Indirect effect through X_4		0.0091	
Air humidity (X4)	-0.159		-0.127
Indirect effect through X_1		-0.040	
Indirect effect through X_3		0.072	
November			
Air temperature (X_1)	-0.159		-0.185*
Indirect effect through X_3		-0.060	
Indirect effect through X_4		0.0342	
Wind speed (X_3)	-0.364*		-0.337*
Indirect effect through X_1		-0.026	
Indirect effect through X_4		0.053	
Air humidity (X4)	-0.128		0.064
Indirect effect through X_1		0.042	
Indirect effect through X_3		0.150	
December			
Wind speed	-0.487*		-0.487*

4. Discussion

The air quality in Siedlce is affected by pollutants released by industrial facilities, vehicles and household combustion devices. Due to low industrialisation of the town, the main source of pollutants is residential heating with coal.

Due to a complex nature of the relationship between meteorological factors and PM pollution, it is very difficult to clearly determine the effect of individual meteorological elements on PM concentration (Olofson et al. 2009, Weber et al. 2013). In Siedlce, above-standard concentration of PM_{10} and $PM_{2.5}$ was usually directly affected by wind direction and speed although the influence was sometimes insignificant. As wind speed increased (particularly in the winter months), particulate matter concentration declined, which might have been caused by more rapid dispersal of the pollutants. Such a relationship has been reported by Oleniacz et al. (2016a) who confirmed that wind speed in Kraków exceeding 2 m/s contributed to a dispersal of pollution concentration. Similar findings were also reported by Czarnecka and Kalbarczyk (2008) who confirmed a ventilatory role of wind in the Pomerania area, in particular in February and March. No or little wind makes it impossible to effectively ventilate a town area (Cichoń and Hławiczka 2010, Błedowska et al. 2012, Kalbarczyk and Kalbarczyk 2007, Nowicka et al. 2004). Also Drzeniecka-Osiadacz and Netzel 2010 have pointed to a decisive effect of wind speed and direction on PM dispersal. On the basis of regression analysis, the authors confirmed a statistically significant relationship between the average 24-h concentration of PM_{10} and wind speed. Moreover, the authors have emphasised the fact that PM concentration is affected by the range and duration of temperature inversion which is an obstacle to vertical air mixing in the atmosphere. This phenomenon may explain the indirect effect of temperature (through wind speed and direction) in the study reported here on PM concentration in February, March and November. Directly, wind direction affected PM_{10} content in January and $PM_{2.5}$ concentration in October and November. In those months, the most frequent wind direction was WSW and it carried pollutants from single-family housing districts. Similar relationships for Trójmiasto (Tricity) were reported by Czarnecka and Nidzgorska-Lencewicz (2015) who confirmed that wind directions caused inflow emissions from outside of the agglomeration. In the study reported here, a direct effect of air temperature on PM dispersion was confirmed for the winter season, which is associated with intensive heating of buildings, that is the process of solid fuel combustion (particularly hard coal). This relationships is also confirmed by the fact that no above-standard concentrations of PM were recorded outside of the heating season in Siedlce. Similarly to other urban areas located in Poland and Europe, Siedlce struggles to maintain standards of air quality during the winter season. Multi-location research conducted in five European countries (Poland, Czech Republic, Bulgaria, Romania, Slovak Republic) has demonstrated that the concentration of PM_{10} and $PM_{2.5}$ in winter was, on average, twice as high as during the summer, which was mainly due to hard coal being used as fuel for heating in the municipal sector (Houthuijsat al. 2001).

The influence of individual meteorological elements on air quality is a complex process associated with vertical gradients of temperature, wind and humidity in the layer of the atmosphere which is closest to the ground (Majewski et al. 2009, Zhao et al. 2010), which was also confirmed in the present work. Depending on pollution type and study month, above-standard PM concentrations were usually affected by several meteorological elements, all analysed variables entering equations of path analysis in several cases. Similar findings were reported by Ćwiek and Majewski (2015) who, using stepwise regression equations, confirmed a simultaneous effect of several elements, including wind speed, atmospheric pressure, air temperature, relative humidity and horizontal visibility, on the concentration of air pollutants.

5. Summary

The effect of meteorological variables on pollutant content in the air is frequently analysed by means of the regression function. However, unlike path analysis, the method does not account for all the relationships between the variables. Path analysis made it possible to assess the direct and indirect effect of four meteorological elements on above-standard concentration of particulate matter in the Siedlce agglomeration. Throughout most of the year, air quality in Siedlce was good, it being satisfactory, poor and very poor in winter (from October to March) only. What is more, path analysis demonstrated that variation in pollutants is directly affected by wind speed and direction as well as air temperature. Increased PM concentrations were recorded mainly on days when wind speed dropped and air temperature was low. The value of the direct effect of temperature is indicative of the fact that as air temperature increased by 1 degree Celsius, PM_{10} content declined by an average of 0.466 μg/m^3 whereas a 1 m/s increase in wind speed was followed by a decline in PM10 content of 0.257 μg/m^3, on average. The indirect effect of the examined meteorological elements on PM dispersion varied and was predominantly influenced by the study month.

Further research into the dispersion of pollution in urban agglomerations is recommended as well as action to be taken to improve air quality, such as urban planning which considers location of buildings in terms of optimum air circulation. The action, although not commensurable with the effects of elimination of pollution sources, will definitely improve the inhabitants' quality of life.

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Abstract

The work is based on results of hourly measurements of the particles PM_{10} and $PM_{2.5}$ as well as 24-h measurements of meteorological elements in Siedlce. Analysis spanned the years 2012-2016. Based on the Polish Index of Air Quality developed by the Chief Inspectorate of Environmental Protection (GIOŚ), there were determined numbers of days in six air quality classes. Analysis of the effect of meteorological conditions on particulate matter content in the air was based on 24-h concentrations of PM_{10} and $PM_{2.5}$ exceeding the standard value of 50 $\mu g/m^3$ for PM_{10} and 25 $\mu g/m^3$ for $PM_{2.5}$. Variation in the excessive concentrations in weather conditions described by means of air temperature, air humidity, wind direction and speed was assessed by means of Wright path analysis. Satisfactory, poor and very poor air quality was recorded in winter only. Path analysis revealed that variation in pollution is affected by wind speed and direction as well as air temperature. Increased concentrations of particulate matter were found mainly on days with low wind speed and low air temperature.

Key words:
PM_{10}, $PM_{2.5}$, path analysis, meteorological conditions

Wpływ warunków meteorologicznych na zanieczyszczenie powietrza pyłem zawieszonym PM10 i PM2,5

Streszczenie

W pracy wykorzystano wyniki pomiarów godzinnych stężeń pyłów PM10 i PM2,5 oraz dobowych pomiarów elementów meteorologicznych w Siedlcach. Analizą objęto lata 2012-2016. Na podstawie Polskiego Indeksu Jakości Powietrza opracowanego przez Główny Inspektorat Ochrony Środowiska (GIOŚ) określono liczbę dni w sześciu przedziałach klas jakości powietrza. Analizę wpływu warunków meteorologicznych na zawartość w powietrzu pyłów oparto na stężeniach dobowych PM10 i PM2,5 przekraczających normę: 50 $\mu g/m^3$ dla PM10 i 25 $\mu g/m^3$ dla PM2,5. Zmienność ponadnormatywnych stężeń w warunkach pogodowych opisanych temperaturą powietrza, wilgotnością powietrza, kierunkiem i prędkością wiatru oceniono przy zastosowaniu analizy ścieżek Wrighta. Dostateczną, złą i bardzo złą jakość powietrza notowano jedynie w zimnej porze roku. Analiza ścieżek wykazała, że zróżnicowanie zanieczyszczeń zależy od prędkości i kierunku wiatru oraz temperatury powietrza. Podwyższone stężenia pyłów zawieszonych notowano głównie w dniach z małą prędkością wiatru i niską temperaturą.

Słowa kluczowe:
PM10, PM2,5, analiza ścieżek, warunki meteorologiczne

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The Handling of Composted Onion Waste in the Form of Substrates for the Proliferation of the *Trichoderma* sp.

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1. Introduction

Nowadays we can observe an increasingly dynamic development of the cultivation of crops and vegetables, which results in growing amounts of waste. The best way to handle this waste is to re-enter it into the soil environment (Regulation of the Minister of Environment of 20 January 2015), which can be done after proper preparation. The composting process seems to be the safest to the environment and the cheapest method of organic waste handling. The end product of the process is compost, which can be used as an organic fertiliser due to its valuable fertilising properties (Malińska et al. 2014, Starzyk et al. 2015, Czekała et al. 2016, Czekała et al. 2017).

A proper composting process results in compost which contains not only humic substances but also B vitamins and phytohormones. Apart from that, a temperature of 55-75°C at the thermophilic phase makes compost free from animal pathogens and weed seeds (Sánchez et al. 2017).

The assessment of adequacy of the compositing process involves not only the measurement of physical and chemical properties but also the biomass, the count of microorganisms and the enzymatic activity in the compost. These parameters are significant determinants of the degree of mineralisation of organic matter in the composted waste, as they indicate its maturity, stability and possibility of further use (Awasthi et al. 2018, Tiquia 2005).

The product of the composting process may be a good carrier of microorganisms promoting the growth and development of plants, e.g. fungi of the *Trichoderma* sp. genus (Wolna-Maruwka et al. 2016, Wolna-Maruwka et al. 2017). When these microorganisms enter soil, they become adsorbed and grow through the composted organic matter. As a result, they have a greater chance to survive the confrontation with the autochthonous soil microflora. Apart from that, the carrier itself (compost) is a nutrient reservoir.

As results from the studies by Cavalcante et al. (2008), Kancelista et al. (2013) and Smolińska et al. (2014), the adaptive abilities of *Trichoderma* sp. are related both with the type of substrate used as a carrier and the type of strain. The growth and development of these microorganisms are considerably influenced by the pH, humidity and temperature of the substrate as well as the source of carbon and nitrogen.

Moulds of the *Trichoderma* genus are very popular in agriculture because they support the growth of plants and protect them from pathogens (*Fusarium, Alternaria, Rhizoctonia. Botrytis, Sclerotinia*, etc.). They are considered to be biological control agents (BCAs) because of their mycoparasitism and capacity to produce antibiotics and siderophores. Additionally, they are classified as plant growth promoting fungi (PGPF) because they produce phytohormones, provide nutrients to plants and induce systemic resistance (El-Komy et al. 2015, Gajera et al. 2016, Sharma et al. 2017).

What also speaks in favour of applying strains of these microorganisms into soil to promote the growth of plants is the fact that they are resistant to pesticides, phenols and heavy metals. They can be easily isolated from the soil environment. Apart from that, they grow quickly and spore profusely in artificial cultures (Smolińska et al. 2014, Steyaert et al. 2010). There are very few microbial formulations based on *Trichoderma* sp. strains on the Polish market. Only one of them contains Polish strains of these fungi. Microorganisms develop best and exhibit the highest activity in the climate they come from. Therefore, it seems important to develop fertiliser preparations consisting of native Polish strains, which will be applied into soil on an organic carrier, i.e. compost. This will make them more resistant to adverse environmental factors.

The aim of the study was to assess the phytosanitary properties of two strains of *Trichoderma* sp. and their ability to grow and develop in mature compost made from onion waste, rye straw and pig manure.

2. Material and methods

2.1. Experimental design

The experiment was conducted in a laboratory at the Department of General and Environmental Microbiology, Poznań University of Life Sciences, Poland, as part of the project No. UDA-POIG.01.03.01-00-129/09-09 titled 'Polish *Trichoderma* Strains in Plant Protection and Organic Waste Handling', co-financed by the European Union from the European Regional Development Fund under the Innovative Economy Operational Programme.

Mature compost (onion waste compost) made from onion husk (553.8 kg fresh weight), rye straw (21.4 kg fresh weight) and pig manure (21.7 kg) was used in the experiment (Tab. 1).

Table 1. Physicochemical state of compost used in experiments (beginning of experiments)

Characteristic of compost	pH_{H2O}	humidity (%)	C $g{\cdot}kg^{-1}$ d.m.	N $g{\cdot}kg^{-1}$d.m.
Onion compost	8.81	45.11	389.23	24.89

The compost was collected from a 20-tonne prism. It was divided into four equal parts, 10 kg each, and placed in containers with a capacity of 18.8 l. Next, the compost was inoculated with two *Trichoderma* sp. strains, i.e. *T. atroviride* – T1 and *T. harzianum* – T3. In consequence, there were four experimental variants, each in two replicates: 1 – the control sample; onion waste compost (control), 2 – onion waste compost inoculated with *T. atroviride* strain T1 (variant T1), 3 – onion waste compost inoculated with *T. harzianum* strain T3 (variant T3), 4 – onion waste compost inoculated with *T. atroviride* strain T1 and *T. harzianum* strain T3 (variant T1+T3). The *Trichoderma* sp. inoculums came from the collection of strains of the Institute of Horticulture in Skierniewice, Poland. Each of them was applied in the form of conidial spores, at a density of 10^6 per g of fresh mass of compost. The count of spores was measured with a haemocytometer, under a light microscope (Zeiss).

Before the experiment an in vitro test was carried out to exclude antagonism between the *Trichoderma* isolates (Mańka 1974) used in the T1+T3 variant.

The experiment was carried out under controlled conditions in a thermostat, at a constant ambient temperature of 22°C. There were three terms of microbiological and enzymatic analyses: 1st – at the beginning of the experiment, 2nd – on the 30th day of the experiment, 3rd – on the 60th day of the experiment.

2.2. Microbiological analysis

The scope of experiments comprised determination (in five replications) of the total count of moulds and *Trichoderma* sp. The groups of microorganisms were cultured according to the plate method on solid substrates, using appropriate dilutions of soil solutions, expressed as $CFU{\cdot}g^{-1}$ of compost dry matter.

The count of moulds was determined on a medium prepared according to rose bengal agar (Sigma Aldrich) with aureomycin added. Plates were incubated for 6 days at a temperature of 25°C. Colonies of moulds isolated from composts at the end of the thermophilic phase were inoculated to a PDA substrate (Sigma Aldrich) on the day of their inoculation with *Trichoderma* sp. isolates. Next, their systematic position was determined according to mycological keys and the percentage of individual genera in the entire population was calculated (Domsch et al. 1993).

The count of *Trichoderma* sp. strains was determined with the plate method, on a modified rose bengal agar (Sigma Aldrich) with chloramphenicol, streptomycin, metalaxyl and PCNB (pentachloronitrobenzene) added. The plates were exposed to visible light and incubated for 7 days at a temperature of 24°C. In order to confirm the systematic position of *Trichoderma* sp. in the *Trichoderma harzianum* or *Trichoderma atroviride* species the colonies were inoculated to the PDA substrate (Sigma Aldrich). They were initially identified with a microscope. Next, the identification was confirmed by means of in situ hybridisation (FISH), modified according to Amann et al. (1990), where 4% PFA (paraformaldehyde), 0.5% Triton solution, alcohol series (70%, 80%, 96%), 70% formamide solution and two probes, marked at end 3' with marker Cy3 (ACT CCC AAA CCC AAT GTG AA and ATA CCA AAC TGT TGC CTCGG) were applied (Siddiquee et al. 2010).

The rating scale developed by Mańka (1974) was used to determine the type of interactions occurring between strains of autochthonous moulds isolated from the composts at the end of the thermophilic phase and *Trichoderma* sp. isolated applied in the research. The following elements were taken into consideration: the degree to which one colony surrounded another, the width of the inhibitory zone and growth inhibition. A positive result should be interpreted as an effect limiting the development of a particular autochthon (test fungus) by a selected *Trichoderma* sp. isolate (antagonist).

Before the experiment was set up, fungi had been proliferated on a PDA medium (Potato Dextrose Agar). Next, a sterile cork borer was used to cut discs of cultures (10 mm in diameter). The discs were transferred to the PDA medium and spaced at 30 mm from each other. Every day, for 8 days the mycelium diameter was measured in the dual-organism cultures and the type of interaction between the fungi was determined. The cultures were incubated at a temperature of 24°C. Single-organism cultures prepared in an analogical manner were used as control samples. All tests were replicated five times.

2.3. Trends of physicochemical and enzymatic parameters

The dehydrogenase activity (DHA) was determined with the method developed by Camiña (1998) with minor modifications. The compost (5g) was incubated for 24 h with 2, 3, 5-triphenyltetrazolium chloride (TTC) at 30°C, pH 7.4. Triphenylformazan (TPF) was produced, extracted with 96% ethanol and measured spectrophotometrically at a wavelength of 485 nm. The dehydrogenase activity was expressed as μg TPF $\cdot$ g^{-1} DM of compost $\cdot$ $24h^{-1}$.

The chemical analysis of composts was conducted in the laboratory of the Department of Agronomy. The content of carbon was determined with the

Tiurin method. The content of total nitrogen in the fresh weight of composts was measured with the Kjeldahl method by means of a Kjeltec 2200 System analyser (FOSS Tecator). The pH values of compost samples were determined in double distilled water. (pH_{H2O}). The content of dry weight of composts was measured by drying and weighing at a temperature of 105°C in the laboratory of the Institute of Biosystem Engineering.

2.4. Statistical analysis

Statistical analyses were conducted by means of Statistica 12.0 software (StatSoft Inc. 2012). We used two-way analysis of variance to determine the significance of variation in the number of moulds under analysis, depending on the compost combination and term of analysis. Homogeneous subsets of means were identified by means of Tukey´s test at a significance level of $p = 0.05$.

Principal Component Analysis (PCA) was used to illustrate the dependence between the number of microorganisms, DHA activity, pH and moisture content. Simple regression analysis was applied for evaluating the optimal microorganisms growth and DHA activity.

3. Results and discussion

Apart from bacteria and actinobacteria, moulds also take part in the composting process. These microorganisms play a key role in the degradation of organic matter and the formation of humic compounds. Thanks to their activity it is possible to obtain compost of high fertilising value from organic waste, which is often difficult to handle (Wolna-Maruwka et al. 2016, Van Fan et al. 2018).

Before applying *Trichoderma* sp. strains into composts the analysis of the count of moulds showed that there were statistically significant differences already at the first term of analyses. The count ranged from 150 to 340 $\cdot 10^3$ CFU g d.m. of compost, depending on the experimental variant (Fig. 1).

At the subsequent terms of analyses the count of moulds decreased significantly in the variants with *Trichoderma* sp. isolates, especially in the variant with the *T. harzianum* (T3) isolate. The trend based on the daily decrease in the count of moulds fitted the quadratic regression model below (Equ. 1).

Equ. 1. Moulds (combination T3):

$$M = 91.5D^2 - 511.5M + 760$$
$$R^2 = 0.98$$

where:
M – Molds,
D – Days,
R^2 – Coefficient R squared.

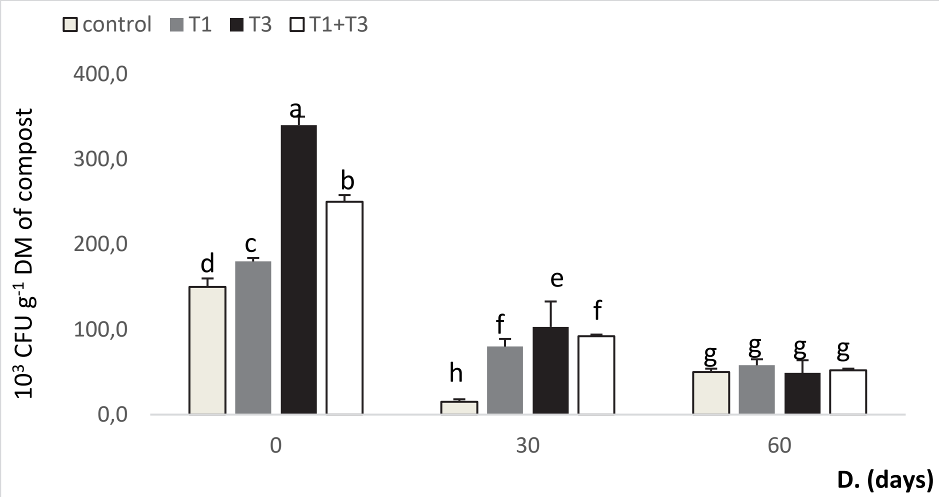

Fig. 1. The changes of total number of moulds in onion composts

Explanation: Means followed by the same letters do not differ significantly at $p = 0.05$; Combination: T1 – onion waste compost inoculated with strain T1, T3 – onion waste compost inoculated with strain T3, T1+T3 – onion waste compost inoculated with strain T1 and T3.

This effect may have been caused both by the addition of *Trichoderma* sp. isolates and by changes in the compost pH and moisture content (Fig. 2), which was confirmed by the principal component analysis (PCA) (Fig. 3).

As results from the study by Steyaert et al. (2010), moulds produce the most spores and develop best when pH ranges from 2.8 to 5.2. In our study the pH of the composts was alkaline, which may have been caused by the gradual decrease in count of moulds as the experiment was incubated.

The substrate moisture is also an important parameter affecting the growth and development of moulds. The study by Natywa et al. (2014) showed that the survival and activity of microorganisms decreased along with the moisture content of the substrate. Moulds became inactive when the moisture content of the environment decreased to 15%. On the other hand, according to Hassen et al. (2001), the development of moulds in compost is inhibited by other factors than pH, humidity or temperature. The development of fungi in compost may be inhibited by microbial antagonism processes, including antibiosis.

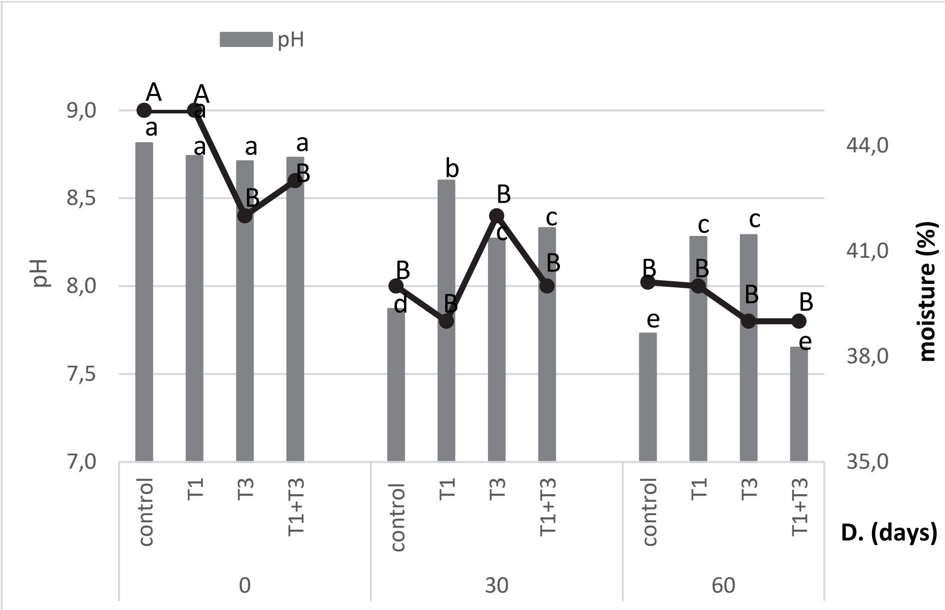

Fig. 2. The changes of pH and moisture value in onion composts

Explanation: Means followed by the same letters do not differ significantly at $p = 0.05$; Combination: OT1 – onion waste compost inoculated with strain T1, OT3 – onion waste compost inoculated with strain T3, OT1+OT3 – onion waste compost inoculated with strain T1 and T3.

This thesis is confirmed by the results of biotic tests shown in Table 2. As can be seen, the *Trichoderma* sp. strains applied into the composts exhibited in vitro antagonism against the autochthonous fungi isolated from the onion compost at the beginning of the experiment.

The results of mycological analyses in Table 3 show that *Penicillium* (31-33%) and *Aspergillus* sp. (4-14%) were the dominant species in the compost. The presence of *Alternaria* sp., *Paecilomyces variotti*, *Rhizopus nigricans* and *Mucor* sp. was also detected. These observations are in agreement with the results of the research by Wolna-Maruwka et al. (2016), where moulds of the *Penicillium* genus were the predominant microflora in compost made from onion waste, wheat straw and pig manure.

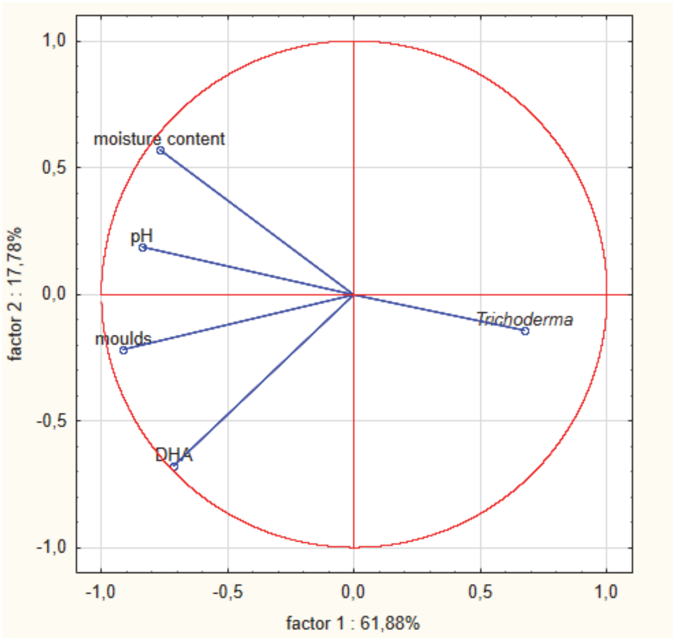

Fig. 3. Dependences between the number of moulds, *Trichoderma* sp, DHA, pH value and humidity (%) of applied in the experimental compost combinations at consecutive terms of analyses (PCA)

The biotic tests (Tab. 2, Phot. 1) showed that the *T. atroviride* strain (T1) exhibited stronger antagonism than the T3 isolate.

Table 2. Results of biotic test in dual cultures

Isolate	*Penicillum* sp. (1)	*Penicillum* sp. (2)	*Aspergillus* sp.	*Aspergillus niger*	*Alternaria* sp.	*Paecilomyces variotti*	*Rhizopus nigricans*	*Mucor* sp.
T1	-6	+8	+4	+6	+6	+6	+8	+6
T3	-6	-4	+4	+4	+6	+4	+6	+6

Explanation: A positive result means that the *Trichoderma* sp. isolate inhibited the growth of the autochthonous colony; 0 – no inhibition, 8 – total inhibition.

Table 3. Isolates of moulds isolated from the compost before inoculation

Isolate	Percentage content (%)
Penicillum sp. (1)	33
Penicillium sp. (2)	31
Aspergillus sp.	14
Aspergillus niger	4
Alternaria sp.	4
Paecilomyces variotti	4
Rhizopus nigricans	5
Mucor sp.	5

Photo 1. Antagonistic relationship between *Trichoderma atroviride* – T1 and *Penicillium* sp. (2)

According to Dłużniewska (2004) and Gajera et al. (2016), *Trichoderma* sp. have numerous antagonistic properties. They are characterised by rapid growth, abundant sporulation, the ability to exist on various substrates, the ability to produce fungitoxic substances, the ease of use of available organic matter and inorganic compounds, and strong parasitic properties resulting from the production of a wide range of antibiotics (alamethicin, tricholine, peptaibols, viridins, gliovirins, gliotoxins, glisoprenin, heptelidic acid, α-pyrrole) and enzymes (cellulase, hemicellulase, xylanase, pectinase, β-1,3-glucanase, chitinase and protease).

According to Perek et al. (2013), the combination of enzymes and antibiotics produced by microorganisms may give a higher level of antagonism than the activity of antibiotics or enzymes alone. The initial degradation of the cell wall by enzymes can facilitate the penetration of antibiotics into the cells of other microorganisms.

However, the interaction tests showed that both *Trichoderma* sp. isolates were susceptible to *Penicillium* sp. strains. According to Wawrzyniak and Waśkiewicz (2014), it resulted from the production of ochratoxin A and citrinin by some *Penicillium* species.

In our research, not only was the count of moulds reduced at the end of the experiment, but also the dehydrogenase activity decreased gradually (Fig. 4). According to Barren et al. (2008), the dehydrogenase activity can be used to monitor the composting process and to assess compost maturity and stability.

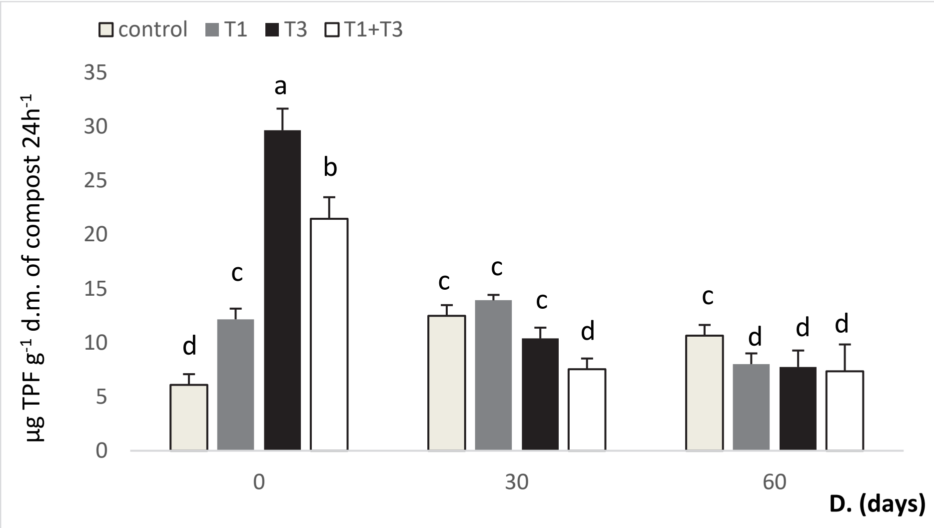

Fig. 4. The changes of dehydrogenase activity in onion composts

Explanation: Means followed by the same letters do not differ significantly at p = 0.05; Combination: T1 – onion waste compost inoculated with strain T1, T3 – onion waste compost inoculated with strain T3, T1+T3 – onion waste compost inoculated with strain T1 and T3.

However, this enzyme reaction was mainly observed in the variants where *Trichoderma* sp. isolates were used. Like the count of moulds, especially in the compost inoculated with the T3 isolate, it assumed the trend that matches the quadratic regression model (Equ. 2).

Equ. 2. Dehydrogenase (combination T3):

$$DHA = 8.3113D^2 - 44.2DHA + 65.539$$
$$R^2 = 0.99$$

where:
DHA – Dehydrogenase Activity,
D – Days,
R^2 – Coefficient R squared.

The principal component analysis (PCA) confirmed the negative relation between the count of *Trichoderma* sp. and the dehydrogenase activity. It also indicated the positive correlation between the dehydrogenase activity (DHA) with the pH of composts (Fig. 3).

The reduced dehydrogenase activity during the experiment shows that the active decomposition of organic matter decreased and the compost reached maturity. According to Tiquia (2005), the DHA in mature compost ranges from 12 to 39 μg TPF$\cdot g^{-1}$ d.m. of compost. In our study at the end of the experiment (3rd term), the DHA in the composts amounted to 7.33-10.64 μg TPF$\cdot g^{-1}$ d.m. of compost, that suggest that obtained composts were fully stable and mature.According to the guidelines presented by the abovementioned author, the composts were fully stable and mature.

At the beginning of the experiment the compost samples were analysed mycologically (Tab. 3) for the occurrence of autochthonous *Trichoderma* sp. fungi. As they were not found in any of the experimental variants, it considerably facilitated the control of the survivability of the isolates applied into the composts. 30 days after the application of the strains the highest count of *Trichoderma* sp. was found in the variant containing both T1 and T3 isolates, whereas the *T. atroviride* isolate (variant T1) exhibited the poorest adaptive properties (Tab. 4).

Table 4. The changes of *Trichoderma* sp. (10^2 CFU g^{-1} DM) in onion composts

Combination	D. (day)		
	0 – beginning of experiment	30	60
control	0.00	0.00	0.00
T1	0.00	4.21^e	14.21^c
T3	0.00	9.11^d	24.55^a
T1+T3	0.00	10.01^d	20.11^b

Explanation: Means followed by the same letters do not differ significantly at $p = 0.05$; Combination: T1 – onion waste compost inoculated with strain T1, T3 – onion waste compost inoculated with strain T3, T1+T3 – onion waste compost inoculated with strain T1 and T3.

Within 30 days following the inoculation of the composts the count of the applied *Trichoderma* isolates was reduced by 4 orders of magnitude, from the initial spore density of 10^6 to 10^2 CFU. There was a similar reduction observed in the study by Wolna-Maruwka et al. (2016).

As results from the observations, on the 30th day of the experiment the *Trichoderma* isolates were adapted to the unfavourable environmental conditions, such as the high pH (Fig. 2) and competition with the autochthonous compost microflora (Tab. 2).

According to Kredics et al. (2003), the optimal pH for the growth and development of *Trichoderma* sp. is 4. This finding was confirmed by the statistical analysis (PCA), which indicated a negative relation between the count of these microorganisms and the pH value of the composts (Fig. 3).

However, Vimala Kumari et al. (2014) found that *Trichoderma* isolates collected from agricultural soil were capable of proliferation in an alkaline substrate (pH 7-10).

On the 60th day of compost incubation, the strain survival phase finished and the reproduction phase began. The count of *Trichoderma* sp. increased by more than 100-150%. It is most likely that the variation in the proliferation of the isolates resulted from their different sensitivity to the pH of the substrate. The smallest variation was noted in the variant inoculated with the T3 strain (Fig. 5).

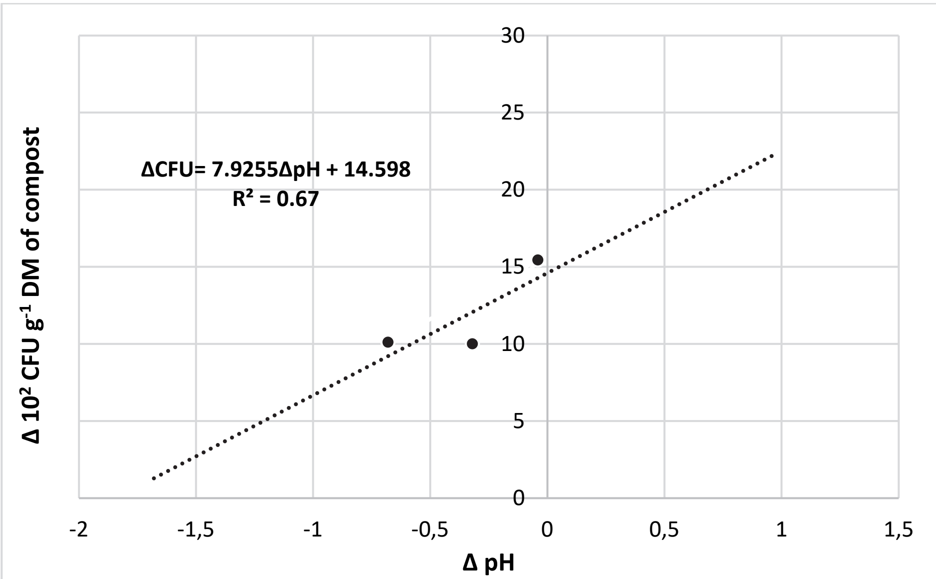

Fig. 5. The effect of the compost pH change during the propagation stage of *Trichoderma* strains on the change of *Trichoderma's* count

As results from the quadratic regression model, the *T. harzianum* strain (variant T3) exhibited the weakest reaction to the change in the compost pH on the 60th day of the experiment. The quadratic regression model shows that the pH decrease of -0.04 from the initial 8.33 resulted in the maximum count of 15.44 · 10^2 CFU *T. harzianum* g^{-1} d.m. of compost. According to Yedid et al. (1999) and Howell (2003), fungi of the *Trichoderma* sp. genus can regulate the pH of the substrate by producing enzymes such as cellulases, pectinases, xylases and proteases, which increase the pH value. On the other hand, they can reduce the pH of the substrate by producing organic acids.

4. Conclusions

1. The strongest trend in the statistically significant reduction of the count of moulds and dehydrogenase activity to the level showing full maturity of the compost was observed in the variant with the *T. harzianum* isolate (T3).
2. The research showed that *Penicillum* sp. and *Aspergillus* sp. were the dominant strains in the onion waste compost. Apart from that, the antagonism test proved that the *Trichoderma* sp. isolates inhibited the growth and development of most of the autochthonous moulds isolated in the analysis.
3. Both the pH and moisture content of the composts significantly influenced changes in the count of fungi as well as the adaptive properties and the proliferation of the *Trichoderma* sp. isolates applied into the composts.
4. The *T. harzianum* strain (T3) was the least sensitive to the environmental conditions, which resulted in its highest count. The *T. atroviride* isolate (T1) exhibited stronger phytosanitary properties.
5. The research showed that the alkaline onion waste compost enabled the growth and development of antagonistic fungi of the *Trichoderma* spp. genus and that it was a good way of handling nuisance waste.

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Abstract

In spite of the alkaline reaction of onion waste composted together with rye straw and pig manure, these materials can be used as a substrate for the growth of moulds of the *Trichoderma* genus, with proven phytosanitary properties against plant pathogens. This hypothesis was verified in a laboratory experiment with four variants: a control sample and three variants with two *Trichoderma* sp. strains (*T. atroviride* T1 and *T. harzianum* T3). The isolates were entered into compost individually or simultaneously (T1 + T3). The research included microbial analyses, in which the survivability of *Trichoderma* sp. strains was monitored and the total count of moulds and the dehydrogenase activity were estimated. The analyses were made three times: before applying the strains into compost, one month and two months after the inoculation. Apart from that, the type of interaction between autochthonous fungi isolated from mature compost at the beginning of the experiment and the *Trichoderma* sp. strains was determined.

The count of moulds was most reduced and the lowest dehydrogenase activity was observed in the compost with the *T. harzianum* isolate. Apart from that, the strain also exhibited the strongest adaptive properties to the compost substrate. The *T. atroviride* isolate proved to be the more effective antagonist of autochthonous moulds isolated on the first day of the experiment, including fungi of the *Alternaria* genus. The pH and moisture content of the substrates proved to be significant factors affecting the growth, proliferation and the antagonistic properties of *Trichoderma* sp. isolates.

The simultaneous inoculation of compost with two *Trichoderma* sp. isolates resulted in the worst growth and proliferation of the *Trichoderma* sp. strains, although the two isolates were not antagonistic to each other in vitro.

Keywords:
compost, *Trichoderma*, physicochemical properties, fungi survival test

Zagospodarowanie przekompostowanych odpadów cebulowych w postaci podłoży do namnażania *Trichoderma* sp.

Streszczenie

Przekompostowane odpady cebulowe wraz ze słomą żytnią i obornikiem świńskim pomimo zasadowego odczynu stanowią podłoże umożliwiające wzrost grzybów pleśniowych z rodzaju *Trichoderma*, with proven phytosanitary properties against plant pathogens. Hipotezę tę zweryfikowano na podstawie doświadczenia przeprowadzonego w warunkach laboratoryjnych, w którym zastosowano cztery warianty doświadczalne: kontrolny oraz trzy z dodatkiem dwóch szczepów *Trichoderma* sp. (*T. atroviride* T1 oraz *T. harzianum* T3). Izolaty wprowadzano pojedynczo lub oba jednocześnie (T1+T3) do kompostu. Analizy mikrobiologiczne polegające na monitorowaniu przeżywalności wprowadzonych szczepów *Trichoderma* sp., oszacowaniu ogólnej liczby grzybów pleśniowych oraz aktywności dehydrogenaz przeprowadzono trzykrotnie: przed wprowadzeniem szczepów do kompostu, miesiąc oraz dwa miesiące po inokulacji. Dodatkowo określano rodzaj interakcji zachodzącej między autochtonicznymi grzybami wyizolowanymi z dojrzałego kompostu w momencie zakładania doświadczenia a zastosowanymi szczepami *Trichoderma* sp..

Wykazano, że największą redukcję grzybów pleśniowych oraz najniższą aktywność dehydrogenaz uzyskano w kompoście, do którego wprowadzono izolat *T. harzianum*. Niniejszy szczep wykazał ponadto najsilniejsze właściwości adaptacyjne w kompostowym podłożu. Izolat *T. atroviride* okazał się natomiast skuteczniejszym antagonistą wobec wyizolowanych w dniu zakładania doświadczenia autochtonicznych grzybów pleśniowych, w tym z rodzaju *Alternaria*. Wartość pH i poziom wilgotności podłoży okazały się istotnymi czynnikami warunkującymi wzrost, namnażanie, jak również właściwości antagonistyczne izolatów *Trichoderma* sp.

Stwierdzono, że wprowadzając do kompostu jednocześnie dwa izolaty *Trichoderma* sp. uzyskano najgorszy efekt wzrostu i namnażania się zastosowanych szczepów *Trichoderma* sp., pomimo, że warunkach in vitro izolaty nie oddziaływały na siebie antagonistycznie.

Słowa kluczowe:
kompost, *Trichoderma*, właściwości fizyczno-chemiczne, test przetrwania grzybów

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Water Needs of Bird Cherry Trees at the Period over Three Years after Reclamation in Different Regions of Poland

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1. Introduction

Bird cherry (*Padus avium* Mill.) is not only a popular ornamental plant, but also a medicinal plant often used in herbal medicine (Podbielkowski 1989, Olszewska & Kwapisz 2011). Different plant tissues, such as fruits, flowers, leaves and bark of bird cherry have been traditionally used as ingredients of mildly diuretic, anodyne, febrifuge, anti-rheumatic, antibiotic, anti-diarrhoeal and sedative ethnomedicines (Launert 1989, Strzelecka & Kowalski 2000, Olszewska & Kwapisz 2011). Bird cherry is also frequently used as a decorative plant; it is planted in parks and along roads, as well as used in landscape and reclamation plantings (Krüssmann 1986, Podbielkowski 1989, Hammatt et al. 1998). Due to decorative advantages of bird cherry flowers and fruits, as well as beautiful yellow and red colors of autumn leaves, and also the plenty of fruits, which are a source of food for birds, it is worth using this species more often in the park and landscape plantings (Karczmarczuk 2012).

The survival rate of plants in the reclaimed areas depends mainly on ensuring optimal water conditions of the soil, which in turn can be effectively controlled by the irrigation treatments (Żakowicz 2010). However, designing and programming an irrigation system requires determination of the water needs, as well as specific requirements of individual plant species. In the case of bird cherry plants, it should also be taken into account that these species prefer soils with mobile and flowable water, and thus does not tolerate habitats with stagnant water (Lasota et al. 2014).

The aim of the present study was to estimate the water needs of bird cherry plants at the period over three years after planting on the reclaimed areas located in five different regions of Poland.

2. Material and methods

The water needs of bird cherry (*Padus avium* Mill.) were determined using the plant coefficient method. The plant coefficients for the bird cherry trees over three years after planting on the reclamation area were adapted to the reference evapotranspiration that was calculated using the Blaney-Criddle's formula, modified for Polish conditions by Żakowicz (2010).

The water requirements of bird cherry plants were estimated in the years from 1981 to 2010 for five different agro-climatic regions of Poland with the representative meteorological stations located in Olsztyn, Bydgoszcz, Warsaw, Wroclaw and Krakow (Łabędzki et al. 2013) (Fig. 1). The calculations were performed for the period of two months, including July and August, critical in terms of the amount of water available to the plants.

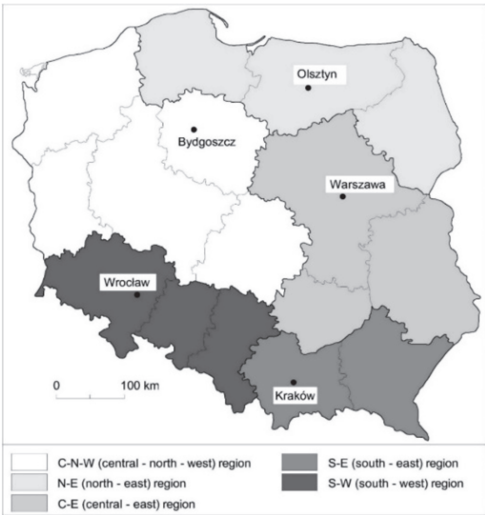

Fig. 1. Agro-climatic regions of Poland with the representative meteorological stations (according to Łabędzki et al. 2013)

The precipitation deficit with the occurrence probability of average dry years ($N_{50\%}$), medium dry years ($N_{25\%}$) and very dry years ($N_{10\%}$) was determined according to the Ostromęcki's method (Żakowicz et al. 2009).

The results of currently presented study are the continuation of research published by Rolbiecki et al. (2018 b) that analyzed the water needs of bird cherry plants during the first three years of growing on the reclaimed areas.

3. Results and discussion

The variability of bird cherry water requirements in the period of July-August ranged from 4.2% in the S-E region of Poland to 4.7% in the N-E and C-N-W region of the country (Table 1). In August, the variation coefficient of bird cherry water needs was higher than in the period from July 1 to August 31 and ranged from 4.5% in the C-E region to 5.1% in the C-N-W region of Poland.

Table 1. Characteristics of the bird cherry water needs during the growing period

Specification	Region of Poland	July-August	August
Minimum (mm)	north-east (N-E)	237.0	100.9
	central-north-west (C-N-W)	249.0	106.5
	central-east (C-E)	249.9	106.9
	south-west (S-W)	221.0	99.0
	south-east (S-E)	230.0	100.9
Maximum (mm)	north-east (N-E)	281.5	127.3
	central-north-west (C-N-W)	292.9	133.7
	central-east (C-E)	294.6	138.5
	south-west (S-W)	261.0	126.0
	south-east (S-E)	273.3	130.5
Median (mm)	north-east (N-E)	258.7	114.2
	central-north-west (C-N-W)	271.7	121.8
	central-east (C-E)	270.0	120.2
	south-west (S-W)	241.1	111.8
	south-east (S-E)	251.7	111.4

Table 1. cont.

Specification	Region of Poland	July-August	August
Standard Deviation (mm)	north-east (N-E)	12.1	5.7
	central-north-west (C-N-W)	12.8	6.1
	central-east (C-E)	11.9	5.5
	south-west (S-W)	10.7	5.1
	south-east (S-E)	10.4	5.4
Variation Coefficient (%)	north-east (N-E)	4.7	5.0
	central-north-west (C-N-W)	4.7	5.1
	central-east (C-E)	4.4	4.5
	south-west (S-W)	4.5	4.6
	south-east (S-E)	4.2	4.8

In each considered region of Poland, during the thirty-year period (1981-2010), a visible tendency to increase the water requirements of bird cherry plants in July and August, were noted (Fig. 2). With the exception of the C-N-W region of Poland, the temporal variability of bird cherry water needs were significant in each considered region of the country. The highest increase of bird cherry water requirements, by 6.7 mm in every ten-year period, in the S-E region of Poland were observed. On average, throughout Poland, during the considered thirty-year period, the water needs of bird cherry in July and August increased in each ten years period by 5.6 mm. In the studies reported by Rolbiecki et al. (2018 b), in each subsequent ten-year period of the considered thirty years, the water requirements of bird cherry plants, calculated for the first three years of growing on the reclaimed areas, increased in the period from July 1 to August 31 in the range from 5.2 to 5.7 mm in the S-W and N-E regions of Poland, respectively. The differences between current results and results presented by Rolbiecki et al. (2018 b) are an effect of the lower values of plant coefficients applied according to Żakowicz (2010) for young plants (first three years after planting) than older plants (over three years after planting).

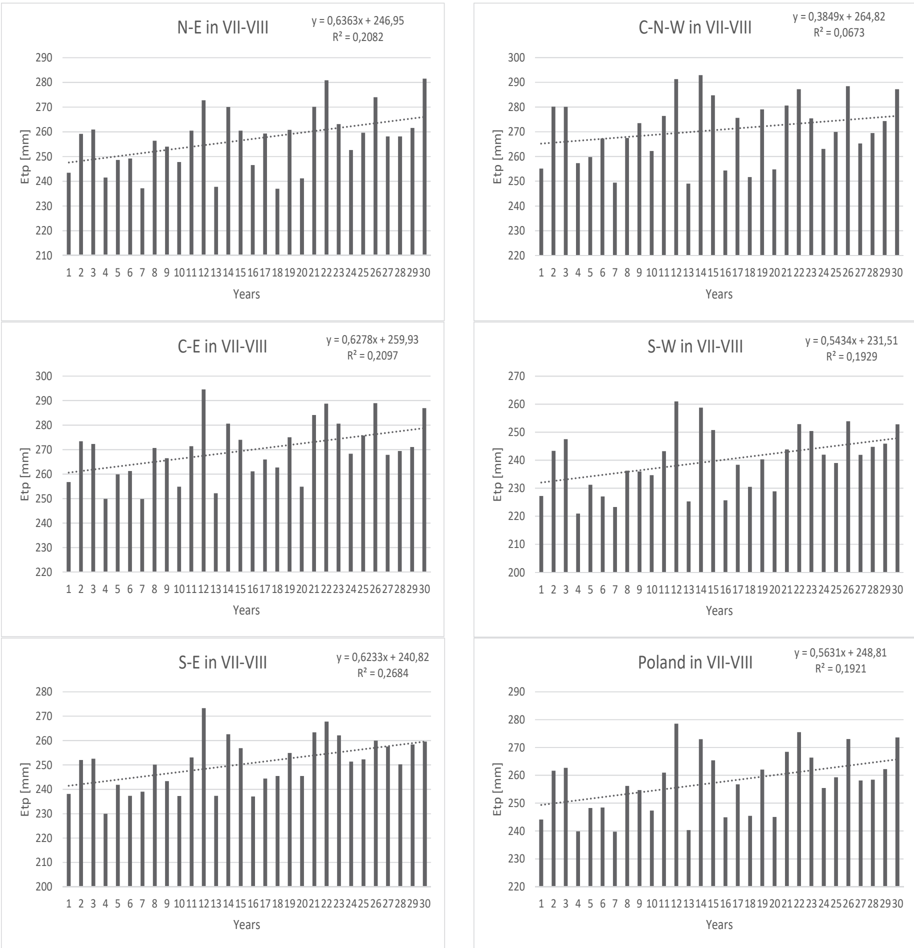

Fig. 2. Temporal variability of water needs of bird cherry plants, over three years after planting, in July and August, in the different regions of Poland

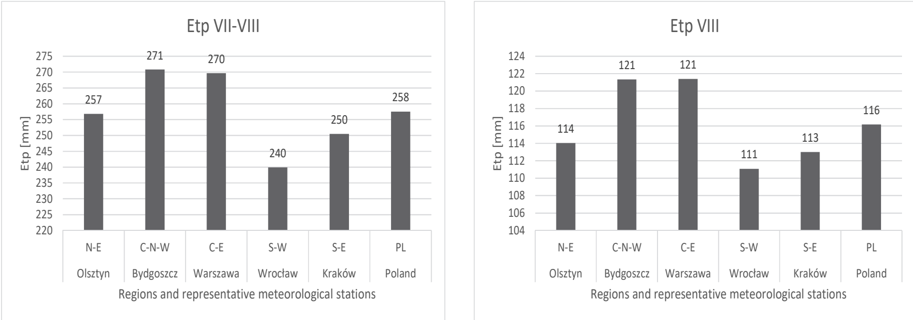

Fig 3. Water needs (Etp) of bird cherry, over three years after planting, in the period from July 1 to August 31 and in August in the different regions of Poland

On average, in the years 1981-2010, the highest water needs (Etp) of bird cherry trees, over three years after planting, in the period from July 1 to August 31, was noted in the C-N-W (271 mm) and C-E region (270 mm), while the lowest water requirements (240 mm) in the S-W region of Poland was calculated (Fig. 3). In August, the highest bird cherry water needs (121 mm) also in the C-N-W and C-E region of Poland were estimated, whereas the smallest water requirements (111 mm) in the S-W region of the country was observed. For comparison, the water needs of bird during the first three years after planting in the period of July-August, calculated as the long-term average from the years 1981-2010 for five different regions of Poland, was 233 mm (Rolbiecki et al. 2018 b). The highest water requirements of young bird cherry plants were estimated in the C-N-W (242 mm) and C-E (241 mm) region of Poland, while the lowest water needs were noted in the N-E (229 mm) and S-E (223 mm) region of the country.

Generally, in the present study, throughout Poland, a visible increase in water requirements of bird cherry plants in August were noted (Fig. 4). In every considered region of Poland, except the C-N-W region, the temporal variability of bird cherry water needs was significant. That confirm the results published by Rolbiecki et al. (2018 b).

In the years 1981-2010, the highest increase (by 2.1 mm in each ten-year period) of the bird cherry water requirements in August was noted in the N-E and S-E region of Poland. Non-significant upward trend of the bird cherry water needs in the C-N-W region of the country was only 1.2 mm. On average, in the thirty-year period from 1981 to 2010, throughout Poland, the water requirements of bird cherry plants, over three years after planting, in August increased by 1.8 mm in each subsequent ten-year period.

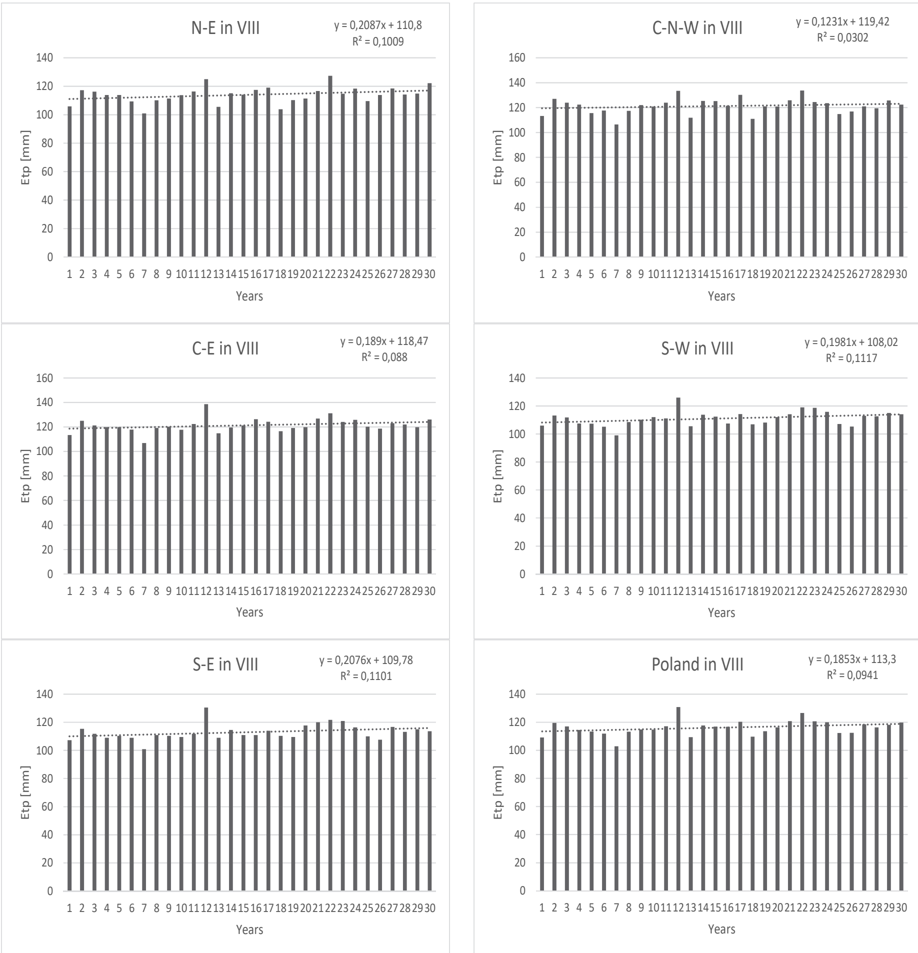

Fig. 4. Temporal variability of bird cherry water needs, over three years after planting, in August in the different regions of Poland

In the period from July 1 and August 31, the highest precipitation deficiencies, 131 and 133 mm, in the average dry years ($N_{50\%}$) were noted in the C-E and C-N-W region of Poland, respectively (Table 2). In the N-E, C-N-W and C-E region of the country, the rainfall deficit in the medium dry years ($N_{25\%}$ ranging from 206 to 214 mm) and in the very dry years ($N_{10\%}$ ranging from 269 to 300 mm) was higher than in the S-W and S-E region of Poland ($N_{25\%}$ ranging from 146 to 159 mm and $N_{10\%}$ ranging from 195 to 211 mm). It should be reminded that according to Żakowicz et al. (2009), the value of $N_{10\%}$ covers the water needs of the plants in 90% and thus the value of $N_{50\%}$ covers the plant water needs in 50%.

A similar tendency was observed in August, when also the highest rainfall deficit ($N_{50\%}$ ranging from 49 to 61 mm, $N_{25\%}$ ranging from 74 to 87 mm and $N_{10\%}$ ranging from 94 to 133 mm) in N-E, C-N-W and C-E region of Poland was noted, while much lower precipitation deficiencies ($N_{50\%}$ ranging from 36 to 42 mm, $N_{25\%}$ ranging from 56 to 58 mm and $N_{10\%}$ ranging from 65 to 75 mm) occurred in the S-E and S-E region of the country.

Table 2. Rainfall deficit of bird cherry plants, over three years after planting, in the period of the highest water needs (July-August) in the different regions of Poland (mm)

Rainfall deficit	Region of Poland				
	N-E	C-N-W	C-E	S-W	S-E
July-August					
$N_{50\%}$	118	133	131	91	85
$N_{25\%}$	206	208	214	146	159
$N_{10\%}$	274	269	300	211	195
August					
$N_{50\%}$	49	61	59	42	36
$N_{25\%}$	82	74	87	58	56
$N_{10\%}$	126	94	133	75	65

According to the study reported by Rolbiecki et al. (2018 b), throughout Poland, during the period from July 1 to August 31, in the years 1981-2010, the average rainfall deficit in the growing of bird cherry plants during the first three years after planting was 87 mm. Additionally, the highest precipitation deficiencies in the C-N-W (103 mm) and C-E (102 mm) region of Poland, was calculated.

In the present study, a visible increase in bird cherry water requirements calculated for the period from July 1 to August 31, in the years 1981-2010, was noted in all considered regions of Poland. Similar observations have already been published by Łabędzki (2009) and Rolbiecki et al. (2018 b). Researchers involved in studying the water needs of the plants consider that the observed climatic changes will result, in the near future, in an increase of the water requirements of most plant species, including also reclamation plantings. Therefore, it is necessary to undertake some adaptation activities, such as developing a program of irrigation techniques, the meaning of which will grow with the intensification of climate changes (Łabędzki 2009, Stachowski 2009, Stachowski & Markiewicz 2011, Kuchar & Iwanski 2011, 2013, Żarski et al. 2013, Kuchar at al. 2015, 2017, Rolbiecki et al. 2018 a).

The survival rate of the plants introduced to the reclaimed areas depends, on the one hand, on the selection of suitable species of trees and shrubs, and on the other hand, on the ensuring suitable soil moisture by applying the irrigation treatments (Żakowicz 2010). Irrigation is considered as one of the most important melioration techniques that guarantee the proper growth of the trees and shrubs seedlings in the plantings and cultivations carried out, among others, in the different plantings and forest nurseries (Rzekanowski & Pierzgalski 2006, Ptach et al. 2018). The results of the present study may be helpful in planning and programming of the bird cherry plants irrigation treatments. The usefulness of the micro-irrigation system in the bird cherry nest reclamation plantings have been confirmed also by Żakowicz (2010), as well as Żakowicz & Hewelke (2012).

The bird cherry plants, on the one hand belong to the species that tolerate the wide types of the soil (Houston Durrant & Caudullo 2016), on the other hand, bird cherry is not drought and shade tolerant plant (USDA 2002). The bird cherry trees especially often inhabit the soils with mobile water, as well as the marshy meadows (Lasota et al. 2014). The results of some experiments carried out in the region of Bydgoszcz indicate a positive effect of irrigation – often also in interaction with other irrigation treatments i.e. revitalization – on the growth of seedlings of many trees species, among others such as: Scots pine (Klimek et al. 2008), white birch (Klimek et al. 2009), European larch (Klimek et al. 2011), littleleaf linden (Klimek et al. 2013) and paulownia (Ptach et al. 2018).

4. Conclusions

1. In the years 1981-2010, in the period from July 1 to August 31, the highest water needs of bird cherry trees over three years after planting, grown on the reclaimed areas, were estimated in the central-north-west (271 mm) and central-east (270 mm) region of Poland, while the lowest (240 mm) – in the south-east region of the country.
2 In August, the highest bird cherry plants water requirements (121 mm) were calculated in the central-north-west and central-east region of Poland, while the lowest (111 mm) – in the south-east region of the country.
3. A visible increase in bird cherry water needs in the period of the highest water requirements (July-August), in the years 1981-2010, was noted in all considered regions of Poland. With the exception of the central-north-west region of the country, the temporal variability of bird cherry water requirements was significant throughout Poland. The highest increase of the bird cherry water needs (by 6.7 mm per every ten years) was found in the south-east region of Poland.
4. In the period of July and August, the highest rainfall deficit, 131 and 133 mm, in the average dry years ($N_{50\%}$) was noted in the central-east and central-north-west region of Poland, respectively. In the north-east, central-north-west and

central-east region of the country, the precipitation deficiencies in the medium dry years ($N_{25\%}$ ranging from 206 to 214 mm) and in the very dry years ($N_{10\%}$ ranging from 269 to 300 mm) was higher than in the south-west and south-east region of Poland ($N_{25\%}$ ranging from 146 to 159 mm and $N_{10\%}$ ranging from 195 to 211 mm).

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Abstract

The purpose of the present study was to determine the water needs of bird cherry (*Padus avium* Mill.) over three years after planting on the reclaimed areas. The estimations were performed for the period of two months, including July and August, which are critical in terms of the amount of water available to the plants. The water requirements of bird cherry plants were calculated in the years 1981-2010 for five agro-climatic regions of Poland with the representative meteorological stations located in Olsztyn, Bydgoszcz, Warsaw, Wrocław and Krakow. The bird cherry water needs were determined using the plant coefficient method. The plant coefficients for bird cherry trees over three years after planting were adapted to the reference evapotranspiration that was calculated using the Blaney-Criddle's formula, modified for Polish conditions by Żakowicz. The rainfall deficit with the probability of occurrence of average dry years ($N_{50\%}$), medium dry years ($N_{25\%}$) and very dry years ($N_{10\%}$) was determined according to the Ostromęcki's method. On average, in the years 1981-2010, in July and August, the highest water needs of bird cherry trees, grown on the reclaimed areas over three years, were estimated in the central-north-west (271 mm) and central-east (270 mm) region of Poland. While, the lowest water requirements of bird cherry (240 mm) in the south-east region of the country was calculated. In August, the highest bird cherry water needs (121 mm) were estimated also in the central-north-west and central-east region of Poland, whereas the lowest water requirements (111 mm) occurred in the south-east region of the country. In each considered region of Poland, in the years 1981-2010, a visible increase in bird cherry water needs in the period of the highest water requirements, was noted. With the exception of the central-north-west region of the country, the temporal variability of bird cherry water needs was significant throughout Poland. The highest increase of the water requirements (by 6.7 mm per every ten-year period) in the south-east region of Poland was found. In the period covering July and August, the highest rainfall deficit, 131 and 133 mm, in the average dry years ($N_{50\%}$) was noted in the central-east and central-north-west region of Poland, respectively. In the north-east, central-north-west and central-east region of the country, the rainfall deficit in the medium dry years ($N_{25\%}$ ranging from 206 to 214 mm) and very dry years ($N_{10\%}$ ranging from 269 to 300 mm) was higher than in the south-west and south-east region of Poland ($N_{25\%}$ ranging from 146 to 159 mm and $N_{10\%}$ ranging from 195 to 211 mm).

Keywords:
crop evapotranspiration, *Padus avium* Mill., precipitation deficit,
reference evapotranspiration, water requirements

Potrzeby wodne czeremchy zwyczajnej w okresie powyżej trzech lat po nasadzeniach rekultywacyjnych w różnych regionach Polski

Streszczenie

Celem przedstawionych badań było oszacowanie zapotrzebowania na wodę czeremchy zwyczajnej (*Padus avium* Mill.) w okresie powyżej trzech lat po wykonaniu nasadzeń na obszarach objętych rekultywacją. Obliczenia przeprowadzono dla okresu obejmującego dwa miesiące, lipiec i sierpień, które są krytyczne pod względem ilości wody dostępnej dla roślin. Wymagania wodne roślin czeremchy zwyczajnej zostały oszacowane w latach 1981-2010 dla pięciu agro-klimatycznych regionów Polski wraz z reprezentatywnymi stacjami meteorologicznymi zlokalizowanymi w Olsztynie, Bydgoszczy, Warszawie, Wrocławiu i Krakowie. Potrzeby wodne drzew czeremchy zwyczajnej zostały określone za pomocą metody współczynników roślinnych. Współczynniki roślinne dla drzew czeremchy zwyczajnej w okresie powyżej trzech lat po wykonaniu nasadzeń na obszarach objętych rekultywacją dostosowano do ewapotranspiracji wskaźnikowej, którą obliczono za pomocą wzoru Blaneya-Criddle'a, zmodyfikowanego dla warunków polskich przez Żakowicza. Niedobory opadów atmosferycznych z prawdopodobieństwem wystąpienia roku przeciętnie suchego (N50%), roku średnio suchego (N25%) oraz roku bardzo suchego (N10%) oznaczono za pomocą metody Ostromęckiego. Średnio, w latach 1981-2010, w okresie od 1 lipca do 31 sierpnia, najwyższe zapotrzebowanie na wodę drzew czeremchy zwyczajnej w okresie powyżej trzech lat po wysadzeniu na obszarach zrekultywowanych obliczono w centralno-północno-zachodnim (271 mm) oraz centralno-wschodnim regionie Polski (270 mm). Z kolei najniższe zapotrzebowanie na wodę czeremchy zwyczajnej (240 mm) wystąpiło w południowo-wschodnim regionie kraju. W sierpniu najwyższe zapotrzebowanie na wodę drzew czeremchy zwyczajnej (121 mm) obliczono również w centralno-północno-zachodnim oraz centralno wschodnim regionie Polski, natomiast najniższe zapotrzebowanie na wodę (111 mm) wystąpiło w południowo-wschodnim regionie kraju. We wszystkich rozpatrywanych regionach Polski, w okresie od 1981 do 2010, odnotowano tendencję do zwiększania się potrzeb wodnych czeremchy zwyczajnej w czasie największego zapotrzebowania na wodę, czyli w lipcu i w sierpniu. Z wyjątkiem centralno-północno-zachodnim regionu Polski, trend zmienności czasowej potrzeb wodnych czeremchy zwyczajnej był istotny we wszystkich pozostałych regionach kraju. Najwyższy wzrost zapotrzebowania na wodę (o 6,7 mm w każdym kolejnym dziesięcioleciu) wystąpił w południowo-wschodnim regionie Polski. W okresie od 1 lipca do 31 sierpnia największe niedobory opadów atmosferycznych, 131 i 133 mm, w przeciętnie suchym roku (N50%) odnotowano odpowiednio w środkowo-wschodnim oraz środkowo północno-zachodnim regionie Polski. W północno-wschodnim, środkowo-północno-zachodnim i środkowo-wschodnim regionie kraju niedobory opadów atmosferycznych w średnio suchym roku (N25% w zakresie od 206 do 214 mm) i w bardzo suchym roku (N10% w przedziale od 269 do 300 mm) był wyższy niż w południowo-zachodnim i południowo-wschodnim regionie Polski (N25% od 146 do 159 mm i N10% od 195 do 211 mm).

Słowa kluczowe:
niedobory opadów, *Padus avium* Mill., potencjalna ewapotranspiracja, potrzeby wodne, wskaźnikowa evapotranspiracja

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Problems of Nitrogen Oxides Emission Decreasing from Marine Diesel Engines to Fulfil the Limit of Tier 3

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1. Introduction

International shipping is the reason of emission about one million ton of the nitrogen oxides yearly to the atmosphere only on Baltic and the North Sea areas (Winnes 2016). Due to annex VI of International Convention on the Prevention of Pollution from Ships (MARPOL) the NO_x emission is limited. The International Maritime Organization (IMO) emission standards are commonly referred to Tier 1, Tier 2 and Tier 3 (see Fig. 1). The limit of Tier 1 was obligatory for new diesel engines (over 130 kW of power) built or installed on vessels from 1st January of 2000. The limit of Tier 2 is obligatory on vessels built after 1st July 2010 and limit of Tier 1 for existing pre-2000 engines. The more stringent requirements applicable to ships in Emission Control Area (ECA) where the emission limits concern to sulfur oxides (SO_x), particulate matters (PM) and nitrogen oxides (NO_x) (ABS Publication 2015, Herdzik 2011).

The NO_x emission limits are set for marine diesel engines depending on maximum operating speed (only) as graphically presented in Fig. 1.

2. The possibility of emission limits fulfillment

All marine diesel engines (installed on vessels) built after 2010 should comply with Tier 2 emission. Tier 3 is required on ECA-s: from 1st January 2016 on two hundred mile zone of USA waters and will be from 1st January 2021 on Baltic and North Sea. It debates about next areas i.e. Mediterranean or Black Sea.

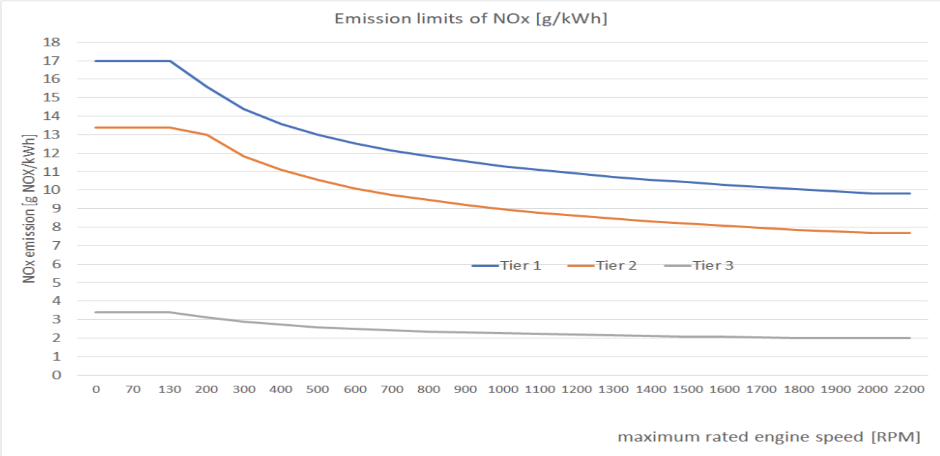

Fig. 1. MARPOL Annex VI NO_x emission limits

Tier 2 emission standard is expected to be met by combustion process optimization. The engine manufacturer may prepare the combustion process to fulfil the requirements through (Lloyd's Register 2005, Moreno-Gutierez et al. 2007, MAN B&W 2010, Pavlenko et al. 2014):

- fuel injection timing (delayed and divided into parts),
- decreasing the compression ratio and maximum combustion pressure,
- change fuel nozzle flow area,
- exhaust valve timing,
- cylinder compression volume,
- special water injectors,
- injectors for fuel-water emulsion, etc.

Tier 3 emission standard requires dedicated NO_x technologies working many often in co-operation of few lower mentioned, such (MAN Energy 2018, ABS 2017a, ABS 2017b):

- water induction into combustion process with fuel emulsion, scavenging air (humified air) or injection into cylinder,
- exhaust gas recirculation (EGR) systems,
- turbocharger cut-out matching,
- selective catalytic reduction (SCR) systems,
- other methods approved by marine administration as equivalent to above mentioned.

In reality into operation there are two alternative methods to meet the Tier 2 and Tier 3 NO_x requirement for two-stroke engines depending on the area of vessel sailing. The exhaust gas recirculation (EGR) is an internal engine process to prevent the formation of NO_x by controlling the combustion process. The decreasing of oxygen content in and parallel by moisturizing the scavenging air results in decreasing of NO_x formation. The selective catalytic reduction (SCR) is an after-treatment method using a catalyst to reduce the generated NO_x into oxygen and water. It needs the proper and stable temperature of the process (unfortunately exhaust gas temperature depends of the engine load) and additional reagents like ammonia or solution of urea in proper quantity to NO_x concentration in exhaust gas. The SCR system is available in a high-pressure system (SCR-HP) and a low-pressure system (SCR-LP).

3. NO_x decreasing emission systems

The installation of NO_x decreasing emission systems increases the prize of engines. There is a necessary of using an additional equipment. The lifetime of proper robust work of mentioned equipment is not known. It should be specified by the supplier.

The dedicated systems are complicated and needs additional electric energy for work about 1-5 kW per 1MW.

An example of such complex system working in EGR mode for MAN 7G80ME-C engine is presented in Fig. 2.

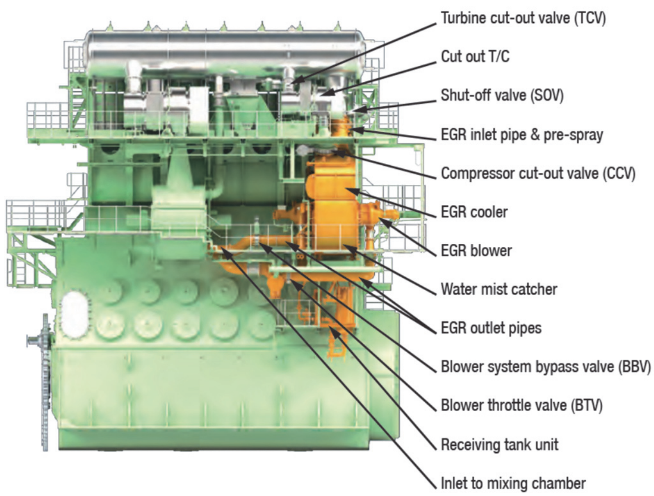

Fig. 2. Integrated EGR layout for by-pass matching (MAN Energy 2018)

The final effect of decreasing NO_x emission depends on co-operation of these elements of the system. The control valve operation depends on the power of engine and Tier 2 or Tier 3 mode. The idea of EGR system is presented in Fig. 3.

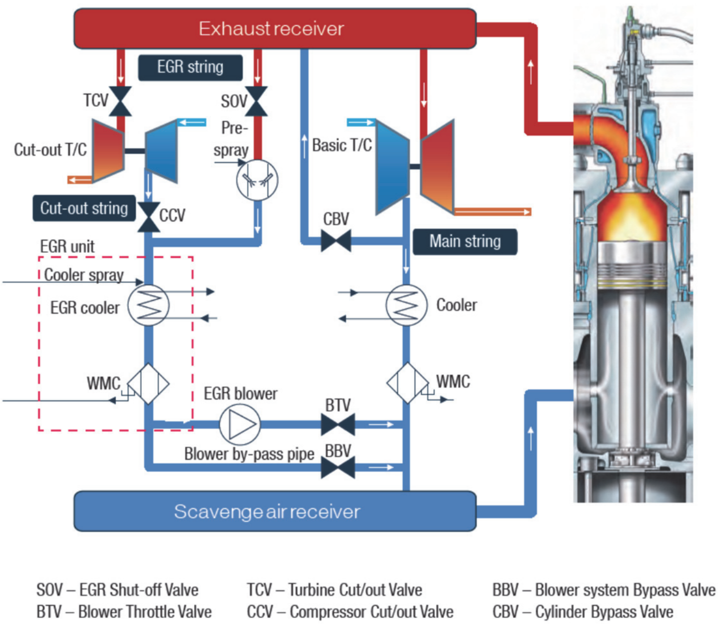

Fig. 3. EGR process diagram with turbocharger cut-out matching (MAN Energy 2018)

Control valve operation for engines of bore ≥80 cm is presented in Table 1. It means that only inside ECA areas the engine is switched on Tier 3 mode, on other areas may work on Tier 2 mode.

Two parameters are measured in exhaust gas receiver before the EGR system: NO_x and oxygen concentrations. Of course the load of engine and pressure in scavenge air receiver should be known as well.

Engine emissions are measured on the test bed according to the mode of work. The ISO 8178 gives various cycles for various types of engine. E3 cycle is applied for propeller-law-operated engine. The test cycle type E3 is presented in Table 2.

Table 1. Control valve operation for engines of bore ≥80 cm (used abbreviations explained in Fig. 3) (MAN Energy 2018)

<table>
<tr><th></th><th colspan="3">Tier 2 mode</th><th colspan="3">Tier 2 mode – TC cut-out</th><th colspan="3">Tier 3 mode</th></tr>
<tr><th>% of load</th><th>SOV BTV</th><th>CBV</th><th>TCV CCV BBV</th><th>SOV BTV</th><th>CBV</th><th>TCV CCV BBV</th><th>SOV BTV</th><th>CBV</th><th>TCV CCV BBV</th></tr>
<tr><td>100</td><td rowspan="5">closed</td><td rowspan="5">closed</td><td rowspan="5">open</td><td colspan="3">Not applicable</td><td rowspan="5">open</td><td>closed</td><td rowspan="5">closed</td></tr>
<tr><td>75</td><td rowspan="4">closed</td><td rowspan="4">closed</td><td rowspan="4">closed</td><td rowspan="3">partly open</td></tr>
<tr><td>65</td></tr>
<tr><td>50</td></tr>
<tr><td>25</td><td>closed</td></tr>
</table>

Table 2. Parameters of engine during NO_x test bed measurement (CIMAC 2012)

<table>
<tr><td rowspan="3">Test cycle type E3</td><td>Speed</td><td>100%</td><td>91%</td><td>80%</td><td>63%</td></tr>
<tr><td>Power</td><td>100%</td><td>75%</td><td>50%</td><td>25%</td></tr>
<tr><td>Weighting factor</td><td>0.2</td><td>0.5</td><td>0.15</td><td>0.15</td></tr>
</table>

It means that the NO_x emission is estimated (according to requirements presented in Fig. 1) only in four points on one of propeller-law-operated characteristics. The marine diesel engines work on different propeller-law-operated characteristics due to changing hull resistance during vessel operation. So addition of not-to-exceed (NTE) testing requirements is being debated. Probably it will be agreed that NTE limits with multiplier 1.5 would be applicable to NO_x emissions at any individual load point in the E3 (and E2) type cycle (CIMAC 2012). Important remark – engines are tested using distillate diesel fuels, in real life operation they work on residual oils (heavy fuels). The real emission of NO_x is not recognized in that case.

The SCR systems are dedicated for four-stroke medium speed engines due to higher than in two-stroke low speed engines exhaust gas temperatures. There are solutions of SCR systems for two-stroke engines as well (UK Maritime 2009, US Code 2009, IMO Resolution 2009, IMO Resolution 2015).

An essential parameter of proper process of SCR system is an exhaust gas temperature on the inlet to this system. The problem is the formation of sulfuric acid in the gas at low temperature which forms a sticky product ammonium bisulfate, which may accumulate in the SCR elements. The required minimum temperature is presented in Fig. 4.

On the other hand, the exhaust gas temperature (better in the inlet to SCR systems) must not be too high. The upper limit is up to about 500°C.

If temperature is increased the oxidation of ammonia is accelerated and the dose of urea should be increased. Additionally, the catalyst material starts to sinter at temperatures above 500-550°C. The exhaust gas temperatures should be within a certain temperature window 300-500°C.

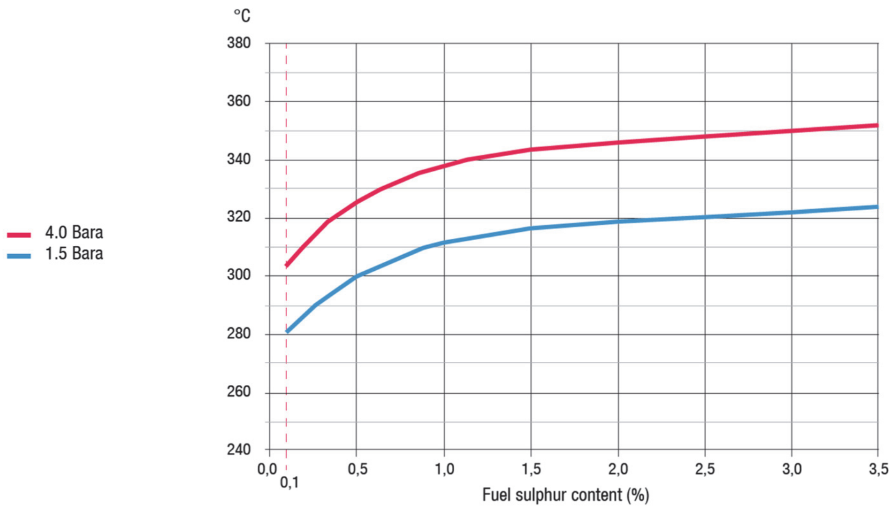

Fig. 4. Required temperatures for SCR related to sulfur content and exhaust gas pressure (in bar absolute pressure) (MAN Energy 2018)

Other methods are under research process to decrease the NO_x emission like ballast water injection into exhaust gas (to remove the NO_x) (Szkarowski et al. 2017a, Szkarowski et al. 2017b).

4. Reasons for change of vessel resistance and propeller characteristics

During vessel operation the size of ship total resistance depends on many reasons in general named sailing conditions. They can change according to outer conditions e.g. weather and sea conditions (state of sea, force and direction of currents and winds), technical state of hull (hull fouling due to corrosion, sea grows, hull deformation, paint layers damages), change of draft due to weight of cargo and ballast, sailing on shallow and narrow water etc. In stable conditions the vessel resistance is approximately proportional to vessel speed in square exponent but the power of engine is proportional to vessel speed in the third exponent. The extended marine engine work area is presented in Fig. 5. There is shown MAN engine contract parameters area (area inside lines L1-L2-L3-L4-L1) and point "O" as nominal parameters (power and speed) of engine. Because the diagram is executed in logarithmic scale propeller curves are shown as straight lines (here is presented: normal operation and heavy running operation, there is no line for light running operation) (MAN B&W 2010, MAN Energy 2018).

As a result the point of engine work should be inside the allowed area (inside engine work area), better inside the area of no restrictions (with possibility of continuous rating). Due to the possibility of propeller curve modification during vessel operation, the point of engine parameter shifts so it is one of the reasons of change the NO_x emission.

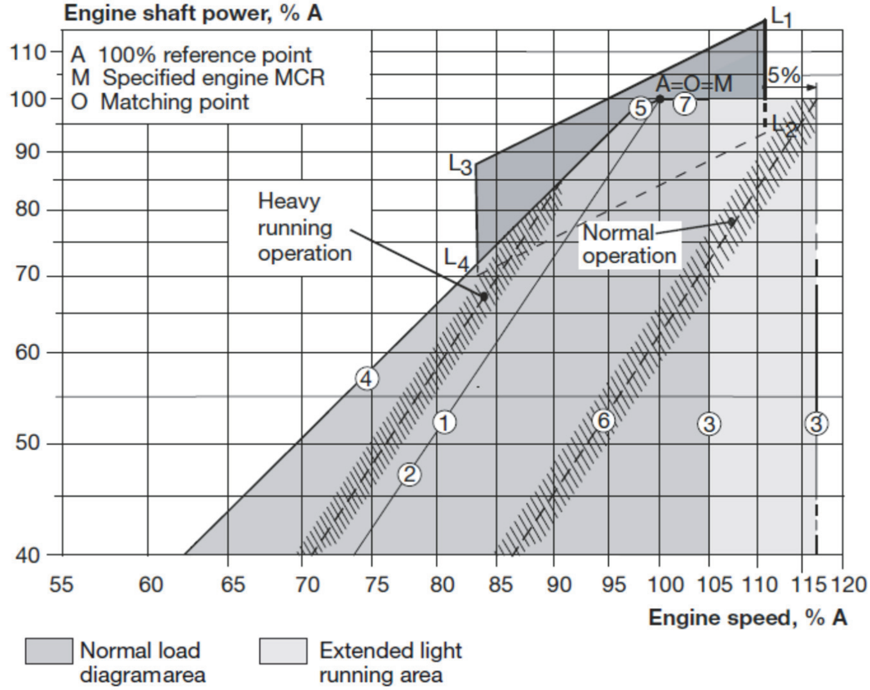

Fig. 5. Extended marine engine work area (MAN B&W 2010)
Line 1 – propeller curve through matching point "O" – layout curve for engine,
Line 2 – heavy propeller curve – fouled hull and heavy seas (extreme hull resistance),
Line 3 – speed limit,
Line 4 – extended speed limit (provided torsional vibration conditions permit),
Line 5 – mean effective pressure limit,
Line 6 – increased light running propeller curve (clean hull, calm weather);
possible lighter condition for ballast voyage,
Line 7 – power limit for continuous rating.

5. Problems of proper work controlling the systems of NO_x emission decreasing

All manufacturers of marine diesel engines have tried to solve the problems of proper work controlling the systems of NO_x emission decreasing. The Onboard Survey Methods should be prepared for the vessel crew by engine manufacturer. By reading or measuring certain performance engine parameters and comparing to limit values, the compliance of NO_x emission is verified. It is not known the real NO_x emission because it should be measured the actual exhaust gas mass flow and the NO_x content in exhaust gases. The parameters may be quickly evaluated due to the change of engine load, technical state of the engine, ambient air parameters (pressure, temperature, humidity), sea conditions etc. It is impossible to react quickly in transient states for proper adjustment of NO_x decreasing emission systems (Borkowski et al. 2011).

Certain cases may result of non-error situations where the system is not reducing NO_x (MAN Energy 2018):

- engine load change is faster than the guidance load change curve,
- rough sea conditions resulting in oscillating engine load,
- time during engaging and dis-engaging control valves,
- engine load and ambient conditions are outside the operating window for the emission control system as specified in the NO_x Technical File,
- other transient situations.

At low loads (below 15% of maximum continuous rating power) depending on type of the engine and sulfur content in fuel the urea injection (SCR system) will be suspended in order to prevent deposits in SCR system caused by insufficient exhaust gas temperatures (see Fig. 4). The other possibility is an increasing the exhaust gas temperature to the required level, part of the exhaust gas from the high pressure side if the turbine (turbocharger) is bypassed, controlled by an Exhaust Gas Bypass valve or EGR shut-off valve (SOV see Fig. 3), and directed to low pressure side. Using this method increases the specific fuel oil consumption (SFOC) (decreases the engine efficiency and increases the emission of carbon dioxide).

In case of system failures, the engine control system will issue an alarm code and text, allowing for the situation to be corrected. Such cases make many troubles for engineers because they have only few possibilities (like check: the valve positions, urea level in the tank, electric power supply) to remove the alarms and failures. The emission control systems are protected by manufacturers against the undesirable intervention of vessel crew.

6. Dosing of urea. Ammonia and hydrocarbons split

The SCR systems need during work the injection of urea or ammonia solutions. The consumption of reducing agent depends on the agent type, the engine load and the NO_x reduction rate. The urea or ammonia consumption may be calculated by the engine calculation program (CEAS for MAN engines). It is very important because the NO_x reduction rate will be too low due to too low dose, and on other hand the reduction NO_x rate may be proper but the urea or ammonia dose may be too big increasing the consumption (additional costs) and caused the ammonia slip (one of the green-house gases) to the atmosphere. The estimated specific consumption of urea and ammonia to reduce the NO_x from Tier 2 level to Tier 3 level is shown in Tab. 3.

Table 3. The estimated consumption of urea or ammonia solutions in SCR systems to reduce the NO_x emission from Tier 2 to Tier 3 (MAN Energy 2018)

Reducing agent	g/kWh	dm^3/MWh
Urea – 40% solution	17.9	16.1
Ammonia – 24,5% solution	16.6	18.4

The slip of ammonia from SCR system is dangerous to the exhaust gas boilers as well. The ammonia with sulfur originated from fuel can lead to deposits of ammonium bisulfate (ABS) on low temperature surfaces into the boiler. Furthermore, the deposits of ABS formed in the boiler are easily removed by standard cleaning methods of the boiler.

Engine operation on heavy fuel oils may cause of hydrocarbons (HC) split due to unburned hydrocarbons (UHC) directly during combustion process, next their absorption and desorption by the engine lubricating oils. Operation on heavy fuel oils gives the possibility of UHC formation as deposits on the cylinder walls, head and piston crown. Unburned hydrocarbons from within quench region in engines are expelled during the exhaust process. There are many problems (especially for the last 20-30 years) with the usage of heavy fuels in diesel engines due to:

- fuel stability,
- fuel compatibility,
- ignition quality (need heating for proper viscosity),
- contamination with waste products (e.g. used lubricating oils, hydrofluoric acid, organic chlorides, polypropylene, polystyrene, polyethylene, catalyst fines), etc.

Ship-owners or charterers always purchase the cheapest fuels.

7. Final remarks. How to improve the systems of NO_x emission decreasing?

The expectation is minimizing the threats of transport to the sea and environment. Is it possible to reach the Tier 3 limit emission (or better in the future) for the NO_x for all engines in the worldwide marine transport? The answer is difficult. There is a strong pressure for doing it. The new proposed emission limits are the challenge for engineers. They try to find out the remedy but we should remember the efficient marine transport is crucial for worldwide economy. The usage of SCR systems or/and EGR systems to fulfill the Tier 3 limit provides during operation to increasing the specific (and total) fuel consumption up to ten percent. The manufacturers tell that the difference is in a range from three to five percent. That may be true but this is difference between engine operation on mode Tier 2 and Tier 3. Taking account between engines built before 2000 year and now the difference is from five to ten percent. NO_x emission decreasing systems need additional electric energy. It generates costs for ship-owners and decreases the economy of marine transport.

The basic method for decreasing the NO_x emission (and total fuel consumption) is lowering the vessel speed and engine load. The fuel change on low-sulfur fuels on the ECA areas reduces mainly the sulfur oxides and particulate matters emission. Apart from isolated applications biofuels are not a real alternative for marine engines in long distance voyages. The idea of switching the vessel supply in electric energy from the port facilities during vessel stay in the ports only locally decreases the emission to the atmosphere. The Tier 3 limit is in effect only on the ECA areas. Methods for more efficient vessels are during searching. The expectancy is in minimizing the vessel hull resistance, increasing the total propulsion efficiency, finding out the methods of recovering the waste heat from engines for reaching the best energy efficiency operational index (EEOI index), etc.

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Abstract

The paper presents problems of limitation the nitrogen oxides emission from marine diesel engines. The emission of noxious substances from combustion of marine fuels is restricted in respect of the atmosphere protection, International Maritime Organization (IMO) regulations and others. The IMO requirements were determined by time of being in force. The first tier started in 2000 year, the second in 2011, the third is being valid from 2016 on USA waters and in some chosen port areas (from 2021 will be obligatory on Baltic Sea, North Sea and English Channel) and it is a necessity to comply those last requirements. In case of NO_x – between the first and second tier the emission was limited 20%, while the third step was limited 80% of the first one. This is a very great challenge, because in nowadays marine diesel engines and marine heavy and diesel oils generally applied, it would seem impossible comply those requirements. It was formed environmental controlled areas of NO_x emission (ECA) and they will extend. Governments of some countries (USA, Norway) were introduced on own territorial waters the requirements of NO_x and SO_x emission. In case of exceeding the limits (or a lack of the proper certificates) it was imposed an ecological charge (a form of tax) or the interdict of entrance on regulated water zones. In the paper it was given an attention to the new challenges for engine producers and ship-owners of fulfilling tier 3 standards or search new substitute solutions. The applying solutions for nitrogen oxides emission limitations cause the decreasing of engine efficiency and increasing the fuel consumption (and carbon dioxide emission) up to ten percent. Due to regulations of marine environment protection they generate additional investment and operation cost for ship-owners and charterers.

Keywords:
nitrogen oxides, marine engine, emission to the atmosphere, Tier 3 limit

Problemy zmniejszenia emisji tlenków azotu z okrętowych silników wysokoprężnych w celu spełnienia limitu emisji 3

Streszczenie

W artykule przedstawiono problemy ograniczania emisji tlenków azotu z okrętowych silników wysokoprężnych. W celu ochrony atmosfery przed emisją szkodliwych substancji z procesu spalania paliw okrętowych wprowadzono regulacje Międzynarodowej Organizacji Morskiej (IMO) i inne. Wymagania IMO określają czas wejścia w życie (obowiązywania). Pierwsze ograniczenie emisji tlenków azotu (Tier 1) obowiązuje od 2000 roku, drugie (Tier 2) od 2011, natomiast trzecie (Tier 3) obowiązuje od 2016 roku na wodach amerykańskich i wybranych obszarach portowych (od 2021 roku będzie obowiązywać na Morzu Bałtyckim i Północnym oraz Kanale La Manche) oraz zachodzi konieczność spełnienia tych wymagań. Dla tlenków azotu (NO_x) – pomiędzy pierwszym a drugim limitem jest różnica 20%, podczas gdy trzeci limit jest o 80% mniejszy od pierwszego. Jest to wielkie wyzwanie, ponieważ w okrętowych silnikach wysokoprężnych stosuje się paliwa ciężkie i oleje napędowe, wydaje się niemożliwe spełnienie tych wymagań. Utworzono obszary kontroli emisji (ECA) tlenków azotu i te obszary będą się powiększać. Rządy niektórych krajów (USA, Norwegia) wprowadziły własne wymagania na ich wodach terytorialnych odnośnie emisji tlenków azotu i tlenków siarki. W artykule zwrócono uwagę na nowe wyzwania dla producentów silników i armatorów statków w celu spełnienia standardów emisji w limicie Tier 3 lub poszukiwania innych równoważnych rozwiązań. Stosowane rozwiązania ograniczenia emisji tlenków azotu zmniejszają sprawność silników oraz zwiększają zużycie paliwa (i emisji dwutlenku węgla) nawet o dziesięć procent. Z powodu wprowadzenia regulacji chroniących środowisko morskie, generują one dodatkowe koszty inwestycyjne i eksploatacyjne dla armatorów i czarterujących.

Słowa kluczowe:
tlenki azotu, silnik wysokoprężny, emisja do atmosfery, poziom emisji 3

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Statistical Evaluation of Variation of the River Bug Water Chemical Contamination

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1. Introduction and work's aim

Surface water contamination results from natural processes (atmospheric precipitation, rock weathering, erosion) and anthropogenic ones (industrial processes and agricultural activities) (Al-Shami et al. 2011, Brankov et al. 2012, Getirana et al. 2011, Kowalik et al. 2015, Mouri 2012, Sultan 2011, Piekutin 2011, Policht-Latawiec et al. 2014). In agricultural areas, water contamination with biogenic compounds has a marked influence on the condition of biological and physio-chemical elements (Kanclerz et al. 2008). Surface water contamination may be either point source pollution or nonpoint source pollution (Gałczyńska et al. 2011, Kowalik et al. 2015, Policht-Latawiec et al. 2013). In 2014, there were operating 88 entities, including 75 municipal and 13 industrial ones, disposing of their wastewater into the environment, in the area of the River Bug catchment. Nonpoint source pollution in particular includes surface runoff from agricultural areas, runoff of rainfall from road, yard and other paved surfaces (Raport… 2015). In catchments, whose total area includes a large share of agriculturally suitable land, the surface water quality is predominantly affected by nonpoint source pollutants (Bogdał & Ostrowski 2007, Kiryluk & Rauba 2009). They pose a threat to the functioning of water ecosystems, and influence water quality, which in turn affects the attractiveness of rivers and adjoining areas (Jaskuła et al. 2015, Pytka et al. 2013). Water quality status is of special importance as far as the Rive Bug is concerned as the river, due to its marked naturalness, is called the last wild river in Europe (Kuśmierczyk 1999). The results of water monitoring provide much data which is difficult to analyse and interpret (Przybyła et al. 2015). To this end, statistical analysis methods are used, mainly descriptive statistics procedures with visualisation in the form of box plots, non-parametric tests and multidimensional analyses (Brahman et al. 2013, Grzywna et al. 2017, Kowalik et al. 2015). It was attempted in the present work to conduct a complex statistical analysis of variation in chemical parameters of the River Bug as affected by locality and season (month).

2. Materials and methods

The international catchment of the River Bug covers an area of 39.4 th km^2 and is part of the Baltic Sea basin. Almost half (49.2%) of the catchment area is located in Poland, 23.4% in Belarus and 27.4% in Ukraine. Total nitrogen and phosphorus loads from the Ukrainian stretch of the Bug as well as the Belarusian rivers Muchawca and Leśna account for around 50% of the cross-border pollution recorded in the Polish Baltic catchment area. Of the overall 10.5 th tonnes per year of cross-border nitrogen and phosphorus pollution entering the River Bug, 72% (7.6 th tonnes) originated in Ukraine, and 28% (2.9 th tonnes) in Belarus (Raport …, 2015). The Polish part of the Bug catchment is located in the following voivodeships: Lubelskie, Podlaskie and Mazowieckie. The River Bug is 772 km long. About 14% of the Bug catchment area is protected by the international, national or regional law. In the catchment area, there is located the Polish-Ukrainian International West Polesie Biosphere Reserve as well as 18 areas of the European Ecological network Nature 2000. The area is primarily devoted to agriculture. In the present work, contamination analysis of the River Bug water in Lubelskie Voivodeship was undertaken. The Bug water quality examination is performed by the Voivodeship Inspectorate for Environmental Protection in Lublin (WIOŚ). Hydrothermal conditions are presented in figure 1.

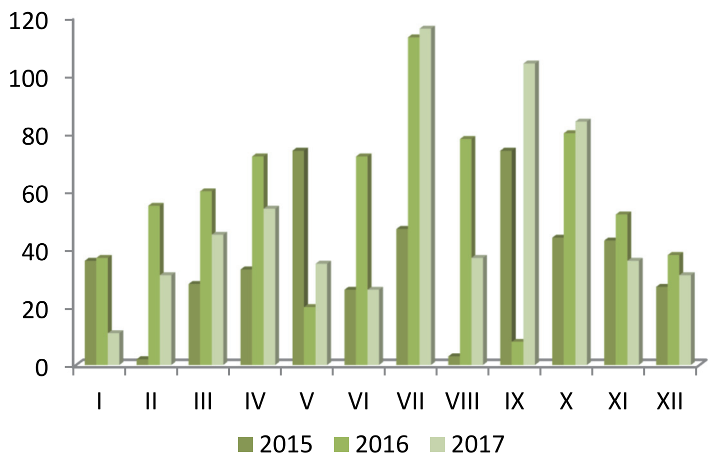

Fig. 1. Precipitation at the Włodawa station in 2015-2017

Analysis was based on the data of monitoring carried out in 2015-2017 at eight measurement points: Kryłów, Zosin, Horodło, Dorohusk, Włodawa, Kuzawka, Kukuryki and Krzyszew (Fig. 2) in February, April, June, August, October and December. The distances between the measurement points were 40, 10, 39, 59, 19, 43, 9.6 km, respectively. Throughout these months, readings were taken at all the localities during three years. As a result, data analysis was conducted for each locality based on eighteen measurements.

Fig. 2. Location of measurement points

The following chemical parameters were analysed: X_1 − dissolved oxygen (mg O_2/l), X_2 – BOD (mg O_2/l), X_3 – sulphates (mg SO_4/l), X_4 – chlorides (mg Cl/l), X_5 – total phosphorus (mgP/l). X_6 – ammonium nitrogen (mg N-NH_4/l), X_7 – nitrate nitrogen (mgN-NO_3/l) and X_8 – nitrite nitrogen (mg N-NO_2/l). Experimental factors were localities and months when measurements were taken. The first stage of statistical analysis involved checking whether the localities and months had an influence on variation in chemical parameters. To that end, a two-way analysis of variance and the Kruskal-Walis test were applied.

Two-way analysis of variance was applied for normally distributed variables (X_1-X_5). It followed the linear model for a completely randomised design:

$$y_{ijl} = m + a_i + b_j + ab_{ij} + e_{ijl} \tag{1}$$

where:

y_{ijl} – value of the examined characteristic,
m − population mean,

a_i – effect of the i-th level of factor A (localities),
b_j – effect of the j-th level of factor B (month of measurement),
ab_{ij} – effect of interaction A x B, e_{ijl} – random error.
Means were separated using Tukey test at $p \leq 0.05$.

For traits X_6-X_8, which were not normally distributed, transformations were used (Bliss, log and arc sin transformation) but they were not effective so Kruskal-Wallis test was applied. Differences between groups were checked by means of multiple comparisons test.

Principal component analysis and cluster analysis were used in order to assess the complex variation in localities in individual months in terms of all the analysed characteristics (chemical parameters). Principal component analysis is a technique of dimension reduction. It transforms original variables into new, non-correlated variables called principal components. They explain to the greatest degree the total variance of a sample of *p* primary variables $x_1, \ldots, x_p$, that is the value:

$$\sum_{j=1}^{p} s_j^2 = tr(S) , \qquad (2)$$

where:
S – sample covariance matrix,
tr – trace of the matrix,
s_j^2 – variance of the variable x_j, $j = 1, \ldots, p$ (Krzyśko 2009).

The first principal component reduces the greatest amount of this variation, the second one reduces the second greatest part of the variation which has not been reduced by the first component, etc.

Analysed and interpreted were the components whose eigenvalue, according to the Kaiser's criterion, was higher than 1 (Kaiser 1958).

Cluster analysis was performed on the basis of the principal components. The analysis is a tool used for grouping *n* objects described by means of a vector of *p* characteristics. It involves grouping of objects which are similar in terms of many characteristics. The groups are determined by means of measures of distance, the Euclidean distance being used in the analysis reported here:

$$d(x_r, x_s) = \sqrt{\sum_{i=1}^{p} (x_{ri} - x_{si})^2} , \qquad (3)$$

where:
x_r and x_s – p-dimensional vectors of observation of r-th and s-th object ($r, s = 1, 2, \ldots, n$) (Marek 1989; Krzyśko 2009).

Ward method, in which sums of squares of deviations within clusters are kept to a minimum, was used in order to estimate the distance between clusters. Mojena rule was applied to determine the cut-off point of the dendrogram (cluster similarity level). The cut-off point is the bond distance for which the following inequality is true:

$$d_{i+1} > \bar{d} + ks_d; \tag{4}$$

where:
$\bar{d}$ and s_d – respectively, mean and standard deviation of d_i,
k – a value within the range 2.75 to 3.50 (Mojena 1977). The value k was selected to be 1.25 as recommended by Milligan and Cooper (1985).
All the calculation were performed in STATISTICA 12.0.

3. Results and discussion

Variance analysis demonstrated significant differences between dissolved oxygen contents in the water of the River Bug stretching from Zosin to Krzyszew. The highest average value of this parameter was observed in Włodawa (10.91 mg O_2/l), Kuzawka (10.77 mg O_2/l) and Dorohusk (10.16 mg O_2/l), and it was significantly higher than in the stretch between Zosin and Kryłów. The amount of dissolved oxygen in Krzyszewo and Kukuryki did not differ significantly from values at the remaining measurement points (tab. 1). Statistical analysis confirmed there were differences in dissolved oxygen content between seasons of the year. Regardless of the measurement point, in the winter months (December and February) dissolved oxygen content was higher than in the summer months (August and June) (Tab. 2). Oxygen content and temperature are the parameters which condition life in the water environment. Also, they are interrelated: oxygen solubility in water is temperature-related and it declines as temperature increases (Kowalik et al. 2015).

Total phosphorus content in water changed along the river course, it being the highest from Kiryłów to Zosin and from Kururyki to Krzyszewo. Phosphorus content in the analysed three-year period was the lowest from Dorohusk to Kuzawka. Phosphorus content in water was significantly affected by season of the year, it being the highest in October and the lowest in April. The concentration of this element in December did not differ from the content in October and February. Statistical analysis demonstrated a significant interaction between localities and month of measurement, which means that phosphorus content for localities dvaried in individual months (Fig. 3). The average phosphorus content in Kryłów, Horodło and Zosin was statistically the same and ranged from 0.207 to 0.363 mg P/l. In Dorohusk, Włodawa and Kuzawka, phosphorus content, averaged across the three study years, was the highest in October and the lowest in April. The respective values were 0.303, 0.347, and 0.327 mg/l in October, and 0.220, 0.110, and 0,113mg/l in April. Phosphorus content in water between Kukuryki to Krzyszew was the lowest in April as well (0.173 and 0.143 mg/l, respectively). Changes in river water chemical composition are caused by surface run-offs from fields fertilised with organic manures and mineral fertilisers which contain high amounts of substances applied seasonally. A higher water content of phosphorus in autumn was reported by Igras & Jadczyszyn (2011) whereas Jaskuła et al. (2015) claimed that a decline in the concentration of phosphorus compounds from January to April may be due to dilution of wastewater caused by more intense flows. High amounts of phosphorus enter the water environment with sewage from households and farm buildings (Dąbkowski & Pawłat-Zawrzykraj 2003, Kiryluk & Ruba 2011, Krasowska 2017).

Sulphate content was related to localities and months of measurement. No significant interaction between the aforementioned factors was observed, which is indicative of the fact that at all the measurement points, the distribution of sulphate content in months was similar. The highest and comparable concentration of sulphates was recorded in Kryłów (89.02 mg SO_4/l), Zosin (81.34 mg SO_4/l) and Horodło (76.67 mg SO_4/l). Sulphates were significantly lower in water from Dorohusk (68.11 mg SO_4/l) through Włodawa (70.39 mg SO_4/l) to Kuzawka (66.00 mg SO_4/l), it being the lowest in Kukuryki (54.44 mg SO_4/l) and Krzyszew (52.89 mg SO_4/l) (tab. 1). The lowest sulphate content was recorded in August (58.41 mg SO_4/l), and the highest in December (86.62 mg SO_4/l). Also Krasowska (2017) recorded the highest concentration of sulphates in December, which according to the author, was due to a low water level. In the period February-June, sulphate content remained at a similar level (Tab. 2).

Chloride content was significantly affected by localities and months. No statistically significant location x month interaction was confirmed. The highest chloride content was determined in the river stretch from Kryłów to Zosin, it being the lowest in Kuzawka and Krzyszew. The amount of this substance in Kukuryki was similar to the quantity determined in Włodawa.

Analysis of variance revealed that, in the three-year study period, BOD values at the measurement points were similar, them being affected by the study months only. An interaction between months and measurement points for this characteristic was insignificant. The lowest BOD value was found in October (3.14 mg O_2/l) and December (3.54 mg O_2/l), it being the highest in June (4,21 mg O_2/l) and August (4,35 mg O_2/l). BOD values in February and April differed insignificantly from values determined for the remaining months.

Table 1. Average dissolved oxygen content, total phosphorus content, sulphates, chlorides and BOD by locality

Locality	Dissolved oxygen	Total phosphorus	Sulphates	Chlorides	BOD
Dorohusk	10.16^{a}	0.24^{b}	68.11^{b}	36.94^{cd}	3.89^{a}
Horodło	9.70^{b}	0.28^{a}	76.67^{ab}	39.82^{bc}	3.94^{a}
Kryłów	9.40^{b}	0.31^{a}	89.02^{a}	46.39^{a}	3.78^{a}
Krzyszew	9.82^{ab}	0.26^{ab}	52.89^{c}	31.61^{de}	3.83^{a}
Kukuryki	9.88^{ab}	0.30^{a}	54.44^{c}	34.13^{de}	4.05^{a}
Kuzawka	10.77^{a}	0.22^{b}	66.00^{bc}	31.50^{e}	3.62^{a}
Włodawa	10.91^{a}	0.24^{b}	70.39^{b}	32.94^{de}	3.42^{a}
Zosin	9.41^{b}	0.28a	81.34^{a}	43.14^{ab}	3.76^{a}

Means followed by the same letters (in columns) differ insignificantly at $p \leq 0.05$.

Table 2. Average dissolved oxygen content, total phosphorus content, sulphates, chlorides and BOD by month

Month	Dissolved oxygen	Total phosphorus	Sulphates	Chlorides	BOD
February	10.64^{ab}	0.25^{b}	72.67^{b}	34.15^{b}	3.81^{ab}
April	9.87^{bc}	0.18^{c}	71.12^{b}	31.85^{b}	3.67^{ab}
June	9.39^{cd}	0.29^{ab}	64.00^{bc}	32.68^{b}	4.21^{a}
August	8.71^{d}	0.26^{b}	58.41^{bc}	40.67^{a}	4.35^{a}
October	9.79^{bcd}	0.33^{a}	66.32^{bc}	43.63^{a}	3.14^{b}
December	11.64^{a}	0.29^{ab}	86.62^{a}	39.40^{a}	3.54^{b}

Means followed by the same letters (in columns) differ insignificantly at $p \leq 0.05$.

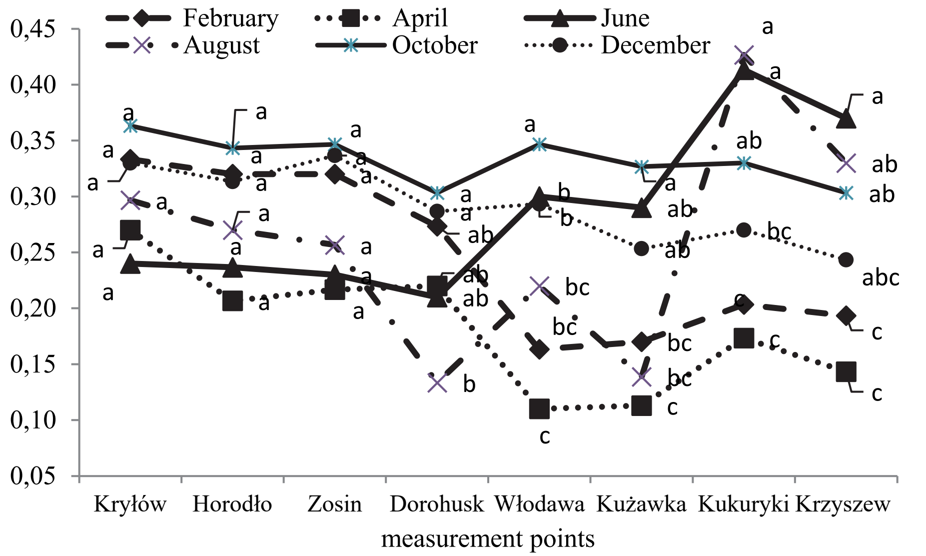

Fig. 3. Total phosphorus content by locality and month
Means accompanied by the same letters (between measurement points) differ insignificantly at $p \leq 0.05$

Ammonium nitrogen content differed at localities, it being the highest in Kukuryki (0.65 mg $N\text{-}NH_4$/l) and Krzyszew (0.56 mg $N\text{-}NH_4$/l). The amount of $N\text{-}NO_4$ in Kukuryki differed significantly from values determined at the remaining measurement points. Moreover, the concentration of this parameter in Krzyszew differed significantly from the content in Dorohusk, Włodawa and Kuzawka. Ammonium nitrogen content was also affected by months, it being higher in December and February than in the remaining months (Fig. 4). In months with higher temperatures, the concentration of ammonium ions is lower due to nitrification and utilisation of ammonium nitrogen by plants (Ligocka 2018). In contrast, in the period when temperatures are lower the concentration of ammonium ions increases (Gałczyńska et al. 2009).

The concentration of nitrate nitrogen in Kryłów, Zosin and Horodło was the highest, as indicated by the maximum values and medians. The highest variation in this characteristic was recorded in Dorohusk, Włodawa and Kuzawka. Nitrate nitrogen content was the lowest and the least variable in August, and the highest in February and December (Fig. 5).

Nitrite nitrogen content in Włodawa, Kuzawka and Kukuryki was lower than in Zosin and Horodło. The Kruskal-Walis test revealed that this parameter was affected by months, whereas the test of multiple comparisons demonstrated that nitrite nitrogen content in October differed from values for the remaining months. The concentration of this substance had the highest median and the greatest variation (Fig. 6). According to Sullivan and Drever (2001) as well as Clark et al. (2004), changes in the concentration of biogenes, nitrates in particular, are associated with the season. A decline in the substances in the spring-summer period may be due to increased decomposition of organic matter.

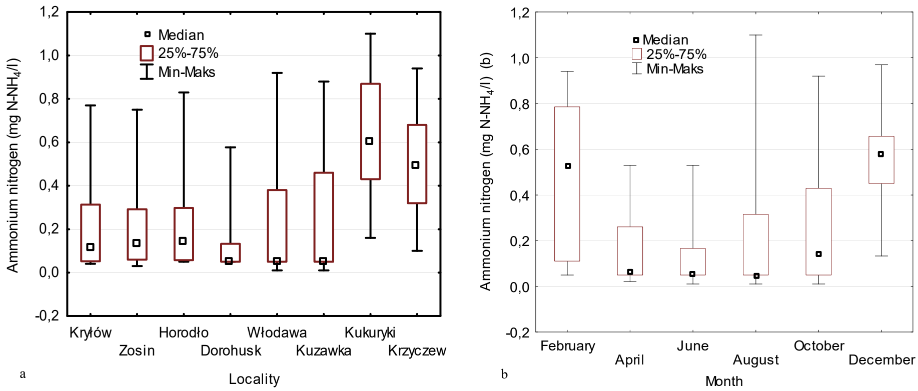

Fig. 4. Total ammonium nitrogen by locality (a) and month (b)

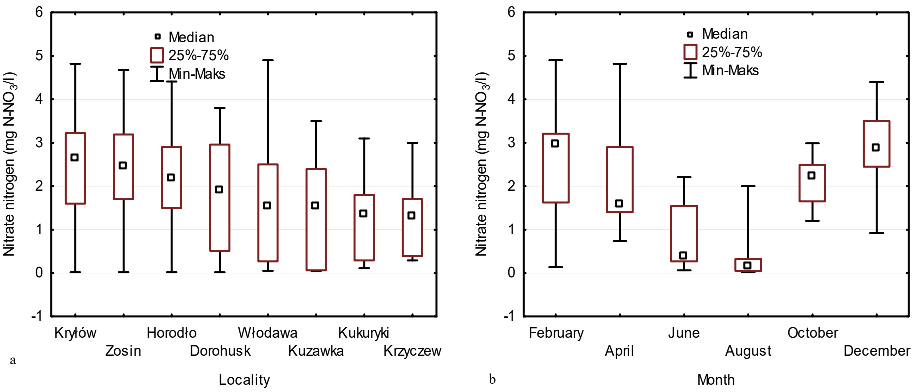

Fig. 5. Total nitrate nitrogen by locality (a) and month (b)

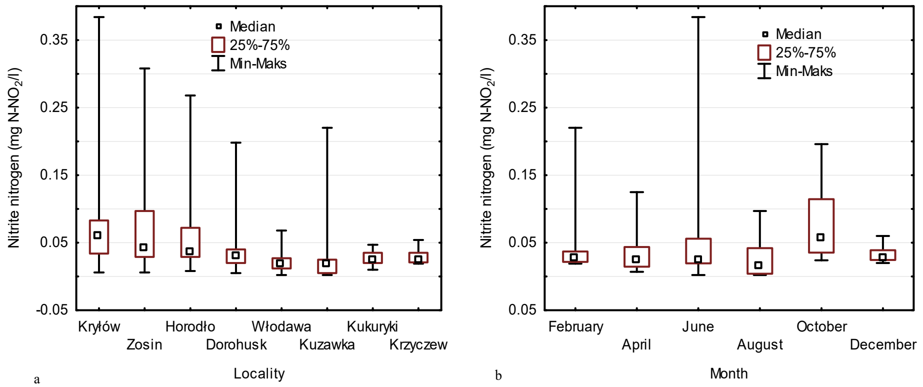

Fig. 6. Total nitrite nitrogen by locality (a) and month (b)

Table 3. Values of Kruskal-Wallis test (H) checking significance of differences between localities and months

	Ammonium nitrogen	Nitrate nitrogen	Nitrite nitrogen
Locality			
Value of the test H	48.61(p = 0.000)	14.96 (p = 0.031)	39.95 (p = 0.000)
Month			
Value of the test H	42.37 (p = 0.000)	78.54 (p = 0.000)	24.68 (p = 0.000)

The applied methods made it possible to compare both localities and months, viewed separately, in terms of the concentration of many chemical parameters. Assessment of variation of objects and their simultaneous grouping according to many characteristics may be achieved by means of multidimensional analyses (Mądry 2007). Multi-trait variation between localities in individual months was assessed using principal component analysis. In February, three principal components accounted for over 91% of variation between localities, the first components explaining over 50% of this variation (Tab. 4). The following characteristics were the most strongly associated with PC1: total phosphorus content, ammonium nitrogen content, sulphates, BOD and chlorides. Mutual multidimensional relationships showed that at localities where phosphorus content was higher, higher concentrations of sulphates, chlorides and BOD where determined in addition to a lower ammonium nitrogen content. Negative associations between ammonium nitrogen content and phosphorus content were reported by Ligocka (2018).

Table. 4. Eigenvalues, share of principal components in the overall variation and correlation coefficients between the components and water chemical parameters

Item	February			April	
	PC1	PC2	PC3	PC1	PC2
X_1 – Dissolved oxygen	0.537	-0.801	-0.096	0.769	0.405
X_2 – BOD	0.827	0.102	-0.442	-0.474	-0.618
X_3 – Sulphates	0.872	0.176	0.424	-0.753	0.504
X_4 – Chlorides	0.785	0.564	0.087	-0.957	0.183
X_5 – Ammonium nitrogen	-0.911	0.348	-0.044	-0.025	-0.859
X_6 – Nitrate nitrogen	0.257	-0.751	0.491	-0.959	0.124
X_7 – Nitrite nitrogen	-0.061	0.331	0.821	-0.997	0.062
X_8 – Total phosphorus	0.932	0.300	-0.147	-0.932	-0.118
Eigenvalue	4.115	1.885	1.330	5.08	1.60
Cumulative variance (%)	51.45	75.01	91.64	63.5	83.56
	June		August		
	PC1	PC2	PC1	PC2	PC3
X_1 – Dissolved oxygen	0.665	0.693	0.905	0.257	0.113
X_2 – BOD	0.978	0.055	-0.648	-0.040	0.734
X_3 – Sulphates	-0.906	0.277	0.924	-0.345	0.144
X_4 – Chlorides	-0.943	-0.142	0.433	-0.749	0.491
X_5 – Ammonium nitrogen	0.542	-0.830	-0.806	-0.351	-0.302
X_6 – Nitrate nitrogen	-0.975	-0.207	0.699	-0.648	-0.261
X_7 – Nitrite nitrogen	-0.955	-0.217	-0.084	-0.961	-0.207
X_8 – Total phosphorus	0.871	-0.410	-0.646	-0.733	0.078
Eigenvalue	6.02	1.52	3.84	2.75	1.02
Cumulative variance (%)	75.28	94.40	48.04	82.44	95.22
	October			December	
	PC1	PC2	PC3	PC1	PC2
X_1 – Dissolved oxygen	0.821	0.496	0.141	0.816	-0.546
X_2 – BOD	-0.688	-0.599	-0.374	-0.869	0.394
X_3 – Sulphates	-0.956	0.203	-0.071	-0.886	-0.425
X_4 – Chlorides	-0.694	-0.501	0.515	-0.991	0.035
X_5 – Ammonium nitrogen	0.585	-0.723	-0.316	0.812	0.324
X_6 – Nitrate nitrogen	-0.930	0.269	-0.061	-0.830	-0.452
X_7 – Nitrite nitrogen	0.359	-0.774	-0.070	-0.951	0.228
X_8 – Total phosphorus	0.073	-0.303	0.949	-0.923	-0.025
Eigenvalue	3.88	2.18	1.44	6.20	1.02
Cumulative variance (%)	48.57	75.85	93.83	78.64	91.11

The second principal component was the most strongly associated with dissolved oxygen content and nitrate nitrogen. At localities where dissolved oxygen content was higher, there was more nitrate nitrogen in water. The third principal component was most strongly correlated with nitrite nitrogen. In April, variation between localities was to the greatest extent affected by nitrogen content (nitrite nitrogen and nitrate nitrogen associated with PC1, and ammonium nitrogen associated with PC2), phosphorus content and chlorides. In June, the first two principal components accounted for over 90% of variation between localities, the parameters with the greatest influence being BOD, nitrate and nitrite nitrogen contents, chlorides, sulphates and phosphorus content. In August, multi-variable differences between river stretches were associated with dissolved oxygen content, nitrite and ammonium nitrogen contents as well as total phosphorus content. The characteristics which affected the multi-trait variation between the measurement points in October included: nitrate nitrogen, sulphates and dissolved oxygen content, all of them being associated with the first principal component which accounted for 48.57% of variation. The second principal component carried information on chlorides whereas the third component was associated with phosphates. PCA demonstrated that in December variation between localities was affected by most of the parameters associated with the first principal component accounting for 78.64% of variation, in particular nitrite nitrogen, total phosphorus and chlorides. Similar associations resulting from principal component analysis were reported by Przybyła et al. (2015) who demonstrated that for river waters the following parameters were positively correlated with the first principal component: dissolved oxygen content, calcium content, magnesium content and water hardiness whereas chlorides, phosphates and conductivity were associated with the second component. Similarly to research by Krasowska (2017), PCA made it possible to analyse season-related variation in the concentration of chemical substances in rivers.

Cluster analysis conducted based on principal components enabled classification of measurement points into two or three groups characterised by different chemical parameters according to month in which measurements were taken. Three groups were formed in August only. The first group was made up of Horodło, Kryłów and Zosin, the second one included Krzyszew and Kukuryki whereas the third one consisted of Włodawa, Kuzawka and Dorohusk. In the remaining months, two clusters were formed. The first cluster of localities with similar chemical parameters was formed by Krzyszew, Kukuryki, Włodawa as well as Kuzawka, and the second one by Zosin, Horodło, Kryłów and Dorohusk (Fig. 7).

Table 5. Average values of characteristics for groups of localities formed based on cluster analysis

Group	Dissolved oxygen	BOD	Sulphates	Chlorides	Ammonium nitrogen	Nitrate nitrogen	Nitrite nitrogen	Total phosphorus
February								
1	10.40	3.24	64.92	29.83	0.69	2.49	0.04	0.18
2	10.88	4.38	81.02	38.48	0.24	2.58	0.04	0.31
April								
1	10.27	3.58	63.50	27.08	0.19	1.28	0.02	0.13
2	9.49	3.77	78.76	36.62	0.13	2.95	0.06	0.23
June								
1	10.39	5.36	54.33	28.33	0.16	0.27	0.02	0.34
2	8.39	3.06	73.68	37.03	0.07	1.28	0.12	0.23
August								
1	9.22	4.28	76.29	45.11	0.15	1.03	0.04	0.26
2	7.78	4.43	42.17	37.50	0.60	0.23	0.04	0.34
3	9.17	4.34	57.49	37.63	0.13	0.11	0.01	0.20
October								
1	10.23	3.57	69.28	34.10	0.64	2.26	0.05	0.23
2	11.05	4.06	76.66	34.21	0.28	2.81	0.03	0.27
December								
1	12.08	3.09	76.75	34.75	0.66	2.58	0.02	0.27
2	11.20	3.98	96.50	44.06	0.43	3.28	0.04	0.32
3	9.22	4.28	76.29	45.11	0.15	1.03	0.04	0.26

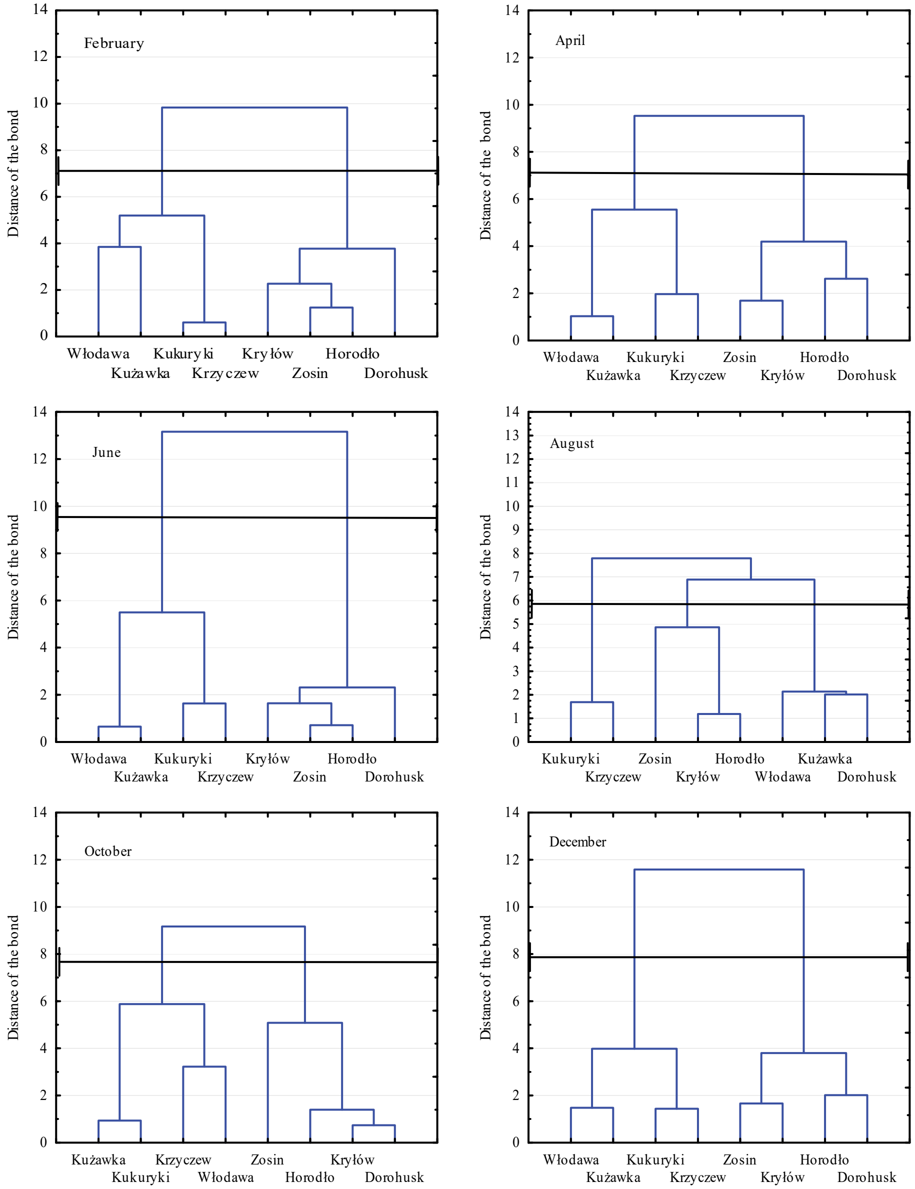

Fig. 7. Dendrogram of division of measurement points

The average ammonium nitrogen content was higher in localities forming the first cluster (ranging from 0.19 to 0.69 mg/l depending on the month). Moreover, at these measurement points, there were recorded higher dissolved oxygen contents in April (10.27 mg/l), June (10.39 mg/l) and December (12.08 mg/l), as well as phosphorus in June (0.34 mg/l). In August, the lowest average sulphate content (42.17 mg/l) and dissolved oxygen content (7.78 mg/l) were determined in Krzyszew and Kukuryki (group 2) in addition to the highest ammonium nitrogen content (0.60 mg/l), phosphorus content (0.34 mg/l) and BOD (4.43). The average dissolved oxygen content (9.22 mg/l), sulphates (76.29 mg/l) and nitrate nitrogen content (1.03 mg/l) were the highest in Horodło, Kryłów and Zosin (group 1). Localities which formed group 3 (Włodawa, Kuzawka and Dorohusk) had a relatively high average dissolved oxygen content (9.17 mg/l), and the lowest amount of nitrite nitrogen (0.01 mg/l) and total phosphorus (90.20 mg/l) (Tab. 5).

4. Conclusions

The concentration of chemical substances and compounds in the River Bug differed at individual measurement points (localities) and in study months.

Phosphorus content, sulphates and chlorides declined along the course of the river. BOD did not differ at individual localities. Dissolved oxygen content was the highest in the stretch from Dorohusk to Włodawa. Ammonium nitrogen content was the highest in Kukuryki and Kuzawka whereas nitrate and nitrite nitrogen contents were the highest from Zosin to Horodło.

In winter months, there was an increase in the concentration of ammonium ions, dissolved oxygen content, sulphates and chlorides. In the summer, BOD and phosphorus content were on the increase whereas sulphates and nitrate nitrogen content declined.

Principal component analysis demonstrated that differences in the chemical sta tus of the River Bug water between the measurement points resulted mainly from the concentration of nitrogen compounds, total phosphorus content and chlorides.

Cluster analysis made it possible to divide the analysed stretch of the River Bug into two parts with different chemical status in February, April, June, October and December. The first part included the following measurement points: Krzyszew, Kukuryki, Włodawa and Kuzawka, all of which had higher average concentrations of ammonium nitrogen, dissolved oxygen and total phosphorus. The second part, consisting of Kryłów, Zosin and Horodło, was characterised by increased average concentrations of BOD, sulphates and chlorides.

In August, the examined river stretch was divided into three clusters. The first cluster was made up of Horodło, Kryłów and Zosin which had the highest dissolved oxygen content, sulphates and nitrate nitrogen. The second cluster, characterised by the highest average dissolved oxygen content and sulphates, consisted of Krzyszew and Kukuryki whereas the third cluster (Włodawa, Kuzawka and Dorohusk) included localities with the lowest amount of nitrite nitrogen and total phosphorus.

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Abstract

The work presents analysis of chemical condition of the water of the River Bug stretch extending from Kiryłowo to Krzyszew. The analysis was preformed based on data of monitoring of surface water quality available on the website of Voivodeship Inspectorate of Environmental Protection in Lublin (WIOŚ) spanning the years 2015-2017. Eight measurement points and the following months were considered: February, April, June, August, October and December. Analysis of variance and Kruskal-Wallis test were used to analyse the effect of localities and months on selected chemical indicators. The concentrations of nearly all the parameters (excluding BOD) were found to be influenced by the localities. Phosphorus content, sulphates and chlorides increased along the course of the river. Also, the analysis revealed that the concentration of ammonium ions, dissolved oxygen, sulphates and chlorides increased in winter. Multidimensional analysis demonstrated that differences in chemical conditions between the localities were predominantly due to nitrogen compound content, total phosphorus content and chlorides. Cluster analysis showed that in nearly all the months (excluding August) the tested stretch of the River Bug could be divided into two parts with different chemical composition parameters. The first part, characterised by higher average values of ammonium nitrogen content, dissolved oxygen content and total phosphorus content, included the following measurement points: Krzyszew, Kukuryki, Włodawa and Kuzawka. The second part was formed by the following localities: Kryłów, Zosin and Horodło, all with higher average BOD values, sulphates and chlorides.

Keywords:
the River Bug, chemical contaminants, principal component analysis, cluster analysis, analysis of variance.

Statystyczna ocena zmienności zanieczyszczenia chemicznego wód rzeki Bug

Streszczenie

W pracy przedstawiano analizę chemicznego stanu wód rzeki Bug na odcinku od Kryłowa do Krzyszewa. Analizy tej dokonano na podstawie danych pochodzących z monitoringu jakości wód powierzchniowych zamieszczonych na stronie Wojewódzkiego Inspektoratu Ochrony Środowiska w Lublinie (WIOŚ) z lat 2015-2017. Pod uwagę wzięto dane z lutego, kwietnia, czerwca, sierpnia, października i grudnia z 8 punktów pomiarowych. Przy pomocy analizy wariancji oraz testu Kruskala-Wallisa przeanalizowano wpływ miejscowości oraz miesięcy na zawartość wybranych wskaźników chemicznych. Stwierdzono, że zawartość prawie wszystkich parametrów (poza BZT5) różnicowana była przez miejscowości. Wraz z biegiem rzeki zmniejszała się zawartość fosforu, siarczanów i chlorków. Analiza wykazała ponadto, że zimą rosło stężenie jonów amonowych, zawartość tlenu rozpuszczonego, siarczanów i chlorków. Wielowymiarowa analiza natomiast dowiodła, że różnice stanu chemicznego pomiędzy miejscowościami związane były głównie z zawartością związków azotu, fosforu ogólnego oraz chlorków. Na podstawie analizy skupień prawie we wszystkich miesiącach (poza sierpniem) odcinek rzeki Bug pod względem stanu chemicznego można podzielić na dwie części. Pierwszą grupę stanowi odcinek rzeki z punktami pomiarowymi w Krzyszewie, Kukurykach, Włodawie i Kuzawce o większych średnich zawartościach azotu amonowego, tlenu rozpuszczalnego i fosforu ogólnego. Drugą grupę utworzyły miejscowości: Kryłów, Zosin i Horodło o wyższych średnich stężeniach BTZ_5, siarczanów i chlorków.

Słowa kluczowe:
rzeka Bug, zanieczyszczenia chemiczne analiza składowych głównych, analiza skupień, analiza wariancji.

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Impact of Street Sweeping and Washing on the PM10 and PM2.5 Concentrations in Cracow (Poland)

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1. Introduction

The growing public interest in the air quality in large cities and urban agglomerations has also been recently observed in Poland. According to the European Environment Agency (EEA) report on air quality in Poland (2010-2015), the percentage of the urban population exposed to concentrations exceeding the EU standards for the particulate matter PM10 was 80-88%. Poland is also listed among the countries leading both in PM10 and PM2.5 emissions. The average concentration of PM2.5 in Poland is 22.8 $\mu g/m^3$ (EEA report 206, 2015, 2016, 2017), and such a high-level results from the burning of solid fuels (mainly coal) in households (Choi et al. 2015, Sówka et al. 2018). Another important source of particulate and gaseous contaminants in urban areas is emissions from transport and industry (Bokwa 2008, Amato et al. 2009, 2009b, 2010, Chirizzi et al. 2017). It is estimated that air pollution in the EU is associated with transport in 12% for PM10, and 15% for PM2.5, and related to industry in: 28 and 24% respectively (Badyda 2009, Gliniak et al. 2015, EEA 2016, 2017).

The research also shows that PM concentrations in urban dust are related not only to sources of emitted flue gases, but also to particulate matter transfer from soils, abrasion of the road surface, construction works, and incineration (Amato et al. 2010, 2010b, Harrison et al. 2001, Lenschow et al. 2001, Bagieński 2015, Chirizzi et al. 2017, Jancsek-Turócziet et al. 2013). Studies have shown that the share of the road transport (emissions from engines and abrasion of tires, claddings, and road surfaces) in shaping the average concentrations of air pollutants in street canyons is also higher than for different type of sites, reaching 27% for PM 10, and 24% for PM 2.5 (Harrison et al. 2008, Kim and Guldman 2011, Bogacki et al. 2012).

One of the ways to reduce PM concentrations in the air is to prevent it from being deposited at the edge of roadways. Sweeping and/or washing of the road surface prevents dust from re-entering the air. In the literature, there is not much research on the impact of street sweeping on air quality (Amato et al. 2009, AIRUSE LIFE 11 2013). However, it has been already established that after sweeping the air dust contains more particles with smaller diameters (Katamaneni et al. 1996, AIRUSE LIFE 11 2013). Measurements performed during the spring season in Stockholm have shown that sweepers can also increase the PM10 levels by raising the dust deposited on the road along the curbs (Kuhns et al. 2003, Norman and Johanson 2006, AIRUSE LIFE 11 2013). In studies conducted in Madrid (Karanasiou et al., 2011), it was observed that daily levels of PM10 on unwashed streets during dry days were 215% higher than those during the day after night cleaning of the streets . Research carried out in urban areas (Karanasiou et al. 2012) showed that the resuspension of road dust should be considered an important source of elevated PM levels. The results showed that traffic intensity is the most important factor affecting the level of hourly PM concentrations, and it has been observed that there is a lower impact of the weather as well as for the frequency of street compaction. The combination of street sweeping and washing (rinsing with water) is one of the methods proposed to limit the share of road traffic in PM concentrations in the environment. Positive examples of street sweeping combined with washing (rinsing with water) caused a drop of PM10 in the air, up to 7-30% of average daily concentrations in Spain, Germany, Sweden, and Taiwan (Vaze and Chiew 2002 Chang et al. 2005, AIRUSE LIFE 11, 2013).

Cracow is the second largest city in Poland, with a population of approx. 800,000, and it is considered one of the EU cities with the highest level of air pollution (155 days with PM10 over the limit in 2014) (EEA 2017, Report GIOS 2014). The average annual concentration of PM10 in Cracow for the period of 2010-2014 was 69.34 $\mu g/m^3$, with 188 days exceeding the daily limit of 50 $\mu g/m^3$ (EU Air Quality Directive 2008) in 2016 (WIOS report 2015, 2016). Elevated concentrations of PM10 are observed regularly from November until March. This situation is caused by the unfavorable location of the city which is in a river valley (Vistula River), and the concentration of local emission sources. The dense housing development and the high traffic volume combined with the limited ventilation of the area further increases concentrations of dust particles in the air. The main sources of air pollution in Cracow are industry, coal-fired heating (central heating plant, and stoves in private houses), and transport(Bokwa 2008, Gliniak et al. 2015). The most significant types of industry in Cracow are ferrous metallurgy, the organic and non-organic chemical industry, rubber industry, mechanical, electric, electronic, and the energy industry. Due to the prevailing influx of air to the city from the west, significant amounts of pollution are also transmitted from the Upper Silesian areas (the main center of coal mining and metallurgy in

Poland). These unfavorable conditions cause that the air pollution is largely retained and accumulated in the area of the city(Bokwa, 2008, Gliniak et al., 2015). The impact of intensive sweeping and subsequent washing of streets in Cracow was investigated in 2015-2016. The field investigations were carried in three locations in the vicinity of air quality monitoring stations. The article also takes into account the impact of air quality on road traffic during the World Youth Days in 2016.

2. Methods

2.1. Sampling area description

This study was focused on the impact of street cleaning on improvement of the air quality performed in Cracow (southern Poland). The experiment was conducted between April 2015 and September 2016 in six series of measurements (Table 1). For technological reasons, the experiments were carried out in periods when the air temperature at night was above 0°C. During the experiments, the wet sweeping and washing streets with water, due to the safety of road users, made it impossible to carry out the experiments in the winter months, when the PM air pollution is the highest. The advantage of the summer period is that the impact of pollution from other sources than public transport is small. The study was conducted in three locations: Avenue of the Three Bards (Krasiński Ave. and Mickiewicz Ave.); Lieut. Halszki Street (from the intersection with F. Bujak Street to the intersection with W. Witosa Street); and at the intersection of Bulwarowa Street and Solidarity Avenue (Fig. 1). Sampling site selection was determined by the localization of the continuous air monitoring stations (Fig. 2). The air quality in the Cracow area is monitored by the Regional Inspectorate for Environmental Protection, and the monitoring network includes three stations: i) at the one of the busiest streets in the Cracow center (the Avenue of Three Bards – site C; ii) at the industrial area (Bulwarowa Street – site I); and iii) at the residential area (Lieut. Halszki Street – site R). Experiments were conducted by the Cracow Municipal Cleaning Company (MPO), together with the Cracow University of Technology (CUT), and the Regional Inspectorate of Environment Protection (WIOŚ).

Site C (the Avenue of Three Bards, Fig. 2a) is characterized by pre-war urban development of a "canyon" nature with residential buildings (2-5 stories), and the service and administrative facilities located on the ground floor. The traffic intensity on this avenue is about 4000 vehicles per hour (~100 thousand per day). According to the WIOŚ data from the local air monitoring station, the number of days with PM10 higher than 50 $\mu g/m^3$ was 260 in 2015, and 165 in 2016 (report WIOŚ 2015, 2016).

Series	Date
I	15.04. 2015-18.04.2015
II	19.05.2015-20.05.2015
III	15.09.2015-18.09.2015
IV	4.04.2016-7.04.2016
V	24.08.2016-27.08.2016
VI	13.09.2016-16.09.2016

Table 1. Experiment Series

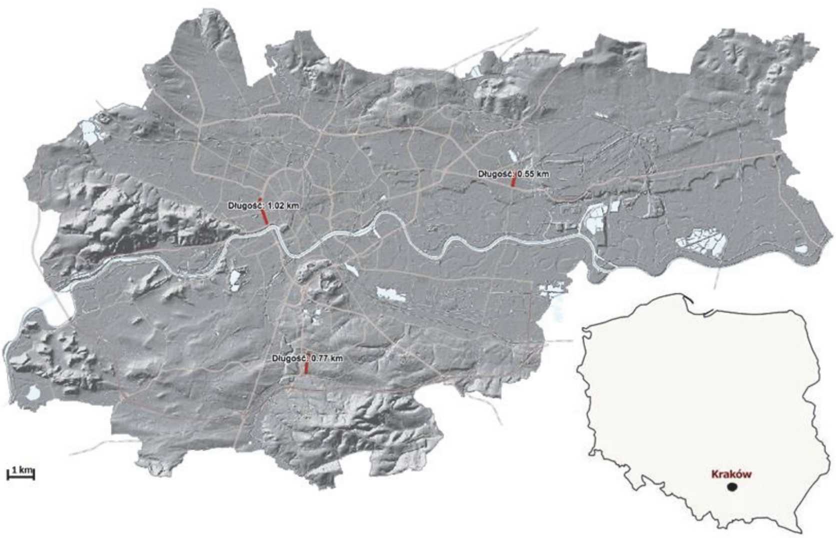

Fig. 1. Localization of the experimental locations in Cracow

Site I (Bulwarowa Street, Fig. 2b) is localized in the industrial/residential district of Nowa Huta, with one of the ArcelorMittal Poland's units, as the main industrial facility in the area. The streets included in the experiment are characterized by a traffic intensity less than 1000 per hour (~ 24 thousand per day), dispersed with residential buildings, and gardens. Access roads to residential development are combined with walking and bicycle paths. Bulwarowa Street is also surrounded from both sides by wide green belts, where the monitoring station is localized as well. The other part of the sampling area consists of the section of the Avenue of John Paul II, which is a two-lane route divided in the middle by tram lines. According to the WIOŚ data from the air monitoring station on Bulwarowa Street, the number of days in which the level of PM10 was higher than 50 μg/m^3 was 120 in 2015, and 74 in 2016 (report WIOŚ 2015, 2016).

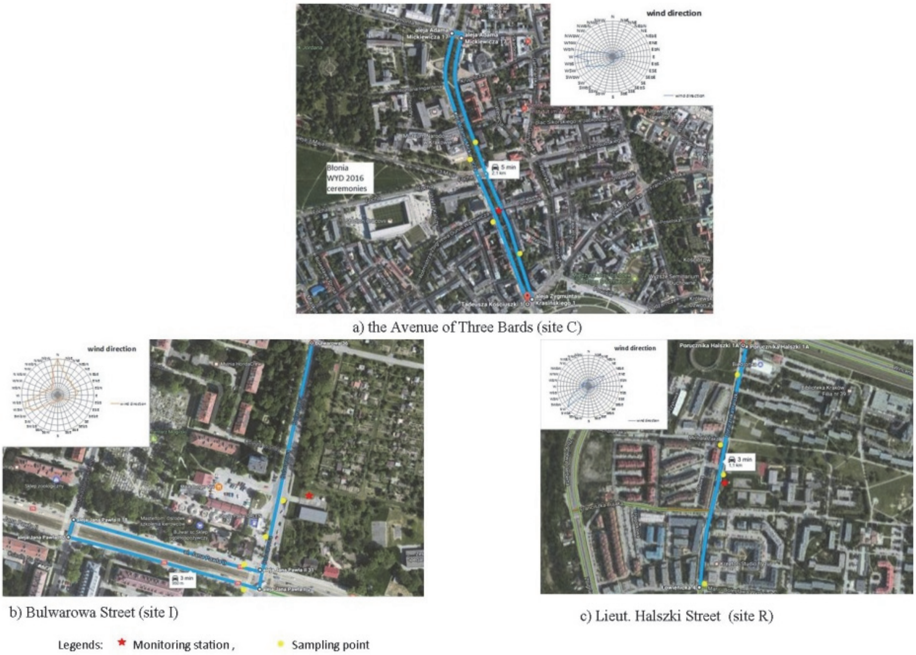

Fig. 2. The route of passing sweepers and washing cars during the experiment in: a) site C, b) site I, c) site R

Site R (Lieut. Halszki Street, Fig. 2c) is located in the Kurdwanów Housing Estate, which is part of the Podgórze District (southern part of Cracow). This housing estate consists mainly of high-rise residential buildings, which is a cause why the streets are mostly access routes to housing buildings and apartments. This estate is considered, and is one of the biggest "bedrooms" in Cracow, and it is inhabited by about 20 thousand residents. Lieut. Halszki Street is a small single-lane street, with a traffic intensity of 2000 per hour (~ 36 thousand per day). According to the WIOŚ data from the local air monitoring station, the number of days in with a level of PM10 higher than 50 $\mu g/m^3$ was 99 in 2015, and 78 in 2016 (report WIOŚ 2015, 2016).

2.2. Sampling pattern

In the first experiment (series I) sampling was only performed at site C (center transportation area). During this experiment the vehicle traffic was limited to only one lane. Every day (from 10 pm), the sidewalks along the road were washed, and both sides of the street were also swept. A moment later, three tankers escorted by police were moving across the width of the street. Washing was repeated every hour, until 4-5 am the next day. After weighing of the sweepers, samples of swept material for chemical analysis were collected. Water samples were collected at four points from the road surface during the first and last street washings. This procedure was repeated for another three days. Between experiments, these streets were swept and washed in accordance with the schedule of the MPO. During the experiments the MPO sweepers were used, which meet the highest ecological standards of EURO 6 exhaust gas. All the equipment was PM10 certified. Sweepers were working in the wet system with water recirculation, which means that water during the sweeping process was used repeatedly. Vehicles were also equipped with a third brush, which allowed sweeping on two different levels. Street washing trucks were equipped with a tank with water, and a sprinkler in the front of the vehicle which was used for street washing (Generowicz et al. 2017).

In the series II-VI sampling was conducted in all three locations (sites C, I, and R). Based on the experience gathered during the first series, the experimental methodology was modified. In these further series, the experiments were started on Tuesdays and ended Friday morning. During the first street washing, street traffic was carried out normally, other than in the first series. During all series the following procedure was implemented: wet sweeping and washing of the streets began at 10 pm with streets washed by the water tankers. This procedure was performed in a few cycles, until 5 am. In all series, sweeping samples after weighing were collected for chemical analysis. Water samples were also collected at four points from the road surface during the first and last washes. The whole procedure was repeated for another three days. During the experiments, the amount of street sweeps was measured and the amount of water and fuel used monitored.

In order to show how traffic impacts air quality in the city during the summer months, the article presents results of PM10 and PM2.5 measurements during the World Youth Days (WYD) in Cracow, in July 2016. In this period, traffic in Cracow was largely restricted, and a major part of the regular city residents left the city. However, the impressive number of visitors (2.5 million) was present in Cracow during the celebrations, with 800,000 people attending the main ceremonies at Błonia Park (recreational area in the direct vicinity of the Three Bards Avenue). During this time the main part of the avenue (Krasiński Ave.) was closed to car traffic, and the MPO was sweeping and washing the streets in a continuous system.

2.3. Laboratory analyses

After sample collection, the samples of sweepings were analyzed among the others for: total (solid) dry weight; mineral dry weight; and organic dry weight. Analyses were performed in the laboratory of the WIOŚ. Dry weight, mineral dry weight, and organic dry weight was determined in according to method PN-EN 12880:2004. In the laboratory of the CUT the size of sweepings, and the size of suspended particles in the wastewater from the streets were also measured.

2.4. Weather and air quality data

Information about weather conditions were downloaded from the WIOŚ and the Faculty of Physics and Applied Computer Sciences of the AGH University of Science and Technology official websites. The data on ambient air quality used in this paper was obtained from the WIOŚ. To control PM10 and PM2.5 concentrations the automatic stations were used. In these automatic measurements the following methods were used: UV fluorescence: beta attenuation: oscillating microbalance; and optical method for PM10 and PM2.5 Met One Instruments, Inc. (Grants Pass, OR, USA, model BAM-1020); and an optical method using orthogonal light scattering to count individual particles with a semiconductor laser as a light source for PM10, PM2.5 GRIMM Aerosol Technik GmbH & Co (Ainring, Germany, Grimm M 180) (Bokwa 2008, Choi et al., 2015).

3. Results and discussion

In series I at site C perfect traffic conditions for the first wash of the streets were provided on the first day of the experiment, since one direction of the vehicle traffic had been completely stopped. During the following days of the experiments, only one side of road was used normally due to the traffic jams being formed. During the first day a clear increase of the dust concentration was observed, although sweepers with the PM10 certificate were used for sweeping (Fig. 3). A similar phenomenon had been noticed in previous studies conducted in Stockholm(Norman and Johanson, 2006). The noticeable increase of the level of dust suspended in the air was caused not only by the resuspension of material previously deposited on the road and sidewalks of the roadway, but also by traffic jams forming at site C. The start time of the experiment, 10 pm, was chosen due to the decrease of traffic. The traffic flow between 10 and 11 pm was more than 2,000 vehicles per hour, while during the rush hours is usually above 6,000 (Gliniak et al., 2015).

On the second day of the experiment, 2/3 (2 lanes out of 3) of one side of the roadway was excluded from traffic, and the resulting blockage was smaller. The increase in PM10 and PM2.5 in the first washing phase was noticeably smaller (Fig. 3). After the end of the series, the highest decreases in PM10 and PM2.5 concentrations were recorded in the 48 hours after the experiment. Comparing the daily concentration of three days after the first cleaning cycle, a decrease of about 25.4% for PM10, and 20.3% for PM2.5 was observed.

Concentrations of PM10 and PM 2.5 during the days when no experiments were carried out, showed an increase of dustiness during the night time, regardless of the day of the week, and season. The analysis of the traffic impact on Krasińskiego Ave., and the particulate matter concentrations carried out by Gliniak et al. (2015) showed no significant dependence, while confirming a strong relationship between PM10 and PM2.5 particulate matter in the air. The tests also showed an increase in the air dustiness at night regardless of the day of week and season. Similar trends were found in the measurements of dust concentration in other WIOŚ measuring stations located in the Kurdwanów and the Nowa Huta districts (Gliniak et al., 2015).

Relatively low concentrations of PM10 and PM2.5 were observed after the experiment despite wind speed lower than before it.. To combine these observations with the current meteorological conditions the average wind conditions during the experiment were also depicted in Fig. 3. The decreasing wind speed during evening/night hours also contributed to the observed PM concentration pattern. A characteristic feature is the predominance of latitudinal directions (east-west) determined by the location of the Cracow agglomeration. At site C, which is located in a street canyon, the impact of these meteorological conditions is somehow limited (Weber et al., 2013, Oleniacz et al., 2016) . At this location, the intensity of vehicle traffic and local air turbulence mainly shape the air quality in a significant way. Based on the available research results (Kozielska et al., 2009, Bogacki et al., 2012), it is possible to assume that in this area (site C) the share of secondary dust (PM2.5) lifted from the road surface by road transport is about 20-25%. Additionally, here is a bigger summer share of road transport in the shape of PM2.5 which exceeds 40%, then the overall share of dust discharged from the road exceeds 30% of the total concentration. Such a high impact of transport on PM results is the fact that in the winter period dust emissions from the heating of houses and the energy industry is increased(Bogacki et al., 2015).

The second series of research was shortened to one day due to weather conditions, i.e. heavy rains. The experiment was discontinued, but the impact of the rain (natural intensive street cleaning during the rain, dust was not only removed from the road surface but also from the air) was taken into consideration during data analyses. During series II, a decrease of PM10 concentration was observed (comparing three days before to three days after) for site C 14.3%, site I 28.7%, and site R 19.9% (Table 3), reduction PM2.5 sites C 25.0%, sites I 22.3%, sites R 12.1% (Table 3).

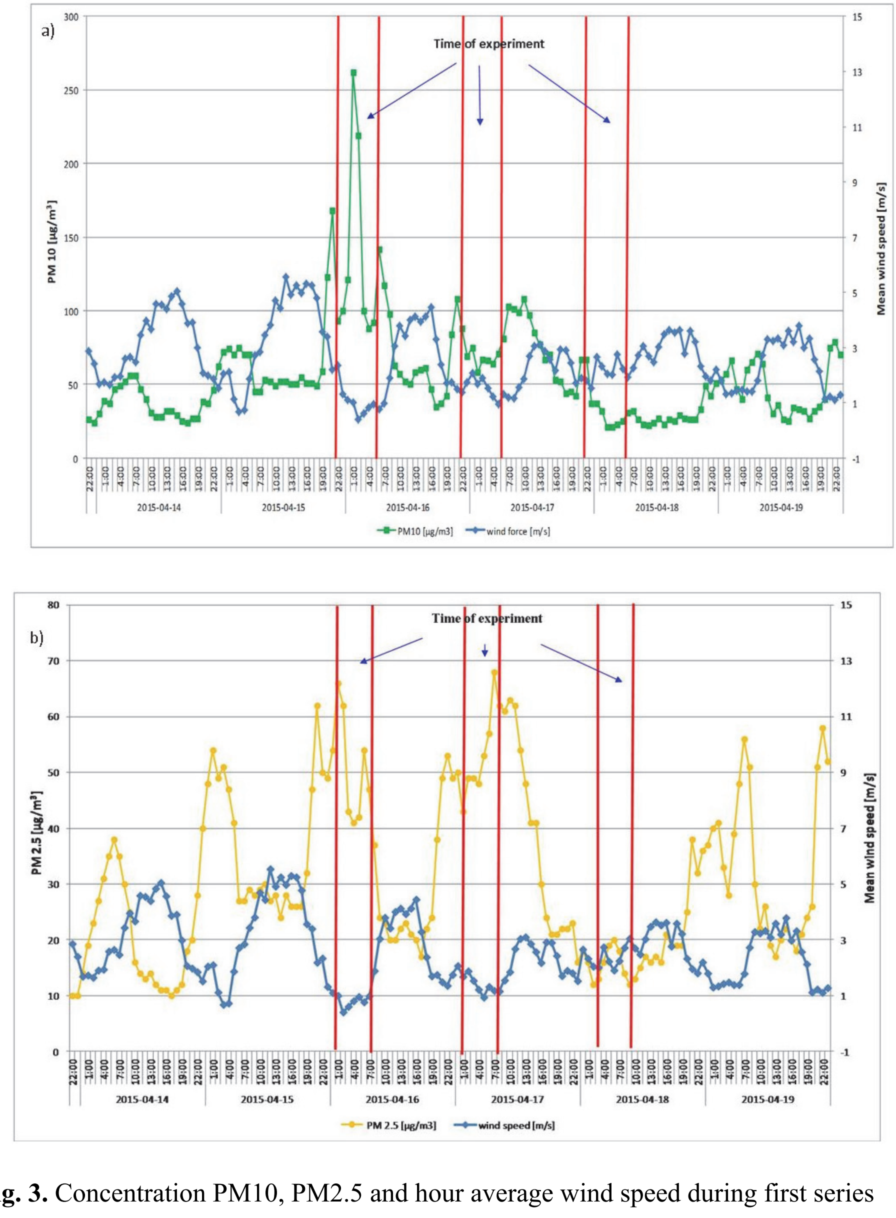

Fig. 3. Concentration PM10, PM2.5 and hour average wind speed during first series

Table 2. Results of chemical composition of water brushes from street washing and cleaning series IV

Site	C			I			R		
Date	2016-04-04	2016-04-05	2016-04-06	2016-04-04	2016-04-05	2016-04-06	2016-04-04	2016-04-05	2016-04-06
Air daily									
PM 10	86.0	106.0	82.0	74.0	90.0	70.0	62.0.0	76.0	57.0
PM 2.5	45.0	51.0	50.0	49.0	56.0	51.0	36	45.0	34.0
Sweeps									
Mass [kg]	860.0	540.0	380.0	1280	440.0	320.0	340.0	180.0	140.0
Total dry weight [g/kgs.s]	779.0	812.0	818.0	663,0	810.0	821.0	836.0	814.0	804.0
Mineral dry weight [g/kgs.s.]	974.0	990	989	91.2	980.0	983.-	984.0	989.0	991.0
Organic dry weight [g/kgs.s.]	26.0	10.0	11.00	88.00	20.00	17.00	16.00	11.00	9.00
Wastewater (Average four sample):									
First wash street									
Total suspended solid [g/dm^3]	13.02	11.86	3.62	6.000	6.860	6.14	18.80	7.890	2.920
Mineral suspended solid [g/dm^3]	12.486	11.726	3.156	5.766	6.684	5.2	15.42	7.102	1.962
Organic suspended solid [g/dm^3]	0.534	0.134	0.464	0.234	0.176	0.94	3.378	0.788	0.958
Last wash street									
Total suspended solid [g/dm^3]	3.4	2.16	0.692	1.98	1.496	2.05	1.830	0.856	0.378
Mineral suspended solid [g/dm^3]	2.946	2.068	0.506	1.782	1.356	1.668	1.650	0.742	0.226
Organic suspended solid [g/dm^3]	0.454	0.092	0.186	0.198	0.140	0.382	0.180	0.114	0.152

Table 3. PM 10 average concentration decreases after washing of streets [%]

Serie	C		R		I	
	daily	hourly	daily	hourly	daily	hourly
I	25.5	30.2	-	-	-	-
II	14.3	37.6	19.9	30.1	28.7	52.6
III	10.5	12.0	2.1	6.4	31.3	12.0
IV	16.7	4.5	5.8	4.1	17.4	24.5
V	25.3	13.8	4.5	1.0	19.2	10.5
VI	11.5	18.1	7.0	20.4	10.0	30.3
average	**17.3**	**19.4**	**7.8**	**12.4**	**21.3**	**26.0**
WYD	14.0	17.3	20.2	2.5	20.4	-5.2

Tables 3 and 4 present the results of PM10 and PM2.5 reduction efficiency calculated from hourly and daily hourly data from the WIOŚ monitoring station. The hourly averages were counted for the day from the end of the tests, i.e. from 5 am to 4 am, and the daily averages provided by the monitoring stations were counted from 0:00 am. Therefore, the daily average does not include the period in which the most effective cleaning of streets is observed. i.e. in the first 24 hours. The higher level of reduction was observed if hourly concentrations of particulate matter were analyzed than for daily concentrations (Table 3, 4) except for series II for site I. For sites R and I, the difference between the average daily and of daily concentrations is about 10% and up to 37% in site R. The average reduction of the PM10 hourly concentration for all series was respectively; for site C 19.4%, for site I 26%, and for site R 12.4%. In the case of reduction, PM2.5 was 21.2% for site C, respectively; 16.6% for site I, and 20.2% for site R.

Table 4. PM2.5 average concentration decreases after washing of streets [%]

Date	C		R		I	
	daily	hourly	daily	hourly	daily	hourly
I	20.3	55.6	-	-	-	
II	21.2	22.1	22.3	31.6	12.1	41.5
III	7.3	5.4	5.5	8.8	37.2	7.2
IV	3.1	2.1	6.7	7.0	15.4	21.1
V	27.4	21.8	24.4	23.6	12.0	3.0
VI	12.2	20.5	33.5	30.0	3.3	10.3
average	**15.4**	**21.2**	**18.5**	**20.2**	**19.2**	**16.6**
WYD	33.3	28.5	31.4	20.8	20.8	1.8

In all the series, a decrease in PM10 and PM 2.5 concentration was observed in the first few days after the end of the experiment, and then the level of air pollution increased. The time and size of the effects of combined mechanical sweeping and intensive street washing was influenced above all, by meteorological conditions and traffic. The shorter effect of decreasing the concentration of solid particles in sites I and R may be related to other factors than meteorological conditions such as, emissions from the ArcelorMittal steelworks, and combined heat and power plants or incinerators (site I). The improvement of air quality was observed for three to four days after such intensive cleaning of the road surface. The increase in particulate matter concentration during the street cleaning process (Fig. 3) is related to raising dust by sweeping vehicles and by creating traffic jams by slower vehicles (especially in site C). Strong winds disperse local air pollutants, but strong winds can also increase PM levels under certain meteorological conditions as a result of resuspension of soil and road dust, especially on warm and dry condition days. (Kukkonen et al., 2005, Kassomenos et al., 2012, Kassomenos et al., 2014). At site C, due to the canyon infrastructure development and the direction of the wind during the experiments, no significant influence of other sources of pollution was noticed than those resulting from road traffic and was related to secondary emissions of dust. In the case of this location, this effect in the summer months was observed in earlier studies (Kozielska et al., 2009, Bogacki et al., 2015, Bogacki et al., 2016). In the case of other locations, a greater impact of factors resulting from meteorological conditions was observed (Fig. 4). Cracow is struggling with poor air quality, especially during periods of calm winds from the south and west.

At the same time, stronger winds from northern directions contribute to periodic dilution of air pollution and improvement of ventilation in the city. Air masses originating from the south are mostly polluted with suspended dust, which can be explained by the inflow of fine particles from areas located further away from Cracow (Szulecka et al., 2017). In the case of site R, the concentration level of PM10 and PM2.5 depends on the quality of air flowing into Cracow, and also industrial sources (in this case mainly EDF Polska and the ARE Power Plant in Skawina), the impact is related in particular to the wind blowing from the east, and to a lesser extent from the south-east (Oleniacz et al 2016, Bajdur et al., 2016). Increased concentration of particulate matter (site I) is observed with the wind blowing from the east and north-east, and is related to the location of industrial plants (ArcelorMittal Poland SA Branch in Cracow, and other plants located in this sector). With the arrival of winds blowing from the west and north-west, the impact on the quality of air in this place also has road transport from nearby busy streets (Oleniacz et al., 2016).

Fig. 4. PM10 and PM2.5 concentration and hour average wind direction during series VI

One of the reasons for the stronger reduction of PM2.5 in relation to PM10 for the R area may be that the roadway on Halszki Street is located on a hillside. During intensive washing, the dust that remains is washed down with water from the street washing. This is due to the particle size distribution of the suspension in water. Based on the analysis of the particle size of the slurry in street washing water, the mean particle diameter of less than 2.5 μm was found to be 30%. On the basis of the obtained results, it can be concluded that the combination of sweeping washing followed by intensive street washing significantly increases the efficiency in removing dust particles with smaller diameters. Systematic removal of residual dust from the road contributes to the improvement of air quality.

Figure 4 present the effect of sweeping and intensive street cleaning on air quality on the example of series VI. They show the concentration of suspended dust depending on the wind direction for three days before, during, and three days after the experiment. It can be seen that during the sweeping and washing process the concentration of PM10 and PM2.5 increased, which is due to the increase of dustiness in the night hours as well as the excitation of dust during the sweeping process; in the afternoon the dustiness level decreases

The average daily concentration was lower after the first day of the experiment in relation to the concentration before the experiment: 61 μg/m^{3}for site C, 50 μg/m^3 for site I, and 44 μg/m^3 for site R; for PM 2.5, a similar phenomenon was observed of approximately 41 μg/m^3 for site I 25 μg/m^3 and 26 μg/m^3 for site R. At the end of the experiment, the concentration of PM10 was observed and decreased in all places, the average hourly concentration in over 60 (μg/m^3) after street cleaning was below the daily limit for PM10 (50 μg/m^3), and only at site C the concentration of PM2.5 was higher than 25 μg/m^3.

To compare the effect of cleaning street surfaces on air quality, the mean values of hourly concentrations of PM10 and PM2.5 were compared in the study area during the experiment, three days before and three days after. The results of dust concentrations in the air were made available by the air quality monitoring station of WIOŚ, Cracow. Figures 5 present the mean values of three-day concentrations, and the values of these concentrations can be reduced by 25.48% to 10.53%. In the case of PM10 particulate matter, their concentration can be reduced to the daily limit (50 μg/m^3) and sometimes even to the permissible annual average (40 μg/m^3).

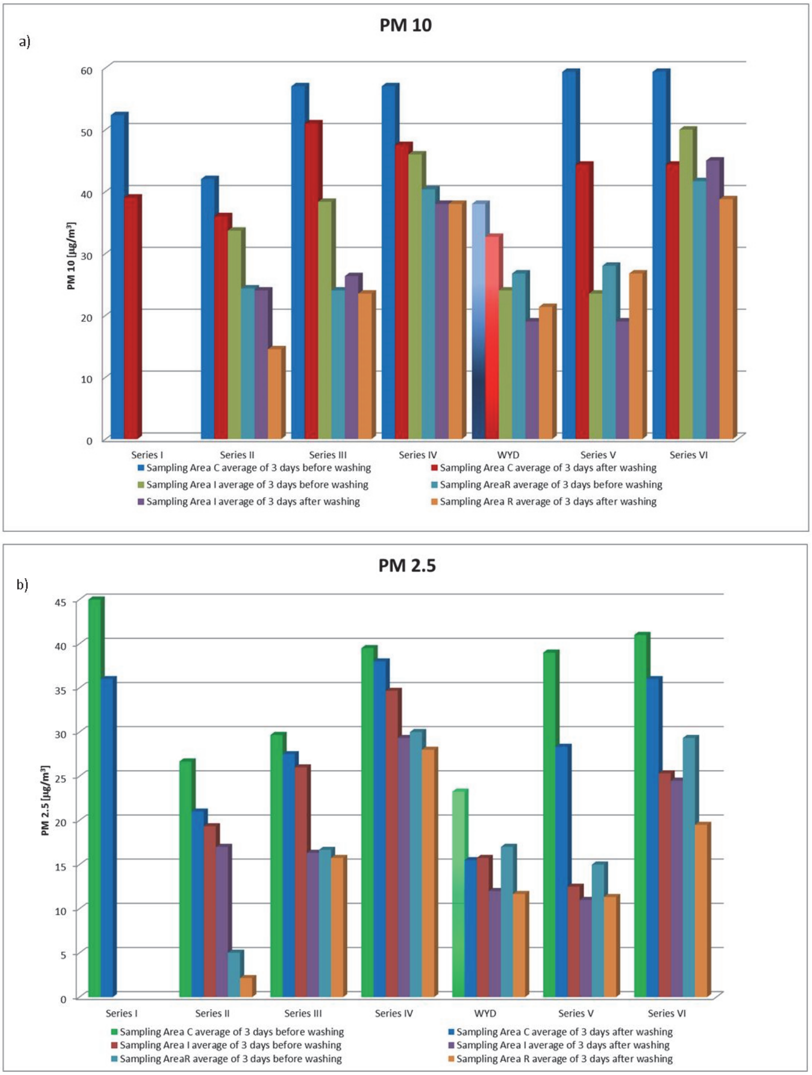

Fig. 5. Mean daily PM10 and PM 2.5 concentration in the air before and after the day experiment

The increase in dust concentration, which was observed after the WYD at the monitoring station located in the industrial area, is caused by the commissioning of the blast furnace at The Steelworks of ArcelorMittal after a few weeks break (Fig. 6). The metallurgical plant is located in the east facing the monitoring station. During the research, it was possible to observe a correlation between the concentrations of individual suspended dust fractions. During the launch of the blast furnace (http://krakow.pl), it was noticed the greater increase in the concentration of PM10 than PM 2.5.

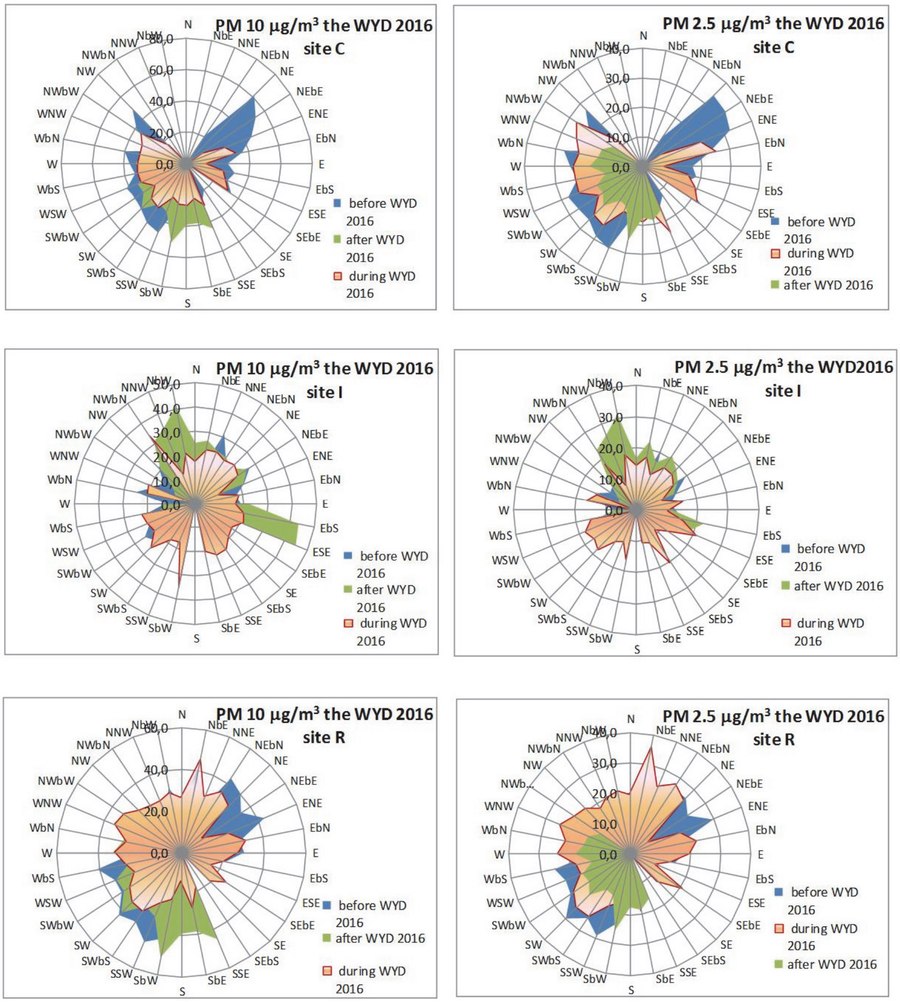

Fig. 6. Observed PM10, PM2.5 and average hour wind speed during WYD 2016

4. Conclusions

Cracow is one of the cities with the most polluted air in Europe, resulting from the combination of being in an unfavorable location (in a valley), as well as coal combustion as the typical heating method for Central and Eastern European cities. In the spring and summer seasons, the biggest impact on quality of air is car traffic, especially in the area of one of the main roads connecting the North and South of Poland, running through the city center (i.e. Three Bards Avenue). This study assessed the impact of street cleaning to reduce the amount of road dust by analyzing PM10, and PM2.5 concentrations after sweeping and street washing. After the experiments, average reductions in PM10 and PM2.5 concentrations were observed, which lasted up to three days from 17.3% for PM10 and from 15.4% for PM2.5.

The level of suspended dust in the air at sites I (industrial area), and R (residential area) was lower than at site C (transportation area) in the spring and summer seasons, and it did not exceed the daily limit (50 μg/ m^3). The effect of sweeping and washing of roads in sites R and I do not make such a big difference, as in site C. The reason is that the quality of air in these locations depends more on other factors than road traffic. The cleaning and intensive street cleaning activities carried out have contributed to the improvement of air quality in the test sites. The greatest impact of this action can be seen at sampling area C in the summer; where the main source of pollution in this place is traffic. Cracow is a city heavily burdened with significant emissions to atmospheric air, both by the location and the number of cars passing through, and industry. The limitation of these pollutants must take place on many levels, and cleaning and washing the streets acts only as a removal due to the consequences of pollution. The obtained results show very clearly the improvement of the state of the environment in terms of reduction of waste, improvement of the quality of urban infrastructure (pavements, and streets), and improvement of the quality of atmospheric air.

The research was carried out thanks to the co-operation of the Krakow City Cleaning Company (MPO), the Cracow University of Technology, and the Provincial Inspectorate for Environmental Protection in Małopolska. Special thanks for the possibility of conducting research and analyses go to President Henryk Kultys, President Andrzej Natkaniec, and the Provincial Inspector for Environmental Protection, Paweł Ciećko, for the involvement and availability of the hardware and technical base. Co-operation like this is a perfect example showing the possibility of combining science and business. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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Abstract

Road traffic is one of the most important factors triggering an increase of suspended dust air pollution in urban areas, especially during the summer. This phenomenon is caused not only by emissions from vehicle combustion engines, but mainly by the formation of dust during road use (tire abrasion, and resuspension of accumulated dust). Sweeping and street washing are the main methods used to remove dust deposited on road surfaces. This article presents the effectiveness of the PM10 and PM2.5 reduction as a result of sweeping, and then intensive street washing in one of the most polluted cities in Europe (Cracow, Poland). The study was carried out in three locations: i) on one of the city's busiest streets; ii) the industrial zone; and iii) at a residential area. The combination of intensive sweeping and roadway cleaning led to the reduction of the suspended dust concentration by 14-20.4% PM10 and 20.8%-33.3% for PM2.5. The greatest impact of this activity was observed in the area where the vehicle traffic was the main source of air pollution. In other places, the obtained effect was reduced by meteorological conditions or emissions from industry.

Keywords:
street cleaning, street sweeping, street washing, PM10, PM2.5

Wpływ zamiatania i mycia ulic na stężenie PM10 i PM2,5 w Krakowie

Streszczenie

Ruch drogowy jest jednym z najważniejszych czynników, który powoduje wzrost zanieczyszczenia powietrza zawieszonym pyłem na obszarach miejskich, zwłaszcza w okresie letnim. Zjawisko to jest spowodowane nie tylko przez emisje z silników spalinowych pojazdów, ale głównie przez tworzenie się pyłu w czasie użytkowania drogi (ścieranie opon i ponowne zawieszanie nagromadzonego pyłu). Zamiatanie i mycie ulic to główne metody usuwania kurzu leżącego na nawierzchniach dróg. W artykule przedstawiono skuteczność redukcji PM10 i PM2,5 w wyniku zamiatania, a następnie intensywnego mycia ulic w jednym z najbardziej zanieczyszczonych miast w Europie (Kraków, Polska). Badanie przeprowadzono w trzech lokalizacjach: i) na jednej z najbardziej ruchliwych ulic w mieście; ii) strefie przemysłowej; oraz iii) w dzielnicy mieszkalnej. Połączenie intensywnego zamiatania i mycia jezdni doprowadziło do zmniejszenia stężenia pyłu zawieszonego o 14-20,4% PM10 i 20,8-33,3% w przypadku PM2,5. Największy wpływ tej aktywności zaobserwowano na obszarze, gdzie ruch pojazdów był głównym źródłem zanieczyszczenia powietrza. W innych miejscach uzyskany efekt został zmniejszony przez warunki meteorologiczne lub emisje z zakładów przemysłowych.

Słowa kluczowe:
sprzątanie ulic, zamiatanie ulic , mycie ulic, PM10, PM2,5

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Time and Space Variability of Water Quality in the Inner-city River in Lublin from the Aspect of Existing Natural and Land Use Conditions

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1. Introduction

The quality of water in a river catchment basin depends on many factors. The method of land management and use plays a decisive role. This is connected with the presence of sources of pollutants, volumes and quality of emissions to the environment as well as the use and efficacy of anti-pollution systems (Hat et al. 2004, Mallin et al. 2009). The protection of water resources must be preceded by detailed, multiple-aspect analysis of the status of respective components of the natural environment and phenomena occurring in the environment-society-economy system. In addition, the current capacity of the ecosystem in terms of anthropogenic impact and its self-purification and water renewal ability must be taken into account (Khan & Ansari 2005, Poskrobko 2007). At present, direct influx of polluted rainwater into inner-city sections of river beds has been a growing problem. Rainwater captures all pollutants it finds on its way – both in the air and on sealed surfaces (among others roofs, roads, parking lots, depots, markets) (Beck & Birch 2012, Jennings & Jarnagin 2002). Limited infiltration and retention result in extremely high run-offs of poor quality (area pollution), which in turn can induce hydrobiological stress in water courses (impact of harmful physical, chemical and biological stimuli) (Geiger & Dreiseitl 1999). These phenomena are random and they have not been satisfactorily examined yet. On the other hand, comprehensive protection of surface water quality is deemed a key factor in catchment management, in particular in territories subject to considerable changes in land use (Carroll et al. 2013).

This paper aims at evaluating the variability of water quality in the Czerniejówka River flowing through the southern and central parts of Lublin city (south-eastern Poland). The analysed river is a right-bank tributary of the Bystrzyca River which, in turn, disembogues into the Wieprz River. The studies were carried out in 2009-2016. They took into account natural factors (such as, for example, weather, rain run-offs, water regime in the valley) and anthropogenic ones (e.g. land development, drainage system, sources of pollution) that could determine high variability of the quality of water in water courses. The sampling points (SP) were situated in sections with various use of adjacent land (agricultural land – 1, high-density building development – 2). The paper also attempts to evaluate the options for protecting the quality of river water resources. The collected results should provide valuable material for experts in environmental protection, water management and spatial planning.

2. Material and methods

2.1. Study area

Lublin is located in south-eastern Poland near the northern edge of the Lublin Upland. It is the largest city on the east bank of the Vistula, covering an area of 147 km^2. Its population is approximately 340 thousand (US 2017). Many industrial plants representing various areas of industry operate within the Lublin conurbation. Road infrastructure and housing as well as commercial and service building development have been growing fast. Unfortunately, many old housing estates and industrial grounds require revitalisation and modernisation. Among other things, the water and sewage and waste management must be put in order.

The Czerniejówka River under observation is a right-bank tributary of the Bystrzyca – Lublin's main river (Fig. 1). The Czerniejówka catchment basin extends over about 170 km^2 and in physiographic terms it is located in the northern part of the Giełczew Elevation. The mean altitude of the basin is 225.5 m a.s.l. with the mouth on the 169 m a.s.l. ordinate. Dusty and sandy-dusty surface formations of good permeability are found here. The Czerniejówka flows in a well-developed valley with a flat bottom and strongly inclined slopes. The valley is filled with Quaternary sandy sediments. It contains numerous springs of little capacity. The water flow in the river in the cold season (autumn-winter) exceeds that in the warm season (spring-summer). The largest amounts of water appear in springtime as a result of intense short-term surface run-offs (thaws). An abundant and even underground water supply determines even daily river flows. The water resources in the basin of the Czerniejówka River are intensely utilised for covering the municipal water supply needs of Lublin (underground water intakes) (Michalczyk et al. 2011).

Outside the city limits the structure of land use in the basin of the Czerniejówka River is dominated by agricultural land with a definite predominance of arable land. The lower part of the catchment, within which the SPs are located, remains under a strong influence of the city. A strong differentiation in land development is clearly visible here, with a predominance of single-family residential buildings. Multi-family buildings are often old unkempt tenement houses. The river basin has about 30 separate sewerage systems disposing rainwater directly into the river bed. All rainwater outlets are located above SP 2 (mouth section of the river). The vast majority of them are situated between points 1 and 2 (inner-city section of the river) (ADAPTCITY 2019). The wide bottom of the valley, in the neighbourhood of SP 1, is covered by arable land with a considerable share of allotment (community) gardens. It spreads on both sides along 0.7 km towards the mouth of the river. Another section of the valley, 1.2 km long, is dominated to a larger extent by single-family houses, and numerous wasteland areas (unbuilt land) were destined for building development. It is also a location of single industrial buildings (among others, the largest brewery in the Lublin Region), warehouses and office buildings. The final part of the valley with SP 2 is densely built-up up till the river bed. This is a location of new multi-family houses, industrial, office, commercial premises, warehouses and utility buildings. The analysed section of the river is crossed by five bridges, including one railway bridge (Geoportal Miejski 2019). The distance between SPs is 2.3 km (Fig. 1). SP 1 is situated 20 m above the bridge at Mickiewicz Street, and SP 2 – 60 m above the bridge at Fabryczna Street. The river bed near the SPs is 4.5 m wide.

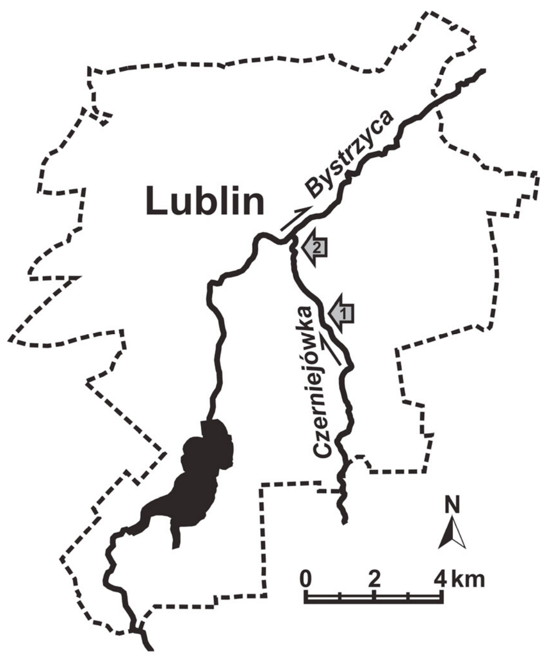

Fig. 1. Location of the Czerniejówka River and SPs 1 and 2

2.2. Climatic conditions

The climatic conditions in the study area were evaluated based on own observations and information available in statistical reports (Table 1). In 2009-2016 the annual precipitation sums were differentiated and they normally exceeded the multiannual average. Precipitation was particularly abundant in 2014. The difference was close to 200 mm in comparison to an average year (1971-2010). In addition, the highest monthly precipitation sum (240 mm in May) was recorded in that year. It accounted for 30% of the annual precipitation. Years 2011 and 2012 were exceptionally dry – precipitation sums amounted to about 500 mm. In November 2011 the precipitation level stopped at only 1 mm. Both in the multiannual period (1971-2010) and in the study period (2009-2016), the lowest monthly supply was observed in February (30 mm), and the highest, respectively, in July (82 mm) and May (102 mm).

Table 1. The lowest and the highest annual precipitation sums and average air temperature in the study period compared with average climatic conditions in a multiannual period (CSO 2009, 2011, 2013, 2014)

	Period	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	I-XII
Precipitation (mm)	2012	43	19	27	31	34	68	58	45	38	87	24	28	502
	2014	67	15	43	54	240	77	76	90	29	24	23	54	792
	1971-2010	32	30	37	39	63	69	82	69	63	43	38	33	598
Temperature (°C)	2010	-8.6	-2.6	2.6	8.8	13.8	17.3	20.8	19.4	11.8	5.2	6.0	-5.0	7.5
	2015	0.6	0.4	4.7	7.9	12.4	16.7	19.3	21.8	14.6	6.8	4.7	3.3	9.4
	1971-2010	-3.1	-2.0	2.0	8.0	13.5	16.1	18.5	17.7	13.0	7.8	3.0	-1.6	7.7

Except in the year 2010, average air temperatures in the study period were considerably above the multiannual average. The difference between average annual temperatures in 2009-2016 and 1971-2010 was 0.7°C. Particularly low average monthly temperatures were noted in January, February and December 2010 (Table 1). As a consequence, the surface water table was frozen and it was necessary to take samples from underneath the ice. The highest average annual temperature (9.4°C) was noted in 2015. Both in the multiannual period and in the study period the warmest month was July. According to Kaszewski (2008), the average annual number of days with snowfall in the study area is 48, while snow cover in the Lublin Region is maintained for about 60 to 80 days.

2.3. Analyses of water quality and flow measurements

The physical and chemical properties of waters were analysed on a seasonal basis (at 32 measurement dates). At both SP samples were taken using ladles at 20-minute intervals. Water temperature was measured upon sampling. At the Water and Wastewater Laboratory of the University of Life Sciences in Lublin the following values were determined: electrolytic conductivity (by conductometry), pH (by potentiometry), total suspended solids (by drying and weighing), dissolved oxygen (O_2), BOD_5 (by dilution), COD (by dichromate method), ammonium ions (NH_4^+), nitrates (NO_3^-), nitrites (NO_2^-), phosphates (PO_4^-), sulphates (SO_4^-), iron (Fe^+), potassium (K^+), and chlorides (Cl^-) (photometric determination). The above-mentioned chemical components were measured using photometers: MPM 2010 (WTW) and LF 205 (Slandi). The physical properties of water were determined using a multi-parameter meter, Multi 340i (WTW). In the evaluation of the quality of river water the extreme and mean values of the analysed indicators were determined for every SP. Statistical variability of the results was based on the standard deviation and the coefficient of variation. The non-parametric Wilcoxon test was used for comparing water quality indicators for both SPs and both half-year seasons (autumn-winter and spring-summer) (significance level $\alpha = 0.05$).

In 2013-2016 water levels and flow intensity were also measured at SP 2. In 2013 measurements were carried out once a month and in the remaining years at water sampling dates. The flow volume was determined by an indirect sectional method after determining the cross-section area of the water course (direct levelling) and measurement of the flow speed (floating element).

3. Results and discussion

The results of studies carried out in 2009-2016 point to a moderate differentiation in water quality in the Czerniejówka River. The coefficient of variation exceeding 50% refers to most indicators. This parameter reaches a considerable value for suspended solids, BOD_5, NO_3^- (at SP 2 – 73.8-96.1%) and PO_4^- (at SP 1 – 77.2%). The highest variability of concentrations approximating 300% is characteristic of NH_4^+ (SP 2). Relatively low variability was recorded for pH, O_2, SO_4^- and Fe^+ (3.2-41.9%). A comparative analysis for both SPs showed similar trends in variability for most parameters. However, the average values of the evaluated indicators often differed in the midstream and downstream. The median values for a definite majority of indicators are similar or identical to their mean values (table 2). It can be determined by the high number of analysed samples (32 values for each indicator at the specific SP).

The variables deteriorating the quality of run-off were NO_2^-, PO_4^- and Fe^+. Mean concentrations of those pollutants were, 0.12, 0.52 and 0.35 mg·dm^{-3}, respectively. The levels of PO_4^-, reaching up to 1.90 mg·dm^{-3}, were particularly alarming. In 2009 and 2012 the average annual concentrations of that component exceeded 0.70 mg·dm^{-3} at both SPs (maximum: 1.20 mg·dm^{-3} at SP 1 in 2009).

Nitrogen and phosphorus are dangerous nutrients contributing to eutrophication of water ecosystems (Khan & Ansari 2005). In turn, iron is deemed a factor reducing the development of cyanobacteria when other nutrients are freely available (Chi et al. 2016). In the analysed river the levels of some pollutants increased after rainfall and surface run-offs. Liu et al. (2012) demonstrated a positive correlation between rainfall and the concentrations of biogenic components in the receiving bodies of water (washing out and transport during run-offs).

The degrees of pollution in the Czerniejówka River at SPs 1 and 2 were compared using a non-parametric Wilcoxon test (level of significance $\alpha = 0.05$). Statistically significant differences in distribution of the analysed characteristics were found for conductivity, O_2, NH_4^+, NO_3^-, SO_4^-, Fe^+ and Cl^- (Table 2). At the mouth of the river (SP 2) water was more polluted than in the midstream (SP 1). Differences between the mean values of the above-mentioned variables ranged from 6.1 (O_2) to 120.4% (NH_4^+). Although the mean concentration of PO_4^- at SP 1 was 13.2% higher than at SP 2, the statistical analysis did not show a different distribution of values for that indicator.

The deterioration in water quality down the river is evidence of an increased number of pollution sources in a highly urbanised part of the city. Some authors demonstrated a relationship between the quality of surface run-off and the use of the catchment basin (Goonetilleke et al. 2005, Peng et al. 2016). Field observations and analysis of maps available at https://www.geoportal.gov.pl and https://geoportal.lublin.eu, confirmed that many very unkempt and contaminated areas existed in the region of the analysed section of the river. This refers, among other things, to old buildings, a road network or some unused grounds. In addition, illegal waste dump sites were discovered. Discharging untreated rainwater directly into the Czerniejówka River is a big problem. The rainwater is discharged by surface run-offs and through open flumes and underground channels (Fig. 2).

Table 2. Characteristic values of basic quality indicators of river water at SPs 1 and 2 in 2009-2016 ("+" statistically significant differences at the level of α = 0.05, "-"no statistically significant differences at the level of α = 0.05)

Variables	Point	Minimum	Maxmum	Average	Standard deviation	Variation coefficient	Significant difference
Temperature (°C)	1 2	2.0 2.5	20.0 20.0	10.5 10.5	5.8 5.6	55.3 53.5	-
Conductivity ($\mu S \cdot cm^{-1}$)	1 2	491 421	787 2460	567 645	67.0 336.4	11.8 52.1	+
pH	1 2	7.0 7.0	8.2 7.9	7.7 7.6	0.3 0.2	3.8 3.2	-
Suspension ($mg \cdot dm^{-3}$)	1 2	2 2	85 97	19 19	17.6 18.6	92.1 96.1	-
O_2 ($mg \cdot dm^{-3}$)	1 2	5.3 5.3	12.4 12.8	9.9 9.3	1.7 1.8	17.4 18.8	+
BOD_5 ($mg \cdot dm^{-3}$)	1 2	0.2 0.4	7.0 11.4	2.6 2.9	1.5 2.2	55.3 75.3	-
COD_{Cr} ($mg \cdot dm^{-3}$)	1 2	2 3	29 37	12 13	6.0 8.3	51.6 64.9	-
NH_4^+ ($mg \cdot dm^{-3}$)	1 2	0.05 0.06	0.47 6.30	0.17 0.38	0.1 1.1	59.5 282.1	+
NO_3^- ($mg \cdot dm^{-3}$)	1 2	0.52 0.79	19.30 31.00	8.27 10.98	5.7 8.1	69.0 73.8	+
NO_2^- ($mg \cdot dm^{-3}$)	1 2	0.03 0.04	0.33 0.31	0.12 0.13	0.06 0.07	52.0 56.6	-
PO_4^- ($mg \cdot dm^{-3}$)	1 2	0.13 0.01	1.90 1.30	0.56 0.48	0.4 0.3	77.2 58.1	-
SO_4^- ($mg \cdot dm^{-3}$)	1 2	32 37	126 144	66 88	22.2 24.1	33.9 27.5	+
Fe^+ ($mg \cdot dm^{-3}$)	1 2	0.12 0.14	0.84 0.79	0.34 0.37	0.1 0.1	41.9 40.7	+
K^+ ($mg \cdot dm^{-3}$)	1 2	1.9 2.1	26.0 28.0	8.0 7.9	5.3 4.9	66.8 62.9	-
Cl^- ($mg \cdot dm^{-3}$)	1 2	10.1 11.3	43.4 78.3	17.1 22.7	6.8 12.5	39.7 55.0	+

Fig. 2. Discharges of polluted rainwater into the Czerniejówka River: a) street gutter and open flume near SP 1, b) outlet of an underground channel near SP 2

Pollutants in rainwater can be very hazardous to natural receiving bodies. Their volume and quality depends on many different factors, e.g. land development method, type of tight surfaces, traffic intensity, degree of air pollution and weather conditions (Petrucci et al. 2014, Zubala 2018). During surface water supply the levels of many pollution indicators in the Czerniejówka River increased. This refers, among other indicators, to conductivity, suspended solids, COD and certain nutrients. During the study period the mean conductivity (mineralisation ratio) at SPs 1 and 2 amounted to 567 and 645 $\mu S \cdot cm^{-1}$, respectively (Table 2). Only at one measurement date was the level of 800 $\mu S \cdot cm^{-1}$ exceeded (2460 $\mu S \cdot cm^{-1}$ in March 2013). Gajkowska-Stefańska et al. (2007) describe that conductivity of natural water ranges from 50 to 1000 $\mu S \cdot cm^{-1}$, and that of wastewater can considerably exceed 1000 $\mu S \cdot cm^{-1}$. The content of suspended solids in the analysed water was not high; on average, it amounted to 19 $mg \cdot dm^{-3}$. Similar to conductivity, the maximum concentrations were recorded in March 2013 (85 and 97 $mg \cdot dm^{-3}$). At that time, turbid melt-waters were discharged (Fig. 2b). It must be emphasized that water was sampled at stabilised flow with a reduced amount of eroded material in agricultural areas. In years characterised by high annual precipitation totals (e.g. 2014) the average level of suspended solids was lower than 10 $mg \cdot dm^{-3}$ (as a result of catchment flushing). The saturation of river water with oxygen was high (on average 9.3-9.9 $mg \cdot dm^{-3}$). This phenomenon is very positive in the context of self-purification processes (mineralisation of organic pollutants) (Juang et al. 2008). Despite good aerobic conditions, BOD_5 and COD at some dates reached hazardous values. This particularly refers to SP 2 where the maximum levels were recorded: 11.4 (BOD_5) and 37.0 $mg \cdot dm^{-3}$ (COD) (Table 2). Among biogenic pollutants the most hazardous for the Czerniejówka River were NO_2^- and PO_4^-. Considering the mean concentrations of pollutants at SP 2 (0.13 and 0.48 mg·dm^{-3}) and average flow intensity at the mouth of the river (0.34 m^3·s^{-1}), the annual discharge of NO_2^- and PO_4^- from the catchment basin could reach 1.39 and 5.15 Mg respectively. In 2013-2016 the extreme flow rates in the measurement section were 0.17 and 0.95 m^3·s^{-1}, whereas water levels ranged from 0.12 to 0.35 m (on average 0.20 m). The group of pollutants with relatively high concentrations also includes Fe^+. The maximum values approximated 0.80 mg·dm^{-3}. The release of this component is fostered by strong humidity at the bottom of certain sections of the valley (Michalczyk et al. 2011). In waterlogging conditions, it is likely that Fe^+ is activated as a result of reduction (gleying processes) (Kabata-Pendias & Pendias 1993).

The study also took into account the characteristics of river water quality in the cold half-year (autumn-winter) and in the warm half-year (spring-summer). Each season was characterised by different weather conditions (Table 1) that could have an influence on the differentiation in the quality of waters in the Czerniejówka River. In the cold season (half-year) 60% of the analysed indicators were more varied than in the warm season (half-year). In particular, this referred to temperature, conductivity, NH_4^+ and Cl^-. In the warm season the coefficient of variation was considerably higher for K^+ only. At the level of confidence of 0.95 (α = 0.05), the Wilcoxon test showed statistically significant differences in temperatures, conductivity, O_2, PO_4^- and Cl^- between half-year periods. In addition, a different distribution of NO_3^- concentrations was found in the statistical test for α = 0.10 (Table 3).

The difference between mean temperatures of water in both half-year periods amounted to as much as 190%. The value of that parameter depended primarily on changes in atmospheric air temperatures. Temperature is an important physical indicator. As it grows, the solubility of solids increases while that of gases, e.g. O_2, decreases (Chełmicki 2002). The average content of oxygen in water in the cold season was about 1 mg·dm^{-3} higher than in the warm season. In the cold season of the year, higher electrolytic conductivity was also observed. Its average value was 658 μS·cm^{-1} (maximum 2460 μS·cm^{-1}). This phenomenon is linked, among other things, to melt-water run-offs carrying high loads of pollutants. Maintained snow cover fosters gradual accumulation of subsequent quantities of pollutants, including anti-slip chemicals (Ociepa et al. 2015). This can be confirmed by increased content of Cl^- in water samples in winter. The mean concentration of Cl^- in the cold season was 22.6% higher than in the warm season. Levels of Cl^- grew down the river, which is most likely due to an increasing share of roads in the river basin area and uncontrolled run-offs from road surface. Discharge of precipitation waters containing high levels of chlorides can disturb the functioning of freshwater ecosystems (Rivett et al. 2016).

Table 3. Characteristic values of basic quality indicators of river water in the cold (1) and warm half-year (2) ("+" statistically significant differences at the level of α = 0.05, "-"no statistically significant differences at the level of α = 0.05)

Variables	Half-year	Minimum	Maxmum	Average	Standard deviation	Variation coefficient	Significant difference
Temperature (°C)	1	2.0	10.0	5.4	2.4	44.6	+
	2	12.0	20.0	15.6	2.3	14.7	
Conductivity ($\mu S \cdot cm^{-1}$)	1	491	2460	658	336.6	51.1	+
	2	421	644	554	42.7	7.7	
pH	1	7.0	8.2	7.6	0.3	4.0	-
	2	7.1	8.0	7.7	0.2	3.0	
Suspension ($mg \cdot dm^{-3}$)	1	2	97	20	21.2	105.1	-
	2	2	65	18	14.4	78.3	
O_2 ($mg \cdot dm^{-3}$)	1	5.3	12.8	10.1	2.1	20.3	+
	2	5.7	10.8	9.2	1.3	13.7	
BOD_5 ($mg \cdot dm^{-3}$)	1	0.4	11.4	3.0	1.9	64.7	-
	2	0.2	8.1	2.5	1.7	69.0	
COD_{Cr} ($mg \cdot dm^{-3}$)	1	2	37	11	6.7	58.7	-
	2	3	36	13	7.8	59.0	
NH_4^+ ($mg \cdot dm^{-3}$)	1	0.07	6.30	0.38	1.1	286.0	-
	2	0.05	0.41	0.18	0.1	58.7	
NO_3^- ($mg \cdot dm^{-3}$)	1	0.52	31.00	8.63	7.0	81.4	-
	2	1.00	26.81	10.62	7.1	67.0	(+ α=0.10)
NO_2^- ($mg \cdot dm^{-3}$)	1	0.03	0.29	0.12	0.07	56.4	-
	2	0.05	0.33	0.13	0.07	53.3	
PO_4^- ($mg \cdot dm^{-3}$)	1	0.01	1.50	0.43	0.3	65.1	+
	2	0.18	1.90	0.60	0.4	68.3	
SO_4^- ($mg \cdot dm^{-3}$)	1	33	125	77	24.9	32.5	-
	2	32	144	77	26.6	34.7	
Fe^+ ($mg \cdot dm^{-3}$)	1	0.14	0.79	0.36	0.1	36.8	-
	2	0.12	0.84	0.35	0.2	45.9	
K^+ ($mg \cdot dm^{-3}$)	1	2.9	14.2	7.2	2.7	37.4	-
	2	1.9	28.0	8.6	6.7	77.7	
Cl^- ($mg \cdot dm^{-3}$)	1	10.1	78.3	22.4	13.2	59.0	+
	2	10.1	33.9	17.3	5.4	31.2	

Despite variations in mean concentrations of nutrients (e.g. NH_4^+ – 52.7%), the statistical test revealed a different distribution of values for PO_4^- and NO_3^- only. The concentrations of both components were higher in the warm season, which contrasts to data presented by some authors. They demonstrated that the content of nutrients in the water environment decreases during vegetation, which is linked to the intense intake of the components by growing plants (Birgand et al. 2007, Jarvie et al. 1998). Increased levels of phosphorus and nitrogen in the waters of the Czerniejówka can be a result of increased supply of these elements in spring and summer; it is considerably higher than the autotrophs require.

Out of 31 systems of rainwater networks connected to the catchment basin of the Czerniejówka River, only 10 have separators installed (ADAPTCITY 2019). In other cases, rainwater is discharged into the river with no treatment at all. Unfortunately, it may be suspected that this is sometimes the case with other wastewater as well (illegal discharge into street inlets). These problems should be solved by providing all rainwater sewerage networks with settling tanks and separators and designing and implementing an efficient inspection and monitoring system. Another good solution is also increasing the retention of rainwater within the catchment, e.g. by creating special reservoirs and permeable surfaces (Zubala & Patro 2015). Illegal waste dump sites must be eliminated and adequate cleanness of the drained areas, including roads, car parks and premises, must be ensured. In addition, it is necessary to run information campaigns encouraging users of arable land in the valley of the river to use good agricultural practice and reduce uncontrolled outflow of fertilizers and other pollutants (DEFRA 2009). The quality of river water can also be protected by supporting self-purification processes. On sections with a deep-cut river bed, weirs providing artificial aeration of water and retaining suspended solids can be built (Imhoff & Imhoff 1996).

4. Summary

The studies showed that the quality of water in the inner city Czerniejówka River was moderately variable. Values of the analysed indicators were relatively highly differentiated for NH_4^+, suspended solids, PO_4^-, BOD_5 and NO_3^-. In turn, low variability was recorded for pH, O_2, SO_4^- and Fe^+. The indicators that considerably deteriorated the quality of water in the river were NO_2^-, PO_4^- and Fe^+ (risk of eutrophication). The annual loads of NO_2^- and PO_4^- discharged from the catchment basin were 1.39 and 5.15 Mg, respectively. Lower quality of water was observed at the strongly urbanised mouth of the river, which may testify to a growing number of pollution sources down the river. The presence of considerably neglected and polluted areas existing within the study area (old buildings, road network, and wasteland) poses a big problem. Illegal waste dump sites were even found there. Discharging untreated rainwater directly into the

river bed is a significant risk (increased values for conductivity, suspended solids, COD and some nutrients). In the study period the examined parameters were also observed to vary during a season. In the cold season 60% of the indicators (mainly temperature, conductivity, NH_4^+ and Cl^-) were characterised by higher differentiation in values than in the warm season. Statistically significant differences were found for temperature, conductivity, O_2, PO_4^-, NO_3^- and Cl^-. In the winter months the values of conductivity and Cl^- levels increased, which is connected with an influx of snowmelt into the river. The concentrations of PO_4^- and NO_3^- were higher in the warm season. This phenomenon is due to the supply of nutrients considerably exceeding the requirement of autotrophs. Due to the variation of seasonal factors, they must be taken into account in developing the water resources management strategy for a catchment. The risk for river water quality must be reduced by undertaking comprehensive measures. These include detection and elimination of all pollution sources within the catchment basin (e.g. pretreatment of rainwater, elimination of illegal waste dump sites and good agricultural practice) and reducing the migration of existing pollutants (e.g. creating precipitation water retention and infiltration sites, forming plant buffer zones in the valley and building weirs in the river).

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Abstract

The paper evaluates the variability of water quality in Lublin's inner-city river taking into account natural and anthropogenic factors that are likely to determine its pollution level. The study period was 2009-2016. The sampling points (SP) were situated in places with different degrees of investment in and use of adjacent grounds. The physical and chemical properties of waters were analysed on a seasonal basis. The values determined for the samples included temperature, conductivity, pH, suspended solids, O_2, BOD_5, COD, NH_4^+, NO_3^-, NO_2^-, PO_4^-, SO_4^-, Fe^+, K^+ and Cl^-. Chemical composition was determined by means of a photometric method. The statistical Wilcoxon test was used for comparing water quality indicators for both SP s and in the cold and warm season. In 2013-2016 water levels and flow intensity (indirect, sectional method) were also measured at the mouth of the river. Most of the analysed indicators were characterised by the coefficient of variation exceeding 50%. The values were relatively highly differentiated for NH_4^+, suspended solids, PO_4^-, BOD_5 and NO_3^- (73.8-282.1%). On the other hand, low variability was observed for pH, O_2, SO_4^- and Fe^+ (3.2-41.9%). The indicators that considerably deteriorated the quality of water in the river were NO_2^-, PO_4^- and Fe^+ (risk of eutrophication). Considering the mean concentrations of pollutants and flow intensity ($0.34\ m^3 \cdot s^{-1}$), the annual discharge of NO_2^- and PO_4^- from the catchment could reach 1.39 and 5.15 Mg respectively. Worse water quality was recorded at the mouth of the river where the adjacent grounds were highly urbanised. This phenomenon can testify to a growing number of pollution sources down the river. Detailed observations confirmed that many considerably neglected and polluted areas existed within the examined section of the river valley (old buildings, road network, wasteland, illegal dump sites). Discharging untreated rainwater directly into the river bed is a huge problem (increased values for conductivity, suspended solids, COD and some nutrients). In the cold season 60% of the analysed indicators (mainly temperature, conductivity, NH_4^+ and Cl^-) were more varied than in the warm season. Statistically significant differences were found for temperature, conductivity, O_2, PO_4^-, NO_3^- and Cl^-. In the winter months the values of conductivity and Cl^- levels increased, which is connected with an influx of strongly polluted snowmelt into the river. The concentrations of PO_4^- and NO_3^- were higher in the warm season. It is likely that the supply of nutrients at that time was higher than required by the autotrophs. Due to a considerable variation of seasonal factors, they must be taken into account in developing the water resources management strategy for a catchment basin. Only a comprehensive approach to the problem of river water quality protection can generate positive effects. The necessary measures include detecting and eliminating all sources of pollution and reducing migration of the existing pollutants.

Keywords:
river water, pollutants, urbanised area, environmental protection

Czasowa i przestrzenna zmienność jakości wody w rzece śródmiejskiej Lublina w aspekcie istniejących warunków naturalnych i użytkowania terenu

Streszczenie

W pracy dokonano oceny zmienności jakości wód śródmiejskiej rzeki Lublina z uwzględnieniem czynników naturalnych i antropogenicznych, mogących decydować o jej zanieczyszczeniu. Badania prowadzono w latach 2009-2016. Punkty kontrolno-pomiarowe usytuowano w miejscach o odmiennym stopniu zainwestowania i użytkowania terenu przyległego. Analizy właściwości fizyczno-chemicznych wód prowadzono sezonowo. W próbkach oznaczano temperaturę, przewodność, pH, zawiesinę, O_2, BZT_5, ChZT, NH_4^+, NO_3^-, NO_2^-, PO_4^-, SO_4^-, Fe^+, K^+ i Cl^-. Składniki chemiczne były określane metodą fotometryczną. Test statystyczny Wilcoxon wykorzystano do porównania wskaźników jakości wody w obydwu punktach pomiarowych oraz w półroczu chłodnym i ciepłym. W latach 2013-2016 w odcinku ujściowym rzeki wykonywano również pomiary stanów wody i natężenia przepływu (metoda pośrednia odcinkowa). Większość analizowanych wskaźników cechował współczynnik zmienności przekraczający 50%. Stosunkowo duże zróżnicowanie wartości dotyczyło NH_4^+, zawiesiny, PO_4^-, BZT_5 i NO_3^- (73,8-282,1%). Natomiast niską zmienność obserwowano w przypadku pH, O_2, SO_4^- i Fe^+ (3,2-41,9%). Wskaźnikami, które w znacznym stopniu obniżały jakość wody rzecznej były NO_2^-, PO_4^- i Fe^+ (zagrożenie eutrofizacją). Uwzględniając średnie stężenia zanieczyszczeń oraz natężenie przepływu (0,34 $m^3 \cdot s^{-1}$), roczne ładunki NO_2^- i PO_4^- odprowadzane ze zlewni mogły osiągnąć kolejno 1,39 oraz 5,15 Mg. Gorszą jakość wody odnotowano w ujściowym odcinku rzeki, z silnie zurbanizowanym terenem przyległym. Zjawisko to może świadczyć o rosnącej ilości źródeł zanieczyszczeń wraz z jej biegiem. Szczegółowe obserwacje potwierdziły istnienie wielu obszarów mocno zaniedbanych i zanieczyszczonych w rejonie badanego fragmentu doliny (stara zabudowa, sieć drogowa, nieużytki, nielegalne składowiska odpadów). Duży problem stanowi odprowadzanie nieoczyszczonych wód deszczowych bezpośrednio do koryta rzeki

(wzrost wartości przewodności, zawiesiny, ChZT i niektórych biogenów). W półroczu chłodnym 60% analizowanych wskaźników cechowała większa zmienność niż w półroczu ciepłym (głównie temperatura, przewodność, NH_4^+ i Cl^-). Ważne statystycznie różnice stwierdzono w przypadku temperatur, przewodności, O_2, PO_4^-, NO_3^- i Cl^-. W miesiącach zimowych rosła wartość przewodności i Cl^-, co wiąże się z dopływem silnie zanieczyszczonych wód roztopowych do rzeki. PO_4^- i NO_3^- miały wyższe stężenia w półroczu ciepłym. Dostawa składników odżywczych w tym okresie prawdopodobnie przewyższała zapotrzebowanie autotrofów. Znaczna zmienność czynników sezonowych wskazuje na konieczność ich uwzględniania w opracowywaniu strategii zarządzania zasobami wodnymi zlewni. Jedynie kompleksowe podejście do problemu ochrony jakości wód rzecznych może przynieść pozytywne efekty. Wśród niezbędnych działań należy wymienić wykrycie i eliminację wszystkich źródeł zanieczyszczeń oraz ograniczanie migracji zanieczyszczeń już powstałych.

Słowa kluczowe:
woda rzeczna, zanieczyszczenia, teren zurbanizowany, ochrona środowiska

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Numerical Analysis of the Influence of the Angle of Inclination of the Screen on the Intensity of Heat Exchange from a Flat Heat Exchanger in a Partially Limited Space

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1. Introduction

Panel radiators appeared in the 1920s and they were originally made of steel. The automation of production, the development of welding technology in the middle of the last century, caused a significant increase in the production of such heaters. In recent years they have been quite popular and their share exceeds 90% of all types of radiators used (Nantka 2006).

The common use of plate heat exchangers has undoubtedly been the advantages resulting from the design itself or the principle of operation, related to, among others with heat exchange conditions (co-or counter-current), performance range, service activities, etc.

In order to properly match the radiator's power to the room, we should take into account primarily the heat demand of this room and the operating parameters of the installation, additional heat sources such as: human heat, lighting, cooking, etc. Also changing factors, such as: wind, sunshine, outside temperature. All these factors affect the amount of heat supplied by the installation, through appropriate regulation (Szpakowska 2010).

When deciding to buy a heater, check whether it has the required marketing authorizations in accordance with PN-EN 442 (Polish Standards, items in literature 17, 18) or the Declaration of Conformity with Technical Approval, which came into force before the creation of the above-mentioned standards (Dąbrowska 2008).

The standard refers to the measurement of thermal power of radiators and informs, among others, about the causes of differences in the power of radiators of the same dimensions. These are, for example, different side surfaces of the radiators, the shape of the pressed plate, the efficiency regulated by the top cover. More interesting requirements and guidelines regarding the features and parameters of heaters according to standards are, for example:

- varnishing and lacquer coating, (paint coat: guilty-protected against corrosion, resistant to damage),
- material properties, (the sheet used to build the wet surfaces of the radiator should be made of low-alloy steel, free from milling defects and corrosion),
- tightness testing, (each radiator should undergo a leak test at a pressure 1.3 times higher than the maximum working pressure, the minimum test pressure should not be lower than 520 kPa),
- strength testing, (the radiator is subjected to a test at a pressure of 1.3 times greater than in case of tightness test) (Guzik 2000).

Other standards for radiators are given in the literature (Polish norms, references in literature 16:29).

Free convection compared to other methods of heat transfer is characterized by relatively low intensity,

- intensified process of free convection affects the economics of the heat exchange process,
- currently, new methods for compensating free convection are sought for and developed.

The intensity of convective heat exchange depends on:

a) field of the fluid temperature and the wall,
b) fluid velocity fields.

The methods for intensifying heat exchange are generally broken down as follows:

- passive - not requiring energy,
- active - requiring the drive with special devices,
- combined - a combination of 2 passive or passive and active methods.

Examples of intensification:

- setting shell-and-tube exchangers with inter-walled interceptors and small cross-sectional areas of the tube bundles (in order to increase the medium flow rate),
- using agitators (intensifying the movement), e.g. in the food industry,

- placing the so-called sieve baffles in the inter-wall spaces of shell-and-tube heat exchangers, which also serve to organize the fluid flow and thus to wash hard-to-reach places,
- application of the electric field in convective heat exchange. This method consists in "bombardment" of the boundary layer with electric charges. There are also known acoustic methods of intensification (Szpakowska 2010).

2. Research methodology

The intensification of convective heat exchange can be followed by the modification of the parameters and flow properties of the convective agent, using properly shaped and positioned elements that influence the convective movements of the fluid.

Modifying the space that exchanges heat allows to shape both temperature fields and fluid velocity in these spaces, affecting the mechanisms that determine the convective heat exchange. The article is a continuation of the author's research on the convective heat exchange (Czapp et al. 2016, Orłowska and Czapp 2012, Orłowska et al. 2017, Orłowska 2017, Orłowska 2018). Natural convection research is a broad field of research for many other researchers (Azzous et al. 2019, Bagai et al. 2019, Kogawa et al. 2019, Oh et al. 2019).

The system proposed for numerical research is a model with a plate heat exchanger, which was supplied in a variable distance x screen-partition Figure 1 (screen-partition) (Fig. 1).

After setting the input parameters for the given geometry and the input conditions, the program proceeds to calculations according to the desired number of iterations.

Boundary conditions:

- T_{sc} – wall temperature (exchanger plates) = const = 55°C
- w_{sc} – velocity on the wall = 0 m/s
- T_{wl} – air inlet temperature = const = 20°C

Assumptions:

- fixed system layout,
- axis x is directed horizontally, perpendicular to the surface of the plate,
- something is directed vertically,
- the heating plate, the front part of the exchanger is isothermal,
- the back plate of the exchanger is insulated,
- T_{sc} – wall temperature (exchanger plates) = const = 55°C, 328 K, (±0,1°C),
- T_{ekr} – temperature of screen.

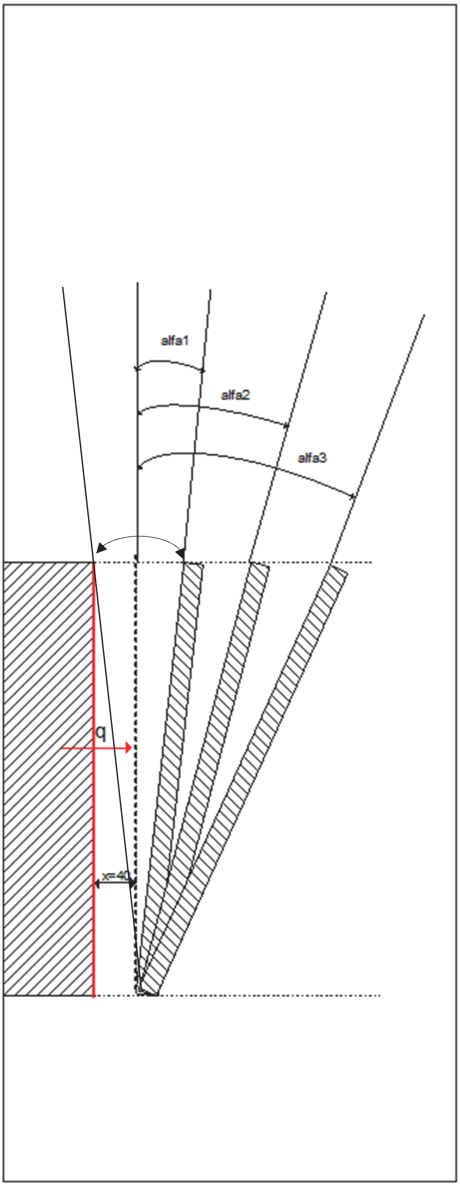

Fig. 1. Heat exchanger with a screen inclined to the various angles alfa

Air:
- compressible,
- fluid movement – turbulent (except for the case without a partition, where the movement is laminar),
- w_{sc} – speed on the wall and partition = 0 m/s,
- T_{wl} – air inlet temperature
- ambient temperature = const = 20℃, 295 K (±0,1°C),
- reference pressure at the outlet of the channel p = 0 Pa, (it is assumed that the pressure level in the outlet section = 0),
- the thermal properties of the working medium are constant except for changes of density in the equation of motion according to the Boussinesquian hypothesis: $\rho = \rho_\infty[1 - \beta \cdot \Delta T]$, gdzie: $\Delta T = T - T_\infty$; T_∞ – opening temperature (T_∞= 293 K, 20 ℃); ρ_∞ – density of the medium at the reference temperature.

Simplifications:
- the pressure gradient in the equations of motion was neglected,
- the buoyancy force direction is consistent with the y axis,
- dissipation of energy and heat conduction in the fluid in the direction along the plate,
- pressure drop along the plate was neglected and brought to the wall layer flow.

The proposed model was solved using the method of numerical modeling in the Ansys commercial package. In this way, velocity and temperature distributions were obtained that allowed to calculate the thermal efficiency of the device. The theoretical description of the phenomenon of heat exchange during free convection with a vertical plate, omitting the pressure drop along the plate, includes equations: continuity, motion and energy.

These equations have the form:

− continuity

$$\frac{\partial w}{\partial x} + \frac{\partial v}{\partial y} = 0, \tag{2.1}$$

− movement

$$\varrho w \frac{\partial w}{\partial x} + \varrho v \frac{\partial w}{\partial y} = \nu \varrho \frac{\partial^2 w}{\partial y^2} + g(\varrho_0 - \varrho), \tag{2.2}$$

where:

$$g(\varrho_0 - \varrho) = g\varrho \frac{T - T_{ekr}}{\theta_\infty}, \tag{2.3}$$

$$g(\varrho_0 - \varrho) = g\varrho \frac{T - T_{ekr}}{\theta_\infty} = g\varrho \frac{T_w - T_{ekr}}{\theta_\infty} \frac{T - T_{ekr}}{T_w - T_{ekr}} = g\varrho \frac{T_w - T_{ekr}}{\theta_\infty} \vartheta, \tag{2.4}$$

– energy

$$w\frac{\partial T}{\partial x}+v\frac{\partial T}{\partial y}=a\frac{\partial^2 T}{\partial y^2}, \tag{2.5}$$

By entering a variable:

$$\vartheta=\frac{T-T_{ekr}}{T_w-T_{ekr}}, \tag{2.6}$$

we transform the energy equation into:

$$w\frac{\partial \vartheta}{\partial x}+v\frac{\partial \vartheta}{\partial y}=a\frac{\partial^2 \vartheta}{\partial y^2}, \tag{2.7}$$

Limit conditions:
$y=0$ $w=0$ $v=0$ and $\vartheta=1$,
$y\rightarrow\infty,$ $w=0$ $\vartheta=0$ (Staniszewski 1979).

All computer simulations were carried out using the Ansys / Flotran (Ansys) computing code. This program is based on the solution of energy balance, momentum and mass equations used in Numeric Fluid Thermomechanics (CFD - Computational Fluid Dynamic). The standard version of the calculation code enables modeling based on traditional phenomena relationships and additional closing equations describing the previously mentioned turbulent momentum and energy streams. The studied system was modeled in two-dimensional space. Two-dimensional so-called the closing model was developed by Launder. At low flow rates, the turbulence model for low Reynolds numbers is often assumed. The presented model can be used both for solving free and forced convection issues. After selecting the desired motion type option (laminar, turbulent), the program takes into account the relevant elements in energy, momentum and mass conservation equations. The calculations were carried out on a computer with a processor with two cores, at 2.1 GHz each and 3 Gb of RAM. At the outset, an analysis was made of the heating plate flow system without a screen. For this purpose, a mesh size 0.0035 (mesh type – free mesh) was used.

The following input data was adopted:

- fixed,
- turbulent or laminar motion depending on the system under consideration,
- the temperature of the heating surface 328 K,
- the ambient temperature 293 K,
- pressure at the outlet from channel 0,
- speed on the walls 0 m/s.

The program was solved by the Solver Tdma Ansys (Ansys) method.

It is worth mentioning that the selection of the appropriate number of iterations and the size of the grid significantly affects the calculation time. After the calculation, the program allows to read the results in the form of colored charts, among others:

- the temperature,
- speed,
- pressure decompositions,
- distribution of air density and related tables (Szpakowska 2010).

3. Results of numerical analyzes

Numerical analyzes were performed for systems with an inclination (screen) inclined by a certain angle of the same height as the heating plate of the heat exchanger, ie 1.15 m (Szpakowska 2010).

The baffle was moved away from the hob at a distance of: at the inlet (bottom) by 4 cm (x = 4 cm), at the outlet (top) at -2 cm (-1°), 5 cm (0.5°), 6 cm (1°), 7 cm (1.5°), 8 cm (2.3°). For comparison, a thermal efficiency value of Q = 448 W, which was obtained in a parallel installation with a plate placed at a distance of x = 4 cm (0°) from the heat exchanger, was also inserted in the collective chart.

Fig. 2 shows the obtained thermal efficiency of the exchanger at different angles of inclination of the partition.

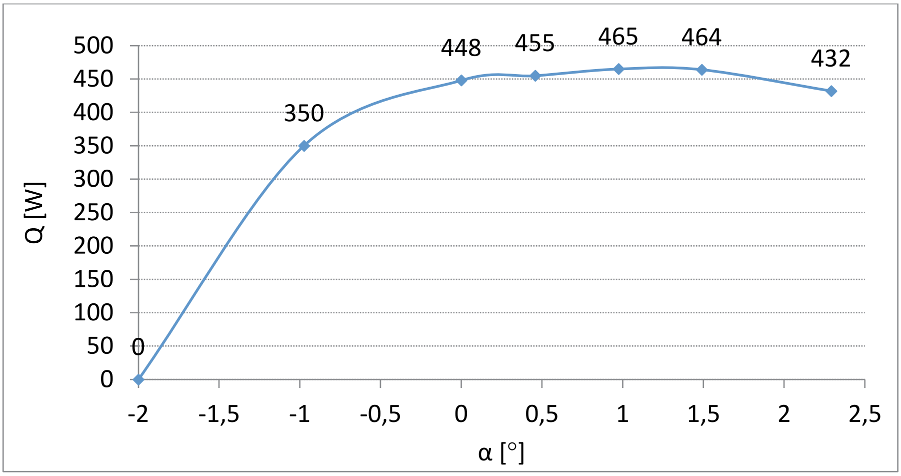

Fig. 2. Thermal efficiency Q [W] of the exchanger as a function of the inclination angle α [°] of the partition

4. Summary and conclusions

In the series of calculations made for the inclination of the screen (screens) – this inclination makes sense to the inclination angle α = 1° (deviation of the upper part of the screen to the distance x = 7 cm, bottom to x = 4 cm), thermal efficiency Q increases. Further tilting the screen reduces the thermal efficiency Q of the exchanger. Tilt of the screen by angle α = 0,5°; 1°, 1.5° makes the thermal efficiency Q of the exchanger higher than the efficiency with parallel geometry, where the screen was moved away to the distance x = 4 cm, Fig. 2. So this is another way to increase the efficiency of the device without the necessity of using energy inputs, i.e. non-mechanical.

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Abstract

The purpose of the work was to perform a numerical analysis enabling to learn the influence of the angle of inclination of a flat partition placed at the plate heat exchanger on the thermal efficiency of the device. It turns out that the inclination of the partition affects this efficiency. Selected systems allowed to capture these changes in the studied range and to visualize them graphically.

Keywords:
radiator, heat transfer coefficient α, convection, inclination

Analiza numeryczna wpływu kąta pochylenia ekranu na intensywność wymiany ciepła od płaskiego wymiennika ciepła w przestrzeni częściowo ograniczonej

Streszczenie

Celem pracy było wykonanie analizy numerycznej umożliwiającej poznanie wpływu kąta pochylenia przegrody płaskiej umieszczonej przy płytowym wymienniku ciepła na wydajność cieplną urządzenia. Okazuje się, że pochylenie przegrody ma wpływ na tą wydajność. Wybrane układy pozwoliły uchwycić te zmiany w badanym zakresie i zobrazować graficznie.

Słowa kluczowe:
grzejnik, współczynnik przejmowania ciepła α, konwekcja, pochylenie

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An Empirical Study of the Variables Affecting the Frequency of Engine Oil Change in the Environmental Aspect

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1. Introduction

In recent years, activities in the road transport segment have focused on various aspects of reducing its harmful environmental impacts. This results both from the global trend related to the fight against global warming, as well as from activities aimed at reducing the use of oil resources. The transport sector is responsible for a significant proportion of air emissions, which directly and indirectly affect people, climate and ecosystems. Moreover, the limited oil reserves have an influence on socio-political and economic relations (Knez et al., 2014). There are a lot of studies related to the reduction of exhaust emissions (CO_2 reduction) in the transport sector (Aditjandra et al., 2016; Kumar Pathak et al., 2016; McBain et al., 2018), and the fuel consumption of vehicles (Matas et al., 2017). There are also several studies on the impact of motor oils, especially low viscosity oils on reducing fuel consumption and CO_2 emissions (Macián et al., 2014, 2015), whereas there is a very limited number of studies concerning the protection of the environment from harmful effects of operating fluids.

Environmental protection activities are an important aspect of almost every area of life and therefore are also vital in the context of waste oils. Transport and industry consume large amounts of lubricant oils, a lot of which later become waste oils. Waste lubricant oil (WLO) is produced in automotive, aviation, marine and industrial sectors but the most significant one (56%) is the automotive sector (IETC, 2013; Osman et al., 2017). In many countries, including Poland, waste oils are considered harmful. They constitute one of the main streams of hazardous waste in Europe and contain many toxic and carcinogenic substances, such as: polycyclic aromatic hydrocarbons (PAHs), products of hydrocarbons oxidation and thermal decomposition, sulphur, phosphor, chlorine and nitrogen compounds, metal derivatives that come from oil additives, products of wear of machinery as well as contaminants from the environment and sometimes also polychlorinated biphenyls (PCB) (Fuentes et al., 2007; Zając et al., 2015). These compounds may cause environmental damage if not properly disposed of and purified (Pelitli et al., 2017; Pinheiro et al., 2017). In their paper, Ramadass et al. confirmed the higher toxity of the used engine oil, compared with fresh oil, based on the tested toxicity parameters (among others activities of soil dehydrogenase and earthworm survival) (Ramadass et al., 2015). Mameli and marletto also indicated used oil as the waste materials which need to be adequately disposed, because of its harmful environmental impact (Mameli & Marletto, 2014).

It is assessed that only 40% of the 45 million tons of the generated waste oil (per year) is gathered and disposed of properly and about 8% is recycled into new lubricant oils (Fuentes et al., 2007; IETC, 2013; Osman et al., 2017). The remaining 60% is discarded (Zhang et al., 2017). In accordance with the guidelines contained in the European Directive 75/439/EEC on the disposal of waste oil, the priority in the management of waste oils has regeneration process (Pinheiro et al., 2017). As much as 19% of the total amount of lubricants available on the market is used in the EU countries. In 2015, around 6.8 million tons of lubricants were used in the EU, while EU handles annually around 3 million tons of WLO (Pinheiro et al., 2017). The resulting difference (around 50%) is due to the fact that part of the oils is irretrievably lost during use (combustion in a combustion chamber, evaporation, leaks, residue in containers, etc.).

Life-cycle of lubricants in industry supply chains and their handling is more and more often considered an important element of good management of environmental issues by suppliers as well as their clients (Guerin, 2008). The degree of the environmental impact of engine oils depends primarily on their chemical composition, production process, distribution and application. The hazard caused by engine oils is caused by a high content of additives resulting from growing expectations as to the quality of oils and by longer periods of use of modern lubricants that lead to the accumulation of harmful substances. On the one hand, trying to prolong the periods of engine oil use leads to a rise in the content of additives (so as to increase viscosity, inhibit oxidation, etc.) and, as a result, also in the content of toxic substances in the oils but, on the other hand, decreases the frequency of oil changes hence reducing its total use. As a result, the amount of waste is lower but the content of harmful substances is higher.

What is considered a serious environmental problem is a significant dispersal of oils resulting from a big number of drivers who use only slight amounts of oils. The usual amount of oil used in an engine of a passenger car is between 4-8 dm^3 (4-50 dm^3 in the case of lorries and machinery). After a certain period, the oil is changed and fresh one is applied. The procedures of handling of the used oil are varied. In the case of passenger cars, oil change takes place at a service station and the used oil is collected by car maintenance companies. More and more frequently, the engine oil and oil strainer change services are included in the price of the products, which encourages car owners to have the oil changed at service stations.

What strongly influences the amount of waste produced is the user awareness. The generally recognized criteria of engine oil change in passenger cars, which are: mileage and oil change schedules based on average figures for different vehicles, are not always sufficient for an adequate approximation of the level oil consumption (Kral et al., 2014; Sejkorová et al., 2017). The frequency of oil change is primarily dependent on the recommendations of the manufacturer. Based on the engine construction, its working parameters and the intended purpose, an oil of appropriate viscosity and performance is chosen. Modern cars are fitted with on-board computers with software that keeps engine performance statistics. It counts not only the mileage but also the number of start-ups, the average speed, trip times, etc. Having collected the data, the software estimates the oil change intervals. However, it should be noted that the intervals are estimated based on certain algorithms which do not necessarily reflect real engine operating conditions and hence do not guarantee optimal oil change time. Changing oil too early leads to an unjustified increase in oil consumption, and therefore to a greater environmental impact due to a bigger amount of waste. Waiting too long with the oil change leads to an increase wear of engine parts and to an excessive concentration of harmful products of degradation in the used oil, which can hinder the regeneration process and have adversely affect on the ecosystems. What is more, in both cases, a car user bears additional costs, either of purchasing the oil in the first case or repairing the worn parts in the second one (Basu et al., 2000; Jun et al., 2006). The aim of this study is to assess the behaviour of car users with regard to frequency of oil change, factors influencing oil change times, place of oil change as well as the need for oil top ups. Moreover, a thorough research has been done to establish a connection between the frequency of oil change and additional factors influencing the degree of oil degradation (car mileage, engine type and capacity as well as the conditions of use). The obtained results can have a positive inluence on the accuracy of assessment of car users' awareness as well as the course of action in terms of a reasonable choice of oil change time. The outcome of this study combined with the results from a thorough investigation regarding travel behaviour and enviornmental-transport policy conducted by Garcia-Sierra et al. can help to understand better why drivers behave as they do (Garcia-Sierra et al., 2015).

The paper is a part of research aiming to assess the awareness of car users in terms of engine oils use. The whole contributes to the existing literature by examining how citizen opinions (collected through a national survey) can be used to select a core set of indicators of monitoring the effectiveness of policies for sustainable management of used oils.

2. Methods and data

2.1. Poland

Poland is a country in Eastern Europe. It is the eleventh country in Europe in terms of area (312,679 km^2). As of 1st January 2018, the population of Poland amounts to nearly 38.5 million people. According to the Central Register of Vehicles, as of 8th June 2017, the number of vehicles registered in Poland amounts to 28,678,674 (including 22,005,578 cars and 3,203,256 lorries – the remaining part includes buses, motorcycles and mopeds). The number of vehicles registered in Poland for the first time in 2016 is 1,822,049 („Central Register of vehicles and drivers, www.cepik.gov.pl", 2018). This includes 26% (475,935) of new cars (lightweight vehicles – passenger cars and light commercial vehicles), which is around 3% of new lightweight vehicles registered in the EU (14.6 millions) (Pocketbook, 2017).

According to a report of the Polish Organisation of Oil Industry and Trade, in 2017 the Polish market of lubricant oils reached the level of 226,896 tonnes, which is a 1.62% y/y increase (POPiHN, 2017). Approximately 47.51% of all lubricant oils sold in Poland are oils for the automotive industry. Within the automotive segment, they account for around 80%. It is particularly worth pointing out that in 2017 the market share of synthetic oils for passenger cars grew from 5.5% in 2007 to 16.29%. Synthetic oils are presently mostly purchased by vehicle users.

2.2. Research framework

Two important aspects have to be taken into account with regard to oil change – firstly, proper engine protection should be provided and secondly, environmental concerns should be addressed. An optimal oil change time is when it is possible to maintain a balance between the two aspects, i.e. when the oil is changed before it loses its properties but not too early so as not to have an unnecessary negative impact on the environment.

Two vital aspects related to oil change have been included in the paper – the place of oil change and the details of use (urban / extra-urban driving). The place of oil change is very important as, when deciding to change oil on their own, car users choose oil based on viscosity classification and do not take into consideration other requirements. However, the choice of oil of certain viscosity class may not fulfil the requirements of a particular engine. The second aspect is concerned with obtaining responses from car users as to the percentage of city-driving. If the percentage is high (i.e. mostly short distances are covered) the engine cannot reach a proper operating temperature, and therefore the oil loses its properties faster. As a result, an increased degradation of engine oil occurs which intensifies the process of engine wear. Abas et al. noticed that engines of cars operating in urban areas work under part-load condition due to low or medium speeds and long idle periods (Abas et al., 2018).

2.3. The environmental protection

After the intended period of use, lubricant oils become waste. Oil waste is the main stream of dangerous waste in Europe. Waste lubricant oils can be further processed to obtain re-refined lubricant oils or they can be burned, in order to generate energy, in installations designed for this purpose. Currently, around 13% of all base oils used in the EU come from re-refined waste oil. Engine oils are the biggest group of lubricant oils in terms of generated waste, which is due to the number of vehicles in use as well as a significant degree of oil recovery. It is estimated that the recovery rate amounts to 52-86% and the remaining part of oil is lost in the process of evaporation, leaks, and combustion in the combustion chamber. Waste framework directive (2008/98/EC) is the main legislation of the EU regulating the handling of waste oils. The regulation determines and establishes inter alia the obligation to apply the waste hierarchy.

The amount of generated waste is strongly influenced by the frequency of oil changes performed by individual users. If an oil change is done too early, particularly when the oil's properties have not been lost yet, it not only leads to increased operating costs, but also to a greater burden on the environment.

From the point of view of environmental protection, the most beneficial way of handling waste oils is their collection and regeneration. However, it should be taken into account that within the stream of waste, there will be cases of informal waste management, that is burning of used oil in the place of collection or even releasing it directly to the environment. Apart from machinery breakdown and unforeseeable events, all the other hazards of polluting the environment with lubricants (oil systems leaks, improper storage, improper maintenance of machinery, deliberate release of oils to rivers and soil) can and should be limited or eliminated through strict compliance with the regulations and proper sealing of the oil systems.

2.4. Questionnaire design and distribution

The statistical study included a group of 1446 drivers from all over Poland. The study was conducted between 1st January and 31st July 2018 and the questionnaire method was used. The questionnaires were submitted online and required providing answers to all questions, which helped to avoid the problem of incomplete data in some questionnaires. The questionnaire included 21 questions – 15 closed-ended and 6 open-ended questions. The questionnaire was addressed to drivers who use fully synthetic engine oils. It was completed solely by drivers who decide or co-decide about the oil change. The study was conducted using probability sampling (random sampling), based on a nationwide, commercial database of drivers.

The formula that was used to determine "the sample size (n) in the estimation of the fraction of elements distinguished in the population" has the following form („Sample size calculator, www.raosoft.com/samplesize.html", 2018):

$$\mathrm{x} = \mathrm{Z}\left(\frac{c}{100}\right)^2 \mathrm{r}(100\text{-}\mathrm{r}) \quad (1)$$

$$n = \frac{Nx}{((\mathrm{N}-1)E^2+x)} \quad (2)$$

$$E = Sqrt\left[\frac{(\mathrm{N}-\mathrm{n})\mathrm{x}}{\mathrm{n}(\mathrm{N}-1)}\right] \quad (3)$$

where:
N – the population size,
r – the fraction of responses that you are interested in,
Z(c/100) – the critical value for the confidence level c.

The margin of error was set at 3.5%. The confidence level was set at 99%. The calculated sample size was 1354. In total, 1446 usable questionnaires were collected.

The questionnaire allowed for identification of the respondents' sex, age, type of the settlement where they live, as well as engine type and engine capacity in their cars, year of car production and car mileage. Moreover, the respondents were asked to stipulate the percentage share (0-100%) of city driving. As mentioned before, the paper is a part of research aiming to assess the awareness of car users in terms of engine oils use.

The authors of the study decided to use correspondence analysis (CA), as it is a descriptive and exploratory data analysis technique whereby results are presented as a bi-plot, i.e. a graphical method which allows for displaying points representing the first variable (rows) as well as the second variable (columns) on one figure. Analysis of their relative positions is subject to certain rules. The row and column coordinates are summarized in a single plot. If data are presented in such a way, the neighbourhood (or distance respectively) between observations and variables provides evidence for strong relationships (or weak relationships respectively). It is important to note that the relative positions of one point in one set should be interpreted with respect to all the points in the other set.

The basic result of correspondence analysis is a scatter diagram – a set of measures that serves to assess the quality of representation of a multidimensional space on a surface. Dimensions are typically plotted to visualize the degree of association between levels of the two categories of variables. In CA, this graphic presentation is called a "map". The origin on the map represents the place where there is no difference among the profiles. The nearer a column(row) profile's vector location is to the origin, the closer it is to the average profile.

The algebraic basis of CA is decomposition of a matrix that represents relations between rows and columns into singular vectors and singular values (singular value decomposition). The sum of the squares of singular values equals the so-called inertia, which is chi-square calculated for a given table, divided by a sample size (n). A given singular value squared allows to assess the proportion of inertia explained by a given dimension. The quality of displaying the correlations within a table on a lower number of dimensions allows to assess the share of inertia of a given dimension in the total inertia of a table.

In the subject literature, it is very difficult to find results of similar studies conducted in the EU. Studies concerning the preferences of drivers in terms of oils are usually commissioned by concerns that produce oils or editors of automotive magazines (for the target groups). The present study fills the gap in the subject literature.

3. Presentation and analysis of study results

3.1. Characteristics of the sample

Table 1 presents the demographic attribute of the sample. As the questionnaire referred to the oil industry, the questionnaire sample was skewed towards male respondents – very often common in literature (Peters et al., 2015). Younger Poles (20-30 years of age) were more inclined to take part in the study, which was compatible with other research conducted in the Polish context (Smol et al., 2018).

The selected sample had the following characteristics:

- 80% of the respondents were between 18 and 40 years old, with those between 20-30 years (50.2%) being dominant,
- 20% of respondents were older than 40,
- 52% of respondents had completed a higher education (bachelor's or master's degree),
- 26% of respondents had a secondary education, 17.7% of respondents indicated that they were in college,
- About 4% of respondents had basic education or relatively lower education levels.

Table 1. The demographic characteristics of the sample (n=1446)

Gender		**Age**	
Male	84.5%	20 and below	4.3%
Female	15.5%	21-30	50.2%
Not specified	–	31-40	25.7%
Place of residence		41-50	12.9%
Rural area	17.2%	51 and over	6.9%
City up to 50,000 residents	12.4%	**Education**	
City up to 100,000 residents	7.1%	Basic education /vocational education and lower secondary education	4.3%
City up to 250,000 residents	10.2%	In college	17.7%
City above 250,000 residents	53.1%	Secondary education	26.0%
		Higher education	52.0%

3.2. Car drivers' knowledge about engine oil

The question about the frequency of oil change was the first issue that respondents were asked to answer. They were to select the best answer from the given alternatives. The results are presented in Fig. 1.

Changing the oil after driving 10,001-15,000 km was indicated by the majority (48%) of participants. Changing the oil after a year regardless of the number of kilometres travelled or during a mandatory inspection according to the service book was the most suitable answer for 17% of respondents. 14% of respondents reported changing oil in their car after driving 15,001-20,000 km, 6% after driving more than 20,000 km and 7% after driving less than 10,000 km. Approximately 8% of those surveyed selected one of the three options: With different frequency – I do not pay attention to mandatory vehicle check periods (5.3%), I do not change it at all (I only top it up) (1.1%), I do not know (1.4%). These participants ignore manufacturer's recommendations as to oil change time and therefore risk damage to their cars as well as to the environment. Used oil is characterised by an increased content of harmful components which then interfere with the recovery process and have toxic effect on ecosystems if released to the environment.

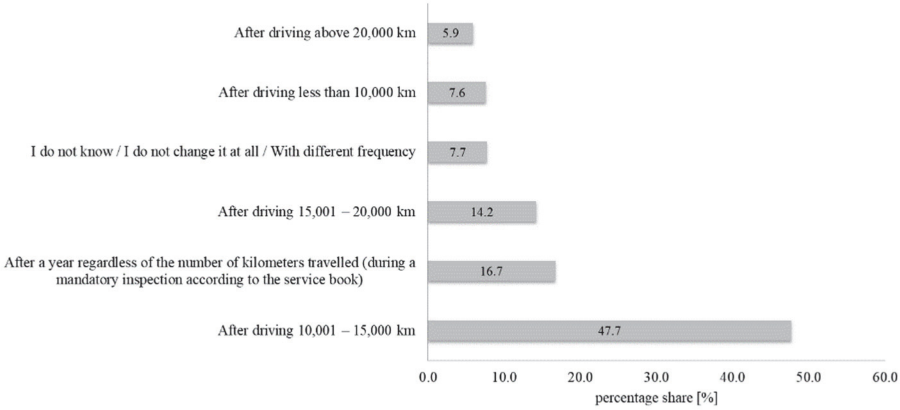


Fig. 1. Frequency of oil change among respondents

The second question was related to the factors influencing the decision of car drivers about the time of engine oil change (Fig. 2).

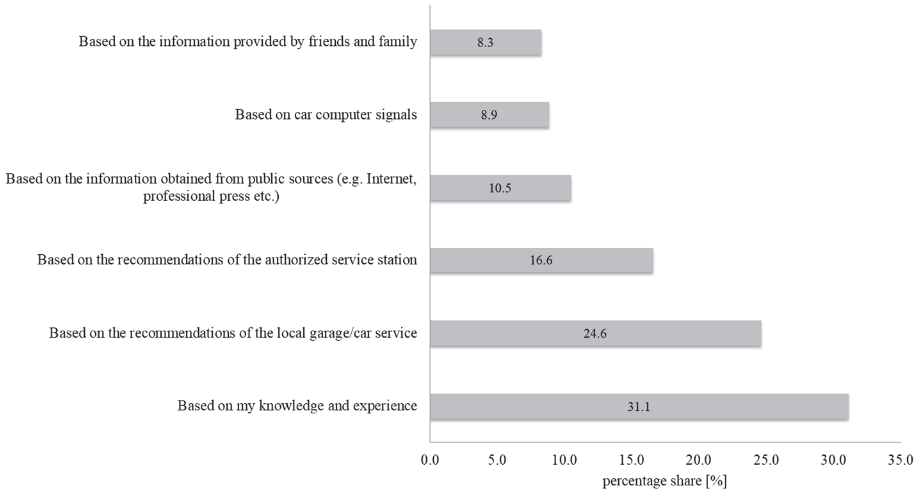
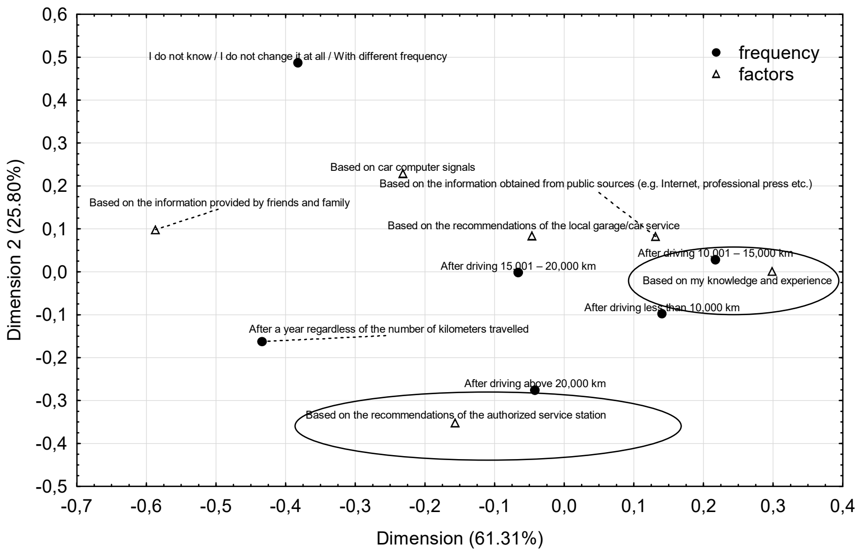


Fig. 2. Factor determining the oil change interval

Almost 1/3 of the respondents (31%) determined the oil change time based on their knowledge and experience. For 42% of respondents, the recommendations of the local garage/car service (25%) or recommendations of the authorized service station (17%) were the most significant factors. Based on the assumption that service stations staff are knowledgeable about engine oils, one can expect that the chosen oil change time will be optimal. Almost 9% of respondents decided on the time of engine oil change based on car computer signals. Approximately 18% of those surveyed believed that the most adequate factor to indicate the suitable time is the information provided by friends and family (8%) or obtained from public sources (e.g. Internet, professional press etc.) (10%). The obtained results confirm the complexity of the studied subject. There is no one dominant criterion which drivers take into consideration when deciding on the optimal use time for their cars (Smith & Sutton, 2011).

Figure 3 depicts the map of frequency of oil change among respondents and factors determining the oil change interval.



Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,26	0,07	61,31	61,31	97,65
2	0,17	0,03	25,80	87,10	41,09

Fig. 3. Correspondence analysis map of the frequency of oil change among respondents plus factors determining the oil change interval and Inertia decomposition

Dimension 1 is represented by the horizontal axis, dimension 2 – by the vertical axis. A two-dimensional space (two axes) explains more than 87% of total inertia. Although distances between categories of frequency of change and factors determining decision are not mathematically set, their degree of "clustering" or nearness of points on the map with regards to their angle from the origin and directs in the same quadrant can be used as outlines to interpret relationships between column and row variables. We can see that respondents changed the oil in their cars after driving 10,001-15,000 km, determining the oil change time based on their knowledge and experience. Therefore, in the case of those who change the engine oil after 10,001-15,000 km, the decision was governed by their knowledge and experience more often than in the case of the rest of respondents. Moreover, dimension 2 indicates that a relatively higher number of drivers who change the oil after driving more than 20,000 km follow the recommendations of authorised service stations. Car manufacturers systematically prolong the oil change intervals by using synthetic oils which, fortified with additives, guarantee long and reliable engine operation. As per the obtained results, prolongation of the oil use periods is noticeable mainly in the case of the group of respondents who follow the recommendations of authorised service stations. Among the people who decide based on their own knowledge, the oil change intervals are shorter. It can be due to incomplete knowledge and following recommendations which are no longer valid or can be caused by difficult conditions of oil use – e.g. short-distance city driving.

A vast majority of respondents (80%) have the oil changed in a garage/car service (67.5%) or in authorised service stations (12.9%) (Fig. 4), which may suggest that the oil will be managed properly and recycled. Changing the oil on one's own (only every fifth respondent changes oil at their own or their friend's garage) there is a significant risk of uncontrolled release of the oil to the environment.

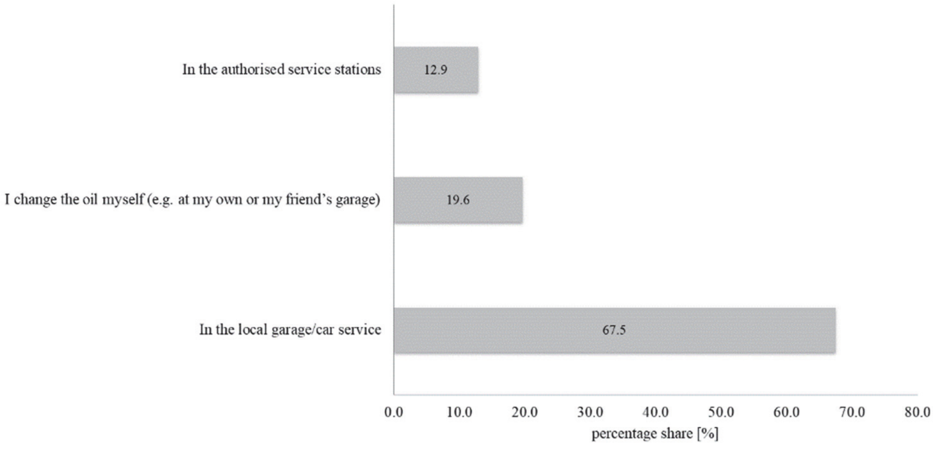
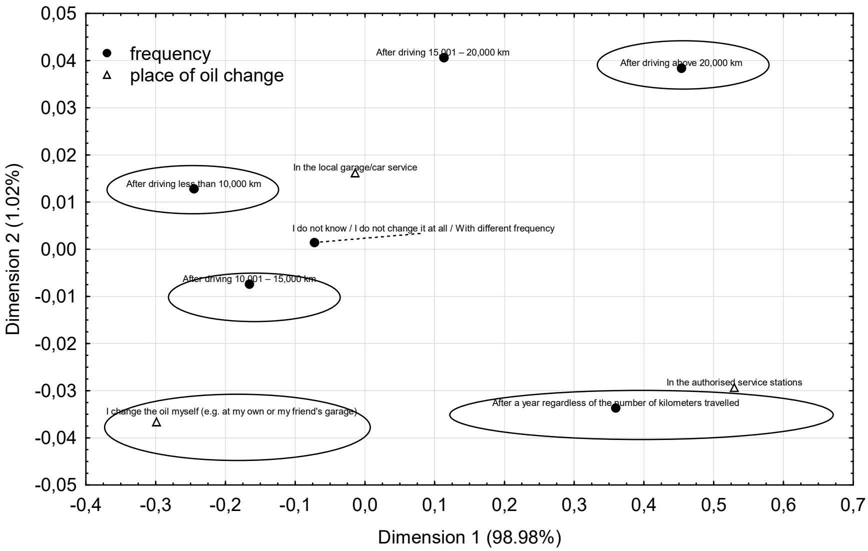


Fig. 4. Place of oil change

Figure 5 depicts the map of the frequency of oil change among respondents and the place of oil change.

The obtained two-dimensional space provides a summative explanation of 100% of total inertia. Changing the oil in authorised service stations has the highest contribution to total inertia. A relatively higher number of drivers who use the services of authorised service stations change the oil once year, regardless of the number of kilometres driven or after driving more than 20,000 km. The results of the correspondence analysis indicate that respondents who change the oil on their own (at their own or their friend's garage, etc.) most often change the oil after driving more than 15,000 km.



Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,23	0,05	98,98	98,98	77,74
2	0,02	0,00	1,02	100,00	0,80

Fig. 5. Correspondence analysis map of the frequency of oil change among respondents plus the place of oil change and Inertia decomposition

In the subject literature, there are no detailed reports of the influence of top-ups on the chemical and physica properties of engine oils and therefore this aspect was also included in the questionnaire. In their paper, Zając et al. focused on determining the influence of topping up the oil during car use on the change of concentration of chosen trace elements (Zając et al., 2018). They have demonstrated that topping up the oil by 10% of the capacity of the oil sump caused an increase in the concentration of the analysed elements from 0.4% to 7% (w/w), depending on the element and the studied oil.

According to the study, 57% of respondents declared topping up engine oil during use – 30% of them declared the amount of less than 0.5l of top-ups between oil changes 19% – 0.5-1l and 8% – more than 1l (Fig. 6). 43% of respondents do not top up the oil in intervals.

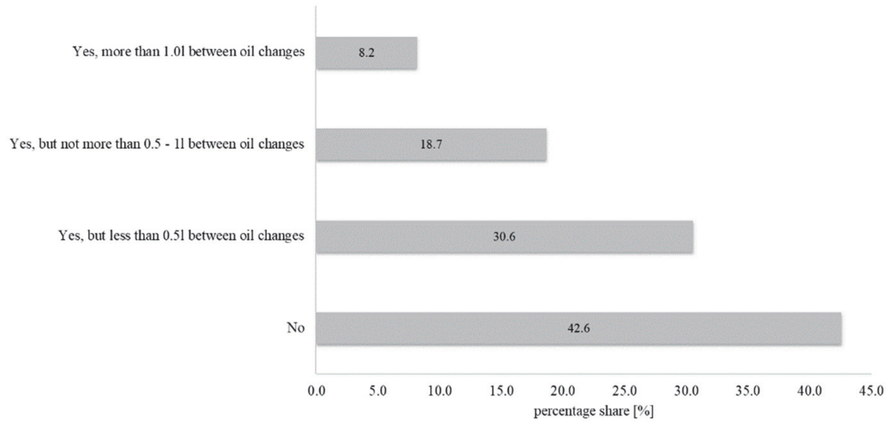
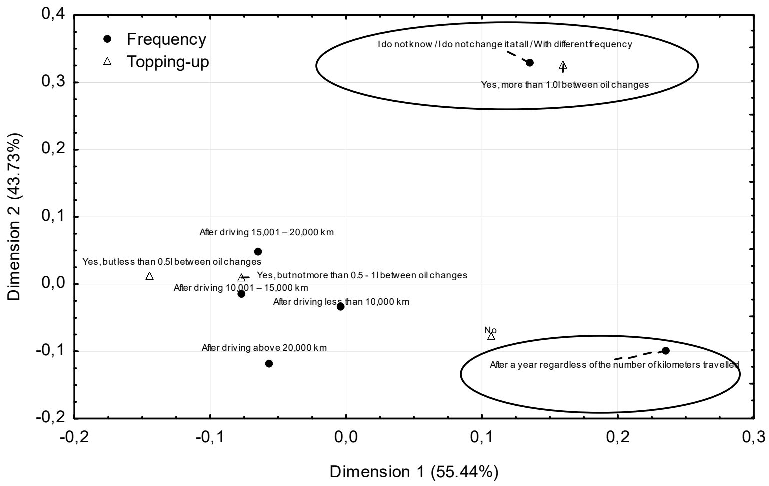


Fig. 6. Topping up engine oil

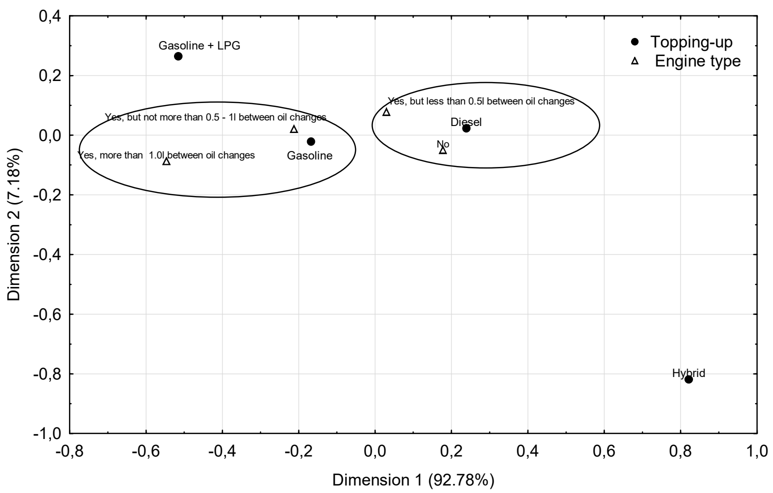
Applying correspondence analysis to the obtained results resulted in a two-dimensional space explaining more than 99% of total inertia (Fig. 7). Drivers who declared topping up the oil by more than 1l in intervals, stated more often than the others that they do not change the oil in their cars or change it with varied frequency, without keeping track of the mileage. A relatively higher number of drivers who do not top up the oil change it regularly once a year, regardless of the number of kilometres driven. Figure 8 shows that diesel car drivers either do not top up the oil or only top it up by less than 0.5l. Diesel engine cars are fitted with DPF systems which increase the content of fuel in engine oil and therefore the level of oil is correct, which does not imply that the oil is in good condition. Among petrol car users, more of them top up the oil by 0.5-1l and above 1l. The top-ups are due to oil loss caused by evaporation or leaks. The top-ups can result in keeping the oil in a good condition for a longer time (oil refreshment).

The next step of the presentation of the obtained results was to examine whether the frequency of oil change is related to the place of residence, level of education and age of car owners. On analysing Fig. 9, it can be noted that dimension 1 that explains nearly 74% of total inertia is the dominating one. Dimension 2 explains only 17.4%. On analysing the perceptual map, a significant division can be noted between the group of people from rural areas who change the oil after a relatively low number of kilometres driven (below 10,000 km).



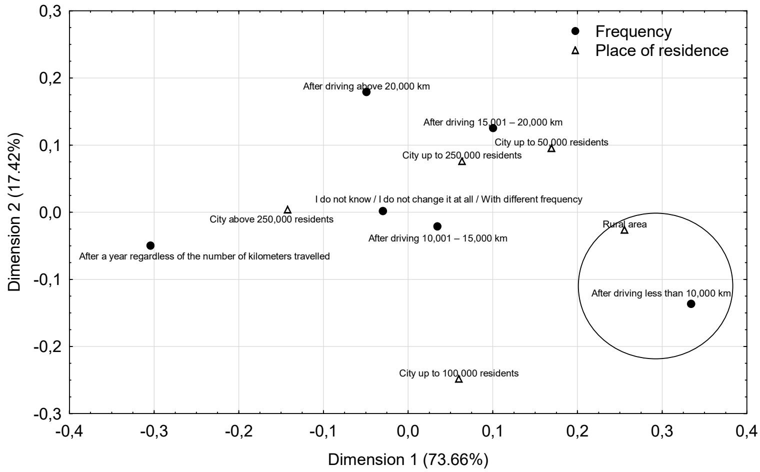
Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,12	0,01	55,44	55,44	20,77
2	0,11	0,01	43,73	99,17	16,38

Fig. 7. Correspondence analysis map of the frequency of oil change among respondents plus topping up the engine oil and Inertia decomposition



Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,22	0,05	92,78	92,78	67,16
2	0,06	0,00	7,18	99,96	5,16

Fig. 8. Correspondence analysis map of engine type plus topping up the engine oil and Inertia decomposition

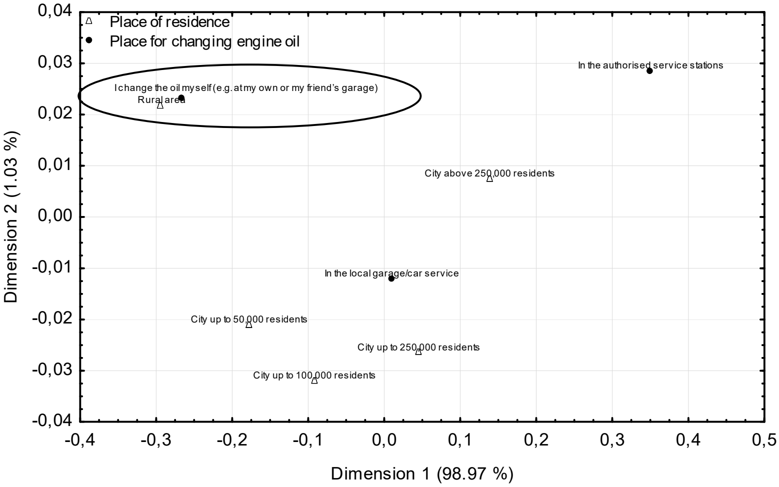


Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,16	0,03	73,63	73,63	37,90
2	0,08	0,01	17,42	91,05	8,96

Fig. 9. Correspondence analysis map of the frequency of oil change among respondents plus place of residence and Inertia decomposition

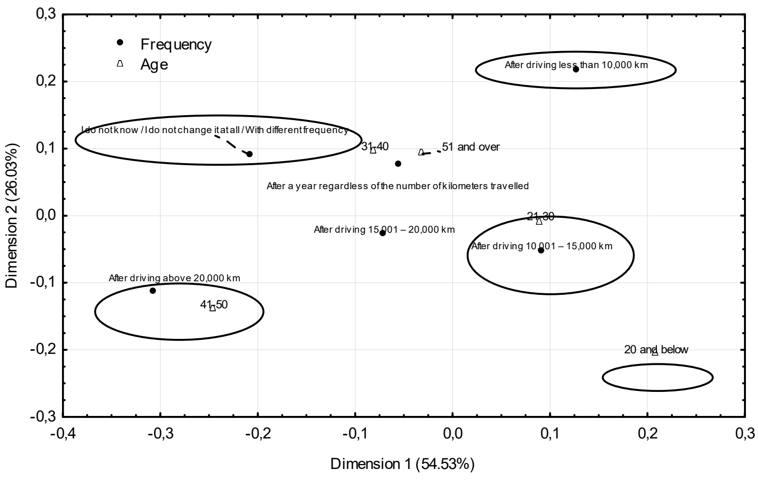
Additional analysis of correlations between the place of residence and place of oil change (Fig. 10) shows that the respondents from rural areas change the oil on their own more often than respondents from those living in agglomerations. It may be due to the fact that in rural areas there are fewer car services and therefore drivers who have basic knowledge about oil change decide to do it in their own garages. However, the place of use (rural area) seems not to be a sufficient reason for changing oil after driving less than 10,000 km. It seems to be rather due to the fact that drivers decide based on their own knowledge which may not be sufficient to determine the time of oil change.

On analysing Fig. 11, it can be noted that, in total, the two-dimensional space explains only above 80% (the least of all the analysed variables). Dimension 1 explains more than 54% of inertia, while dimension 2 – above 26% of total inertia. On analysing the perceptual map, a clear division into two groups can be noted: (1) young drivers (up to 30 years of age) more often than older drivers state that they change the oil after driving up to 15,000 km, (2) drivers between 41-50 years of age relatively more often change the oil after driving more than 20,000 km, do not change it at all or alternatively top up the oil or change it with varied frequency.



Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,17	0,03	98,97	98,97	42,96
2	0,02	0,00	1,03	100,00	0,45

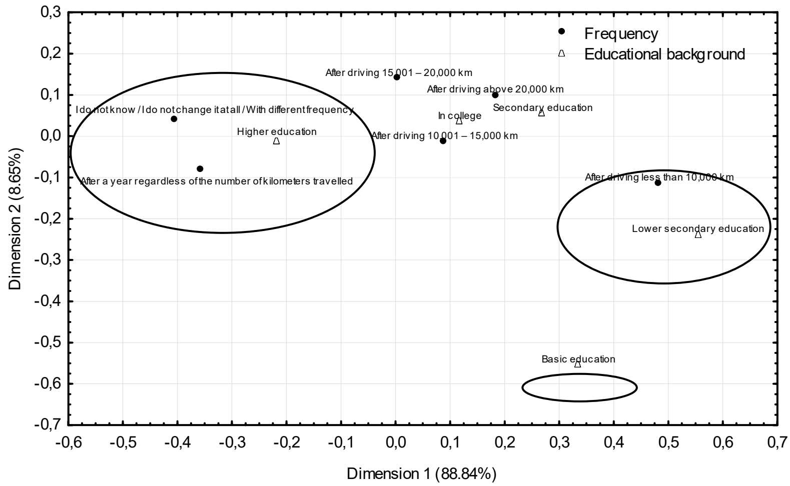
Fig. 10. Correspondence analysis map of place for engine oil change plus place of residence and Inertia decomposition



Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,12	0,02	54,53	54,53	22,26
2	0,09	0,01	26,03	80,56	10,63

Fig. 11. Correspondence analysis map of the frequency of oil change among respondents plus their age and Inertia decomposition

The level of education is another variable for which a perceptual map was created. On analysing it, it can be noted that dimension 1, which explains nearly 90% of inertia, is significantly dominant, whereas dimension 2 explains only nearly 9% (Fig. 12). On analysing the mutual position of the marks representing the frequency of oil change and the level of education, it can be noted that two clusters have been formed: (1) drivers with basic and lower secondary education who relatively more often than those with higher education change the oil after driving not more than 10,000 km, (2) drivers with higher education who change the oil every year regardless of the number of kilometres driven (presumably due to convenience/lack of time) or do not change it at all, top up the oil or alternatively change the oil with varied frequency.



Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,24	0,06	88,84	88,84	83,36
2	0,07	0,01	8,65	97,49	8,12

Fig. 12. Correspondence analysis map of the frequency of oil change among respondents plus educational background and Inertia decomposition

The next step was to analyse whether the frequency of engine oil change is related to the car mileage, year of manufacture, engine type, engine capacity and the percentage share of the car use in urban /extra-urban driving conditions. Table 2 combines respondents' answers related to the specification of cars they drive and the character of use (urban / extra-urban driving).

Table 2. Detailed specifications of the cars used by the survey respondents (n=1446)

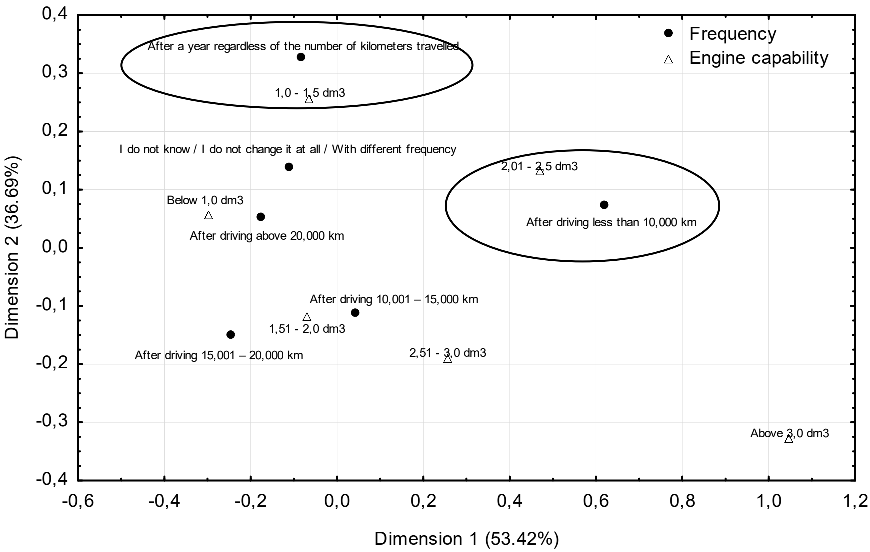
Car mileage [km]		Engine	
<50,000	8.8%	Diesel	55.7%
50,000-99,999	11.1%	Gasoline	42.2%
100,000-149,999	13.9%	Hybrid/Gasoline+LPG	0.3%/1.8%
150,000-199,999	18.1%	**Year of car manufacture**	
200,000-249,999	24.6%	<1994	1.0%
250,000-300,000	14.8%	1995-1999	8.7%
>300,000	8.7%	2000-2004	29.5%
The percentage share (0-100%) of the car use in city driving conditions		2005-2009	33.7%
0%-10%	0.7%	2010-2014	17.8%
11%-20%	1.4%	>2015	9.3%
21%-30%	4.4%	**Engine capacity**	
31%-40%	6.4%	Below 1.0 dm^3	1.8%
41%-50%	6.9%	1.00-1.50 dm^3	25.6%
51%-60%	9.5%	1.51-2.00 dm^3	59.6%
61%-70%	9.3%	2.01-2.50 dm^3	9.1%
71%-80%	18.5%	2.51-3.00 dm^3	2.5%
81%-90%	19.6%	Above 3.00 dm^3	1.4%
91%-100%	23.3%		

The sample had the following characteristics:

- over 50% of the cars covered an overall mileage of more than 200,000 km, with the range of 200,000-249,999 km (24.6%) being dominant,
- almost 20% of the cars covered a mileage lower than 100,000 km,
- the majority of the respondents (61.4%) declared above 70% share of the car use in city driving conditions,
- 55.7%% of respondents had cars with diesel engines, 42.2% of respondents had cars with gasoline engines,
- the year of manufacture of over 60% of cars was later than 2005, with the range of 2005-2009 (33.7%) being dominant,
- less than 10% of respondents drove cars older than 18 years old (year of manufacture earlier than 2000),
- over 85% of the car engines had the capacity below 2.00 dm^3, with the range of 1.51-2.00 (59.6%) being dominant.

The results of correspondence analysis for the variables from Table 2 are displayed in Figures 13-17.

On analysing Figure 13, it can be noted that dimension 1 is strongly influenced by the group of drivers who have cars with engine capacity of 2.0-2.5 dm^3 (inertia = 0.47), whereas dimension 2 is dominated by the group of drivers who drive cars with engine capacity of 1.0-1.5 dm^3 (inertia = 0.58). Relative inertia for the two engine capacities is above 0.5 (0.51). Based on the conducted study, a relation was confirmed between drivers who have cars with engine capacity of 1.0-1.5 dm^3 and changing oil once a year regardless of the number of kilometres driven, as well as between drivers who have cars with engine capacity of 2.0-2.5 dm^3 and changing the engine oil after driving less than 10,000 km.

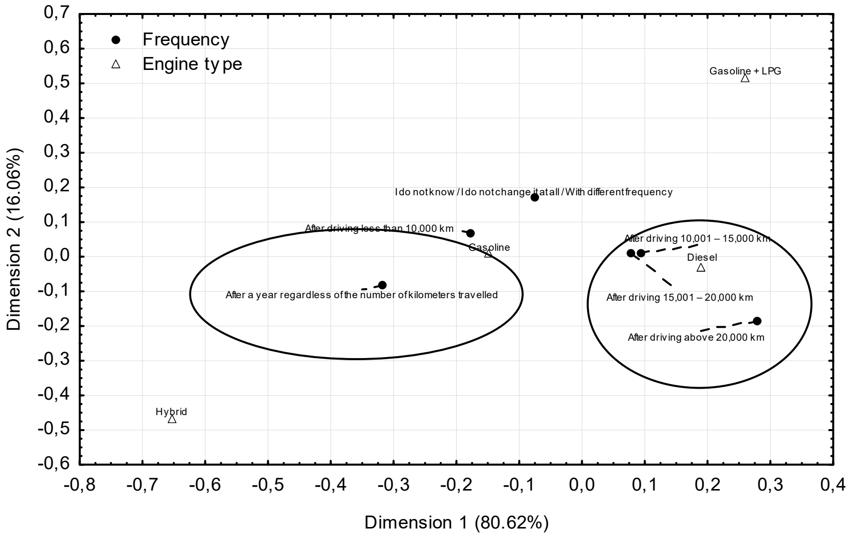


Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,21	0,04	53,42	53,42	61,34
2	0,17	0,03	36,69	90,10	42,12

Fig. 13. Correspondence analysis map of the frequency of oil change among respondents plus engine capability and Inertia decomposition

The obtained two-dimensional space for the type of engine variable indicates that dimension 1 explains more than 80% of inertia and is strongly influenced by both gasoline engines (inertia 0.41) and diesel engines (inertia 0.51) (Fig. 14). The significance of hybrid engines is very low (mass amounts to 0.0027 relative to e.g. 0.5574 for diesel engines). It is due to, inter alia, a low number of respondents driving cars with hybrid engines. Nevertheless, this category is well represented in the dimension. Respondents who drive cars with hybrid engines change the oil once a year regardless of the number of kilometres driven or after driving 15,001-20,000 km.

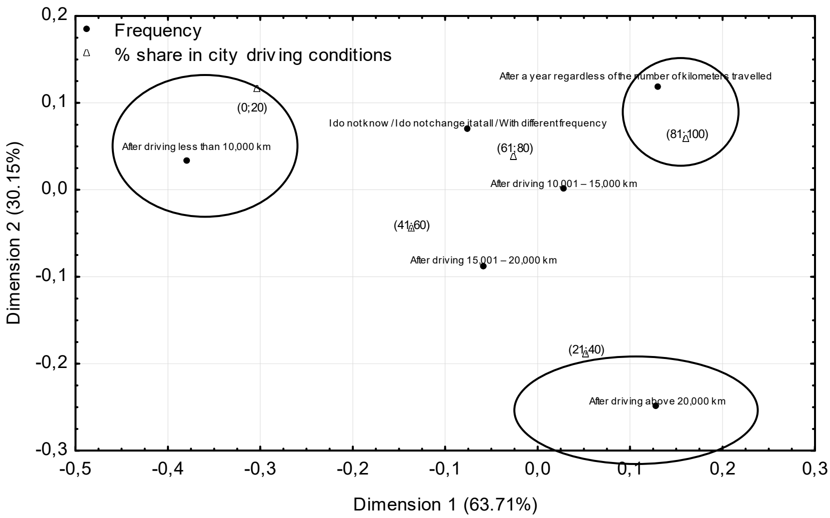
Drivers who drive cars with gasoline engines change the oil more frequently (after driving less than 10,000 km or after a year regardless of the number of kilometres driven) than those who drive cars with diesel engines (after driving more than 10,001 km).



Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,17	0,03	80,62	80,62	42,57
2	0,08	0,01	16,06	96,69	8,48

Fig. 14. Correspondence analysis map of the frequency of oil change among respondents plus engine type and Inertia decomposition

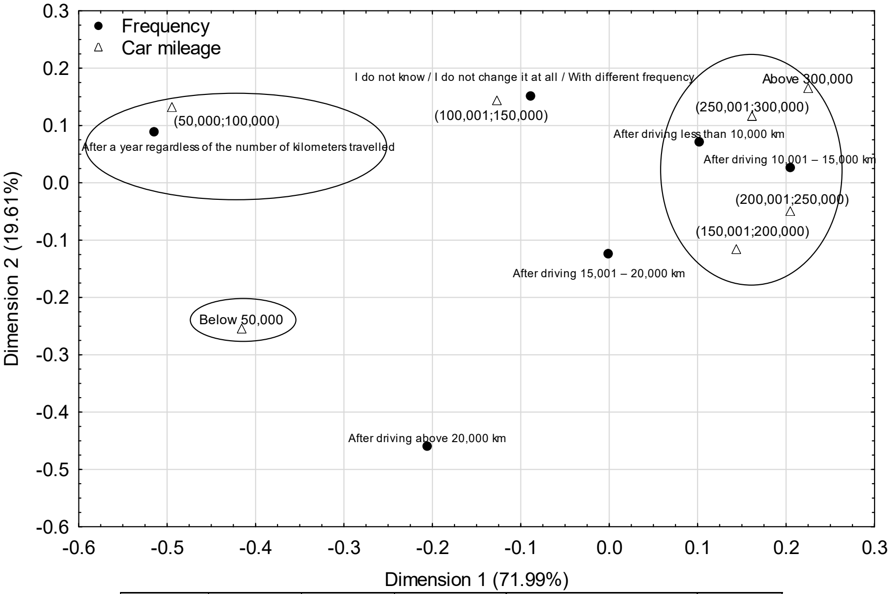
On analysing Figure 15 it can be noted that dimension 1 is strongly influenced by the category of drivers who declare the percentage share of city driving between 80%-100% (inertia = 0.43) and between 0%-20% (inertia = 0.32), whereas dimension 2 is strongly dominated by car drivers who declare the percentage share of city driving between 20-40% of total mileage within oil change intervals (inertia = 0.67). Applying correspondence analysis to establish the relation between the share percentage of city driving and frequency of oil change indicates several correlations: More drivers who use their cars in city driving conditions (around 80%) change the oil after driving less than 10,000 km. Among drivers who declare the share of city driving on the level of 21-40% there is relatively more drivers who change the oil after driving more than 20,000 km. The group of drivers who declare the percentage share of city driving on the level of 61-80% (the lowest relative inertia = 0.05) is underrepresented in the dimension. Its location may be misleading when assigning to an appropriate group representing the frequency of engine oil change.



Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,13	0,02	63,71	63,71	23,14
2	0,09	0,01	30,15	93,86	10,95

Fig. 15. Correspondence analysis map of the frequency of oil change among respondents plus % share in city driving conditions and Inertia decomposition

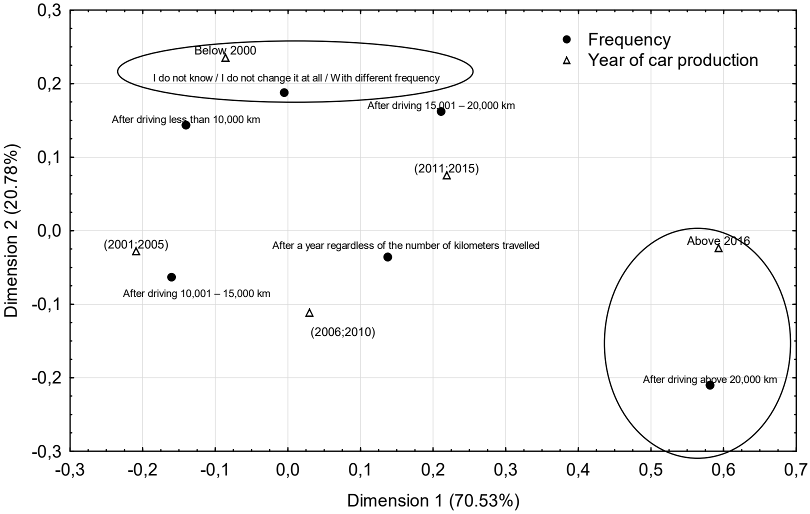
Figure 16 shows that the obtained two-dimensional space explains more than 91% of total inertia. It can be noticed that the group of respondents that changed the oil in their cars once a year regardless of the number of kilometres driven clusters with the group of respondents whose cars covered a mileage of up to 100,000 km (for dimension 1 the two categories are the strongest – "below 50,000" and "50,000-100,000", inertia = 0.26 and 0.40 respectively). Therefore, drivers who have cars with mileage of up to 100,000 km change the oil once a year regardless of the number of kilometres driven more frequently than the rest. Moreover, dimension 1 indicated that relatively more drivers who change the engine oil after driving not more than 15,000 km drive cars with total mileage not exceeding 150,000 km.



Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0.26	0.07	71.99	71.99	98.64
2	0.14	0.02	19.61	91.61	26.87

Fig. 16. Correspondence analysis map of the frequency of oil change among respondents plus car mileage and Inertia decomposition

On analysing Figure 17, it can be noted that dimension 1 explains over 70% of inertia and is strongly influenced by the category of drivers who drive cars not older than 3 years (year of manufacture later than 2015 – inertia = 0.44), whereas dimension 2 is dominated by drivers who drive cars older than 18 years (year of manufacture later than 2000 – inertia = 0.60). Applying correspondence analysis to establish the relation between the year of manufacture and the frequency of oil change indicates several correlations: Drivers who drive older cars (year of manufacture earlier than 2000) more often declare that they do not change the oil but only top it up, or else change the oil with varied frequency without a set schedule. Among drivers who drive new cars (year of manufacture earlier than 2015) the dominant frequency of oil change is after driving more than 20,000 km.



Dimension	Singular value	Eigenvalue	Percent of inertia	Cumulative Percent of inertia	Chi-square
1	0,21	0,04	70,53	70,53	62,75
2	0,11	0,01	20,78	91,31	18,49

Fig. 17. Correspondence analysis map of the frequency of oil change among respondents plus year of car production and Inertia decomposition

New cars are usually serviced in authorised service stations, which entails conducting an interim review and changing the oil regularly. Therefore, the oil change intervals are in line with the recommendations of the service stations, as displayed in Fig. 3. However, old cars (older than 18 years) users take care of their vehicles to a lesser extent, hence the less frequent oil change. Changing the oil is an additional expense, which drivers may perceive as unnecessary if their cars are of low value. For this reason, some respondents in the group do not change the oil at all or do it occasionally.

4. Conclusions

To sum up the study results presented above, it should be emphasised that applying the correspondence analysis tool allowed to prove numerous correlations between the frequency of oil change and particular variables, which can be helpful in the assessment of the behaviour of car users as to oil change. The most important correlations are the following:

1) More than 90% of respondents change the oil regularly (the highest percentage of respondents (48%) change the oil after driving 10,001-15,000 km). However, more than 7% of respondents ignore the significance of regular oil change thus risking damage to their cars and to the environment.

2) Almost 1/3 of the respondents (31%) determined the oil change interval based on their knowledge and experience. For 42% of respondents, the recommendations of a local garage/car service (25%) or recommendations of an authorized service station (17%) were the most important factors.
3) A relatively higher number of drivers who change the engine oil after driving 10,000-15,000 km choose the oil change time following their own knowledge or experience.
4) A relatively higher number of drivers who change the oil after driving more than 20,000 km follow the recommendation of authorised service stations.
5) 57% of respondents declared topping up the oil during use. Drivers who declare topping up the oil by more than 1l in intervals, more often than others indicated not changing the engine oil or changing it with varied frequency, without following any schedule.
6) Young drivers (up to 30 years of age) more often than older drivers declare changing the oil after driving up to 15,000 km. Drivers between 41-50 years of age relatively more often drive more than 20,000 km without changing the oil, or do not change the oil at all, or alternatively top up the oil or change the oil with varied frequency.
7) Drivers with basic or lower secondary education relatively more often than those with higher education change the oil after driving no more than 10,000 km. Drivers with higher education who change the oil once year regardless of the number of kilometres driven or do not change the oil at all tend to top up the oil or change it with varied frequency.
8) Owners of cars with 1.0-1.5 dm^3 engine capacity more often than others change the oil after a year, regardless of the number of kilometres driven. Owners of cars with 2.0-2.5 dm^3 engine capacity more often than others change the oil after driving less than 10,000 km.
9) Drivers who use their car mostly in city-driving conditions (around 80% of time) more often change the oil after driving less than 10,000 km. Among drivers who drive in city-driving conditions for 21%-40% of time, there are relatively more drivers who change the oil after driving more than 20,000 km.
10) Drivers who drive cars with a mileage of up to 100,000 km more often than others change the oil once a year regardless of the number of kilometres driven.
11) Drivers who drive older cars (year of manufacture earlier than 2000) more often than others state that they do not change the oil but only top it up, or alternatively change the oil with varied frequency without a set schedule. Among drivers who drive new cars (year of manufacture later than 2015) the dominant frequency of oil change is after driving 20,000 km.

For obvious reasons related to car use, oil should be changed at a mileage recommended by the car manufacturer. Every oil change is an additional expense for a car owner and therefore one would expect that drivers tend to delay the oil change rather than doing it earlier than recommended. However, the results of the study show that drivers tend to change the engine oil earlier than it is recommended by the car manufacturer. The results of the study also proved that there is no one decisive factor which determines the oil change time. Around 40% of drivers follow the recommendations of authorised service stations or car services when scheduling oil change. Also, around 40% follow either their own experience or recommendations of friends and family. The first group tends towards a maximisation of the number of kilometres driven (more than 20,000 km), whereas according to the second group, oil should be changed earlier (after driving 10,000-15,000 km). Unfortunately, not having conducted a study that includes sampling of used engine oils (a study of physico-chemical properties), it is difficult to determine which choice is the right one.

A positive side of the study is that a vast majority of drivers (80%) have oil changed in car services and authorised service stations and only 20% change it on their own. Such a pattern guarantees that a significant part of waste oil is properly collected and managed. Changing oil on one's own increases the risk of it being released to the environment or managed in a manner contrary to the existing rules.

A bigger education campaign connected with scientific research seems to be necessary in order to establish clear guidelines for optimal oil change intervals. The most important recommendations for a potential educational campaign should include:

1) authorised laboratory test results confirming the actual oil lifetime, expressed as a number of kilometres travelled (about 10% of the respondents ignore the importance of regular oil change)
2) hierarchy of variables affecting the extension / reduction of the lifetime of lubricating oils (e.g. urban driving, extra-urban driving).
3) benefits of changing oil in specialist authorised service centres / car workshops / maintenance institutions.
4) making drivers aware of how the used/waste oil is being recycled.
5) making drivers aware of the serious consequences of the release of used/waste oil into the environment.

Changing oil too early (unconsciously) leads to detrimental effects, including a negative impact on the environment. It is estimated that approximately 45 million tonnes of waste oil are generated each year, which means that about 126,000 tonnes of such waste are collected on a daily basis. So, with each passing day, a conscious use of engine oils becomes a measurable benefit, translating into a reduced amount of used/waste engine oil, of which only a small part is being fully recycled, whereas about 60% of it still poses a potential threat to the environment.

Just like with any research, especially those empirical in nature, the analysis presented in this article has its limitations. These are mainly conditioned by the method of the sample selection and the sample size. Above all, the population was limited to engine oil buying people in Poland. Another potential limitation of the research affecting the correctness of the results obtained are slight deviations in the composition of the studied group from the typical driver population. There is a minor overrepresentation of drivers from cities and drivers with higher education.

Initial steps have been taken to expand the scope of the study to other countries. Scientific centres in the UK, Switzerland, Spain, Slovakia, the Netherlands, Germany, Czech Republic and Belgium are currently conducting studies.

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Abstract

Used engine oils are considered hazardous waste. They contain many potentially harmful substances. The amount of engine oil in passenger cars is not big however, due to the number of cars in use, the overall amount used in the EU amounts to several million tons. Despite the fact that engine oil change interval is generally set by the car manufacturer, usually it is rather determined by the knowledge and attitude of drivers. Timely oil change, apart from having an obvious influence on the engine wear process, also has a big impact on the environment. Therefore, studying the motives and factors which govern the oil change is crucial for optimizing the period of engine oil exploitation. The paper presents the results of a questionnaire on the frequency of oil change, the factors influencing the oil change time, the place of oil change and oil top ups. Moreover, thorough research has been conducted to connect the frequency of oil change with additional factors influencing the level of degradation of the engine oil. More than 1400 drivers participated in the study. The results were analysed with the use of correspondence analysis. The results presented in the paper show various correlations between the frequency of oil change and particular variables thus allowing for an assessment of drivers' behaviour with regard to oil change. A need has been identified to implement a bigger education campaign concerning the oil change time and conduct research in order to establish guidelines for optimal oil change intervals.

Keywords:
waste lubricant oil (WLO), oil degradation, environmental impact and damage, engine oil change schedule, public awareness, public attitudes, questionnaire, predicting car drivers' behaviour

Empiryczna analiza czynników wpływających na częstotliwość wymiany oleju silnikowego w aspekcie środowiskowym

Streszczenie

Oleje silnikowe zalicza się do odpadów niebezpiecznych. Zawierają wiele substancji niebezpiecznych (np. wielopierścieniowe związki oraz węglowodory aromatyczne). W samochodach osobowych ilość oleju silnikowego nie jest duża, niemniej jednak liczba poruszających się pojazdów powoduje, że ilość oleju w obiegu ogólnym w EU jest rzędu kilku milionów ton. Mimo że termin wymiany oleju jest zazwyczaj określany przez producenta pojazdu to w rzeczywistości jest on pochodną wiedzy i zachowania kierowców. Terminowa wymiana oleju silnikowego w pojazdach oprócz oczywistego wpływu na zużycie silnika ma również duży wpływ na środowisko. Zbyt wczesna wymiana zwiększa ilość olejów odpadowych i powoduje większe zużycie zasobów naturalnych, natomiast zbyt późna wymiana oleju powoduje nadmierną akumulację szkodliwych związków w oleju. Stąd poznanie motywów i czynników, jakimi kierują się kierowcy przy wymianie oleju stanowi istotny element w optymalizacji długości eksploatacji oleju silnikowego. W pracy przedstawiono wyniki badań ankietowych w zakresie częstotliwości wymiany oleju, czynników wpływających na termin wymiany, miejsce wymiany oleju oraz stosowania dolewek oleju. Ponadto podjęto próbę powiązania częstotliwości wymiany oleju z dodatkowymi czynnikami (m.in. przebieg samochodu, eksploatacja miasto-trasa, pojemność silnika) wpływającymi na stopień degradacji oleju. Zebrano opinie ponad 1,400 użytkowników pojazdów. Do analizy wyników zastosowano opisową i eksploracyjną technikę analizy danych, jaką jest analiza korespondencji. Przedstawione w pracy wyniki pozwoliły wykazać istnienie wielu zależności pomiędzy częstotliwością wymiany oleju silnikowego a poszczególnymi zmiennymi, które pozwoliły ocenić zachowania użytkowników samochodów w zakresie wymiany olejów. Zdiagnozowano również konieczność przeprowadzenia szerokiej kampanii edukacyjnej w zakresie terminów wymiany olejów oraz badań naukowych, mających na celu opracowanie wytycznych związanych z optymalnym czasem eksploatacji oleju silnikowego.

Słowa kluczowe:
zużyty olej silnikowy, degradacja oleju, wpływ na środowisko i szkody,
harmonogram wymiany oleju silnikowego, świadomość społeczna, postawy społeczne,
ankieta, przewidywanie zachowania kierowców samochodów

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Assessment of the Impact of a Dammed Reservoir on Groundwater Levels in Adjacent Areas Based on the Przebędowo Reservoir

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1. Introduction

At present the term water management is used to refer to the process of water storage, use and protection, the removal of its excess and limitation of the resulting threats, as well as alleviation and elimination of water shortages (Kaca et al. 2011). As it was reported by Mioduszewski (2012) and Przybyła et al. (2014), water resources, modified mainly by precipitation and evapotranspiration, are characterised by considerable spatial and temporal variation, resulting in periods of deleterious water scarcity or floods causing considerable losses in river valleys.

One of the methods applied to counteract these adverse phenomena is connected with the construction of retention reservoirs, frequently located either in the river continuum (such as dam reservoirs) or outside it (lateral). According to Puczyńska and Skrzypski (2009) as well as Szczykowska and Siemieniuk (2011), water retention in dam reservoirs contributes to a considerable improvement of water balance. However, once water is dammed in retention reservoirs we may observe a certain change in the hydrologic conditions in the water systems. It frequently consists in a reduction of the fluctuations in river water stages and flows, as well as an increased depth of groundwater tables and soil moisture in the immediate vicinity of reservoirs (Górniak and Piekarski 1999, Król et al. 2010).Changes in hydrogeological conditions caused by damming structures within their impact zones may be beneficial, neutral or adverse (Michalec 2012). The intensity of changes caused by the constructed dam reservoir depends on the relief of the surrounding area, the size of the reservoir and primarily its capacity.

The higher the shores, the faster this impact declines, while the greater the mass of retained water, the farther its impact is extended (Traczewska 2012).

According to Zieliński (2015), knowledge on the mechanisms of function in anthropogenically transformed, lowland aquatic ecosystems under various hydrometeorological conditions is still insufficient, particularly in the context of sustainable water management, wherever the probability of hydrological stress in high.

The aim of this study was to assess the impact of the Przebędowo dam reservoir on the groundwater tables in adjacent areas after three years of its operation.

2. Material and methods

This paper presents results of studies conducted in 2015, 2016 and 2017 hydrological years in the catchment of the Przebędowo reservoir (in the areas adjacent to the reservoir) located in the Wielkopolskie province, 25 km north of Poznań in the Murowana Goślina commune (Fig. 1).

In terms of the physico-geographical regionalisation of Poland (Kondracki 2000) the study area of early postglacial landscape is located in the Wielkopolskie Lake District in the area of the Poznań Warta Gorge (315.52). In the discussed catchment of approx. 100 km^2 forests predominate, while to a lesser extent arable land is found in the area adjacent to the reservoir.

Overall the areas adjacent to the reservoir are composed of quaternary (Pleistocene) fluvial deposits, while the analysis of layers within piezometers showed a predominance of medium sands up to a depth of approx. 3m, with mean porosity of 36%, in which groundwaters form a continuous phreatic aquifer.

The analysed reservoir was established in the valley of the Trojanka river (from 6+915 km to 8+371 km of its course), being a depositional terrace with its slope towards the reservoir shores. It was constructed by the Greater Poland Provincial Land Drainage and Water Units Board in Poznań and put into operation in November 2014. The reservoir is located at 52°34'28"northern latitude and 17°00'33" eastern longitude. The earth dam of the reservoir is class IV it is 334 meters long and 3.30 meters high. The reservoir with a length of 1450 m and a maximum bed-width of 120 m at a normal pool level with an elevation of 72.5 m a.s.l. has a mean depth of 0.94 m and a flooded surface of 12.03 ha (Table 1). Around the reservoir an ecological buffer zone, the so-called transition zone between the reservoir and the surrounding utilised agricultural areas, with a mean width of approx. 13, was established as grassland with tree and shrub plantings. The role of this buffer zone is to reduce runoff of biogenic compounds and pesticides from adjacent agricultural areas.

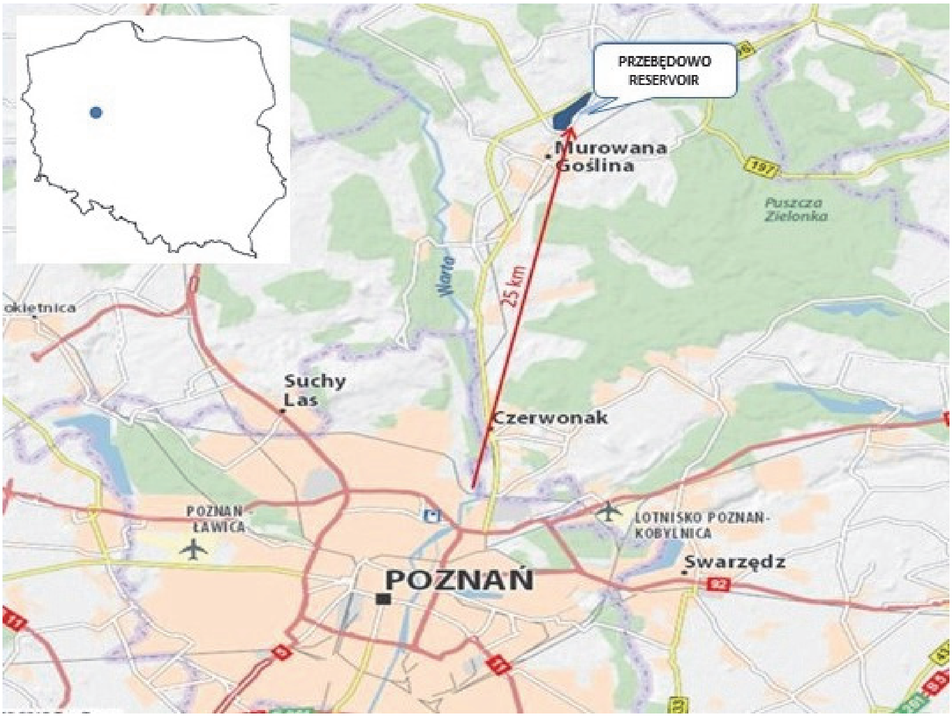

Fig. 1. Location of the Przebędowo reservoir in the Wielkopolskie province

Water levels in the reservoir were measured using a staff gauge located in the damming structure at the outflow of the reservoir (Fig. 2). Additionally water levels in the reservoir were recorded continuously using a hydrostatic probe, from which recorded data were sent to the telemetric module installed at the spillway tower.

In turn, groundwater levels were measured in 21 wells established in seven section lines in the immediate vicinity of the reservoir. Analyses were conducted for data recorded in 7 selected wells: no. P-2 and no. P-3 located in the area adjacent to the reservoir from the west and from no. P16 to. P18, as well as nos. P-20 and P-21 installed from the east. The other wells established during the reservoir construction works were not included in this study due to their location in the dam crest.

In the water year 2015 from mid-January a monitoring system was initiated in the discussed structure; for this reason the characteristics of water levels cover the period since that time point.

Further analysis was expanded to include data from six additional wells installed in April 2016, i.e. wells nos. 1', 2', 3', 4', 5' and 6', in terms of the elevation to the national grid and located in the area adjacent to the reservoir at a distance of approx. 10 m from its shores in three representative cross-sections (Fig. 3).

Water levels in the analysed years were measured once every two weeks. In turn, weekly water levels in the investigated wells were recreated by calculating mean values from the levels measured at 2-week intervals.

The number of days when groundwaters were fed by the water retained in the reservoir was determined in the analysed period based on the difference between the elevation of waters in the reservoir and those of groundwaters in the wells included in the study. Estimate of essentiality relations between water levels in reservoir and groundwater levels in analysed wells carried T-students method.

Table 1. Basic parameters of the Przebędowo retention reservoir

No.	Parameter	Unit	results
1	Structure class (earth dam)	class	IV
2	Length	m	1450
3	Maximum width	m	120
4	Shoreline length	m	2980
5	Pool levels: a/ Max. pool level (at $Q_{K0.5\%}$) b/ normal pool level c/ minimum pool level	 m a.s.l. m a.s.l. m a.s.l.	 73.00 72.50 71.50
6	Reservoir capacity: - maximum at max. pool level - total at normal pool level V_c - active capacity V_U - dead at min. pool level V_m	 m^3 m^3 m^3 m^3	 229 450 162 350 113 350 49 000
7	Flood control capacity between normal damming and maximum pool levels	m^3	67 100
8	Mean reservoir depth at: normal pool level minimum pool level	 m m	 0.94 0.38
9	Reservoir area: - normal pool level - minimum pool level	 ha ha	 12.03 10.64

Fig. 2. A staff gauge with a hydrostatic probe installed at the damming structure at the outflow from the reservoir

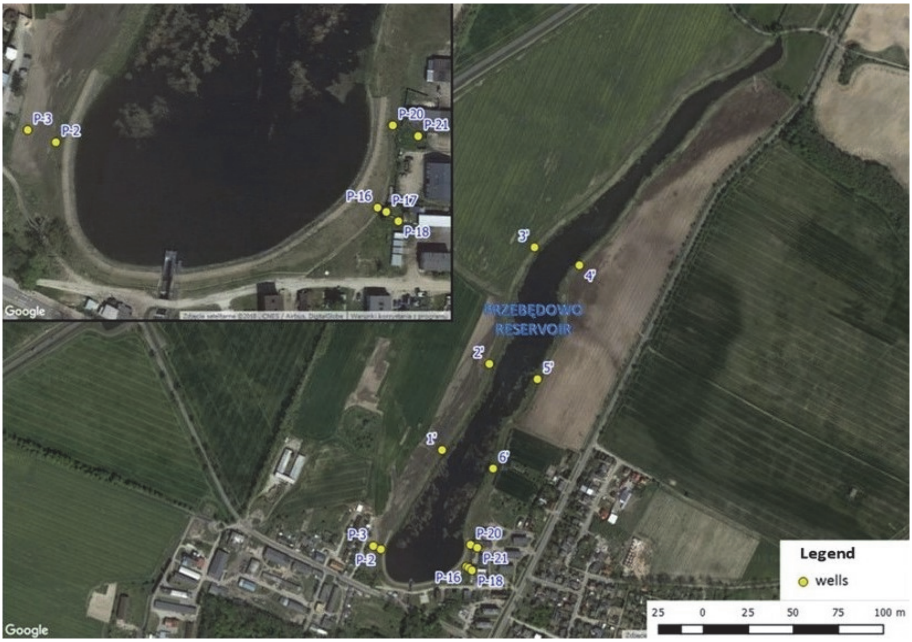

Fig. 3. Location of wells measuring groundwater levels in the area adjacent to the reservoir (source: the authors' study based on Google Earth – https://www.google.pl/intl/pl/earth/)

Results of water level observations in the investigated structure were used by permission of the Director of the former Wielkopolska Board of Land Amelioration and Water Facilities (at present State Water Holding Polish Waters; Regional Water Management Authority in Poznań).
Meteorological conditions in the investigated water years (precipitation and air temperature) in relation to the multiannual means of 2000-2015 were characterised based on the data recorded in the weather station of the Experimental and Teaching Station of the Forest Arboretum in Zielonka, located approx. 8 km south-east from the discussed reservoir. The station is located in the central part of the Puszcza Zielonka Forest at 91.00 m a.s.l., at 52°33′00″ northern latitude and 17°06'33" eastern longitude. It is situated approx. 24 km from the nearest station of the Institute of Meteorology and Water Management in Poznań Ławica (Grajewski 2013).

The characteristics of moisture conditions for the analysed water years was conducted according to Kędziora (1995, after Kaczorowska 1962) taking into consideration criteria contained in Table 2.

Table 2. Characteristics of moisture conditions in hydrological years

Type of year	% normal precipitation
Extremely dry	below 50
very dry	50-74
Dry	75-89
Average	90-110
Wet	111-125
Very wet	126-150
Extremely wet	over 150

This study included also documentation from the execution of geological works connected with the installation of piezometers in the Przebędowo small retention reservoir (2014) prepared by Geoprogram (W. Andrzejewski, R. Urban), the Water utility and water rights report (2009) and the Water management guidelines (2009), as well as the Detailed design of the Przebędowo reservoir (2011) prepared by Biuro Projektów Wodnych Melioracji i Inżynierii Środowiska „BIPROWODMEL” from Poznań.

3. Results and discussion

As it was reported by Bąk (2003), the Wielkopolska region is considered to be one of the driest and warmest regions of Poland. Polar-maritime air masses predominate over the area; as a result the summers are cooler and the winters are warmer when compared to the eastern, more continental part of Poland. Most frequently cold fronts move over the region and in the summer season they are often accompanied by storms, considerable fluctuations in temperature and increased wind speeds. Mean annual atmospheric pressure is approx. 1005 hPa – it is lowest in the spring (in April), slightly higher in the summer, while it reaches the maximum in the autumn (in October). According to that author one of the characteristics of the Wielkopolska climate is also related with the frequent, although irregular occurrence of precipitation-free periods, which has a negative effect on plant growth. In the 20-year period of 1981-2000 the long-term precipitation-free periods (lasting over 30 days) appeared in 9-year intervals. Precipitation-free periods were observed both in dry, average and wet years. The largest numbers of days with precipitation were recorded in the winter, whereas the greatest precipitation totals are observed in the summer.

The first hydrological year analysed in this study (2015) was a dry year, in which precipitation total was 429 mm and it was by 131 mm lower than the multi-annual mean at air temperature exceeding the mean by 0.5°C (Table 3). Both the winter and summer half-years of the discussed year, in which precipitation totals were lower than the multi-annual means by 54 mm and 77 mm, respectively, were classified as dry.

Table 3. Half-year and yearly precipitation totals (P) and mean air temperatures (t) in 2015, 2016 and 2017 hydrological years and their deviations from means of the multi-year period of 2000-2015

Period	precipitation P (mm)			Temperature t (°C)		
	winter XI-IV	summer V-X	year XI-X	winter XI-IV	summer V-X	year XI-X
Multi-year mean	**229**	**330**	**560**	**2.6**	**15.4**	**9.0**
2015	175	253	429	3.8	15.3	9.5
Deviation	**-54**	**-77**	**-131**	**1.2**	**-0.1**	**0.5**
2016	219	463	682	4.1	15.7	9.9
Deviation	**-10**	**133**	**122**	**1.5**	**0.4**	**0.4**
2017	211	593	804	2.5	15.6	9.1
Deviation	**-18**	**263**	**244**	**-0.1**	**0.2**	**0.1**

In turn, the hydrological year of 2016 was a wet year, in which the precipitation total was 682 mm and it was by 122 mm higher than the multi-annual mean, at air temperature exceeding the mean by 0.4°C. The winter half-year of that year with the precipitation total by 10 mm lower than the multi-annual mean and air temperature by 1.5°C higher than the mean was average and warm. In turn, the summer half-year of the discussed year was very wet, at the precipitation total exceeding the mean by 122 mm, at air temperature by 0.4°C higher than the mean.

The last hydrological year analysed in this study, i.e. 2017, was very wet, since precipitation total in that year exceeded the multi-annual mean by as much as 244 mm, at air temperature close to the mean. The winter half-year of that year, in which precipitation total was 211 mm and by 18 mmm lower than the mean, was average. In contrast, the summer half-year was extremely wet, since precipitation total in that half-year was 593 mm and exceeded the multi-year mean by 263 mm, at air temperature exceeding the mean by 0.2°C.

In the winter half-year of the first year analysed in this study, on 18 February the water elevation in the reservoir reached the maximum (72.49 m a.s.l.), which was maintained until 13 April (Fig. 4). In turn, groundwater levels in the analysed wells on that day reached values ranging from 70.72 m. a.s.l. (well P-21) to 71.7 m a.s.l. (well P-3) and it continued to increase. On 7 April maximum groundwater elevations in the investigated wells were recorded and they ranged from 70.85 m a.s.l. (well P-21) to 71.87 m a.s.l. (well P-3). From mid-April to the end of the analysed winter half-year the water table in the reservoir was dropping, while the groundwater tables in the adjacent area showed no greater variability. At the end of this half-year the water pool in the reservoir reached the elevation of 72.39 m a.s.l., while groundwater levels ranged from 70.85 m a.s.l. (well P-21) to 71.85 m a.s.l. (well P-3). From the beginning of the summer half-year of 2015, which in terms of moisture conditions was dry, both the water pool in the reservoir and groundwater levels in the adjacent area were decreasing. The lowest levels of reservoir water and groundwaters were recorded in the beginning of September. The water pool in the reservoir in that period was 71.89 m a.s.l. and it was 61 cm below the normal pool level, while the elevation of groundwaters in the analysed wells ranged from 70.65 m a.s.l. (well P-21) to 71.52 m a.s.l. (well P-3). A considerable effect on this situation was exerted by the adverse course of weather conditions, particularly low precipitation totals and high air temperatures in August. At the end of the discussed half-year, after total precipitation of 30 mm an increase was recorded in the water pool in the reservoir and in the analysed wells, the water pool in the reservoir was 72.26 m a.s.l., while groundwater elevations ranged from 70.7 m a.s.l. in well P-21 to 71.63 m a.s.l. in well P-3. It needs to be stated that over the entire analysed period from January to the end of October, except for the first week of observations, in which the reservoir served the drainage function, waters retained in the investigated reservoir fed groundwaters from the discussed wells, since elevations of the water pool in the reservoir were maintained over the elevations of groundwaters in the adjacent area (Fig. 4).

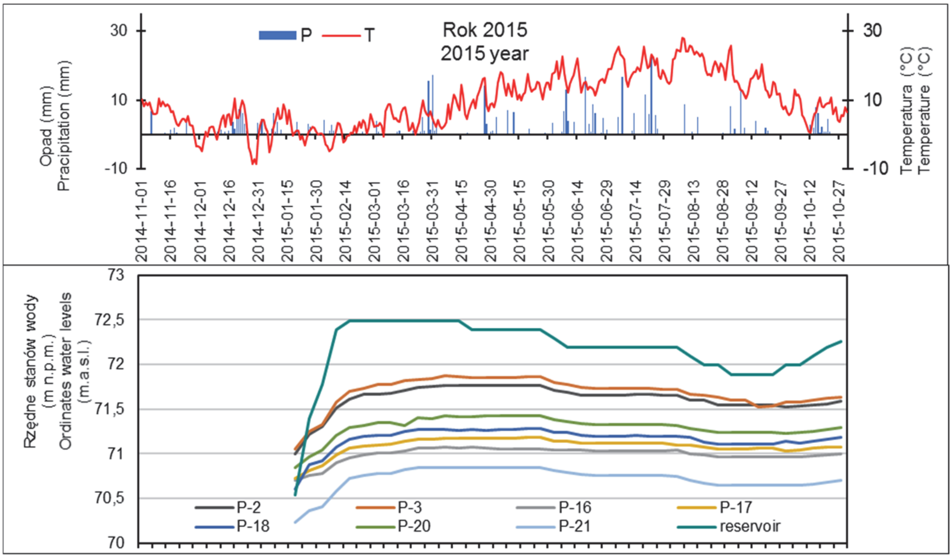

Fig. 4. Elevations of water pool in the reservoir and groundwater in analysed wells (m a.s.l.) against daily precipitation totals and mean daily air temperatures in 2015 hydrological year

In the beginning of the winter half-year of 2016 the water pool in the analysed reservoir was 72.28 m a.s.l., while the groundwater elevations in the adjacent area ranged from 70.72 m a.s.l. in well P-21 to 71.65 m a.s.l. in well P-3 (Fig. 5). Over the entire analysed half-year the water pool in the reservoir and groundwater levels in the adjacent area showed no marked variability, while their maximum values were recorded on 29 March. The water pool in the reservoir on that day reached 72.52 m a.s.l., while the groundwater levels in the area adjacent to the reservoir ranged from 70.88 m a.s.l. in well P-21 to 71.85 m a.s.l. in well P-3. It may be stated that over the entire discussed winter half-year the reservoir served the supply role, since elevations in the water levels exceeded elevations of groundwaters in the discussed wells.

Observations of groundwater levels in the additionally installed wells, i.e. wells 1' to 6', were started in the beginning of the summer half-year. The water pool in the reservoir in that period was 72.46 m a.s.l. and the groundwater elevations in the adjacent area ranged from 70.8 m a.s.l. (well P-21) to 72.96 m a.s.l. (well 5'). At the turn of May and June at low precipitation totals and higher air temperatures the water pool in the reservoir and groundwater levels in the analysed wells were observed to subside. In contrast, precipitation total of 229 mm recorded for the period from 13 June to mid-July caused an increase in water pools in the reservoir and groundwater levels. On 15 July the water pool in the reservoir reached the maximum elevation in that half-year, i.e. 72.59 m a.s.l. In turn, in some of the analysed wells the maximum pool was observed in the same day, while in some of them it was with a delay of 1 or 2 weeks and it ranged from 70.88 m n.p.m in well P-21 up to 73 m n.p.m in well no. 5'. At the end of this half-year the water pool in the reservoir had the elevation of 72.58 m a.s.l., while in the analysed wells the elevations ranged from 70.86 m a.s.l. (well P-21) to 72.89 m a.s.l. (well 5'). In the discussed half-year the elevation of the water pool in the reservoir was above those of groundwaters in most investigated wells. In turn, feeding of reservoir waters by groundwaters was observed over the entire half-year period from the area of well no. 5', as well as wells nos. 4' and 6' - this time to a limited extent. Groundwaters from the side of well no. 4' fed reservoir waters in that half-year for 63 days, while from well no. 6' it was for 28 days.

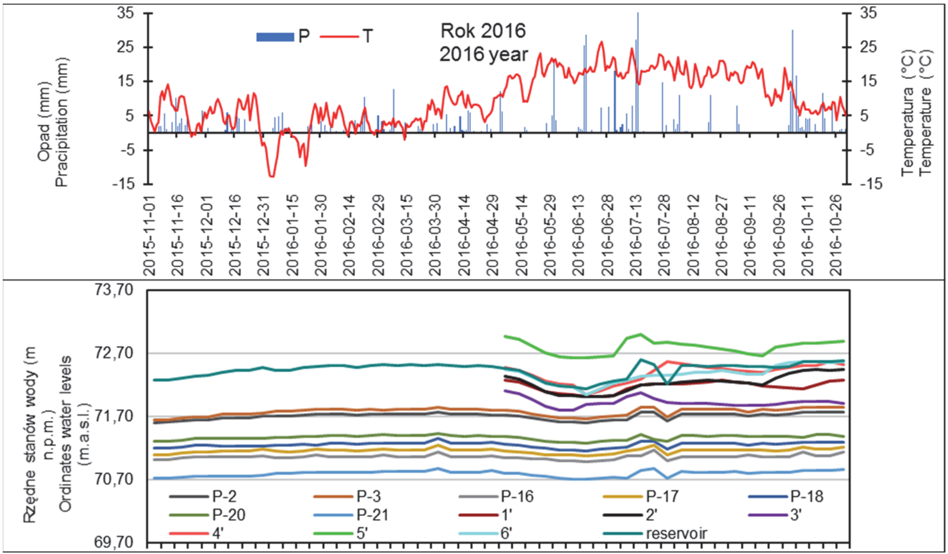

Fig. 5. Elevation of water pool in reservoir and groundwaters in analysed wells (m a.s.l.) against daily precipitation totals and mean daily air temperatures in 2016 hydrological year

In the beginning of the winter half-year of 2017 the water pool in the analysed reservoir ranged from 72.62 m a.s.l., maintained at 12 cm above the normal pool level (Fig. 6). In turn, the groundwater levels in the adjacent area in that period ranged from 70.87 m a.s.l. (well P-21) to 73.12 m a.s.l. (well 5').

The maximum water pool in the reservoir, i.e. the elevation of 72.83 m a.s.l., was recorded in that half-year on 15 December, while groundwater levels in the adjacent area on that day reached elevations close to the maximum and ranged from 70.94 m a.s.l. in well P-21 to 73.33 m a.s.l. in well no. 5'. Over the entire analysed winter half-year (181 days) groundwaters fed the reservoir waters from the side of well no. 5', while to a lesser extent feeding by ground-waters was also observed from wells nos. 1', 2', 3', 4' and 6', with the feeding time ranged from 28 days (well 1') to 112 days (well 4'). In turn, in the case of the other analysed wells, which were located closer to the damming structure, elevations of the water table were recorded below the elevations of the water pool in the reservoir and the direction of feeding was opposite. It may be stated that the recorded results were consistent, among other things, with the results of studies conducted by Głuchowska and Pływaczyk (2008) in the Odra river valley, below the Brzeg Dolny barrage, in which the authors stressed that upstream of the damming structure in its close vicinity water infiltration from the reservoir and feeding of the valley are observed.

In the beginning of the summer half-year of 2017, which in terms of precipitation was extremely wet, the water pool elevation in the reservoir was 72.59m a.s.l., while groundwater levels in the analysed wells ranged from 70.86 m a.s.l. in well P-21 to 73.32 m a.s.l. in well no. 5' (Fig. 6).

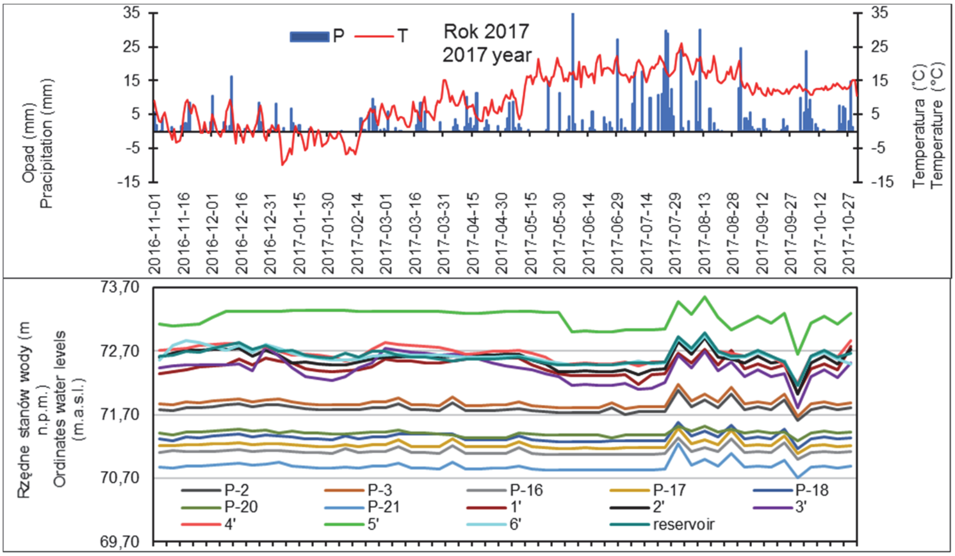

Fig. 6. Elevations of water pool in the reservoir and groundwaters in analysed wells (m a.s.l.) against daily precipitation totals and mean daily air temperatures in 2017 hydrological year

From the second decade of July to mid-August following precipitation total of 209 mm, which had been recorded in that period, an intense increase was observed in the water levels both in the reservoir and groundwaters in the adjacent area. The maximum water pool in the analysed reservoir, at the same time close to the maximum pool of 72.99 m a.s.l., was recorded on 13 August. On that day the maximum elevation was also observed for groundwaters in wells P-2'to P-6', where it reached values ranging from 72.70 m a.s.l. in well no. 3' to 73.55 m a.s.l. in well no. 5', respectively.

In turn, in the other analysed wells the maximum elevation of groundwaters was recorded two weeks earlier and ranged from 71.24 m a.s.l. (well P-21) to 72.17 m a.s.l. (well P-3). The intensive drop in the water pool levels in the reservoir and simultaneously in groundwaters in the adjacent area, which was observed in the second half of August, was not caused by the course of weather conditions, but rather by the opening of the so-called bottom outlets. This was connected with a very high water level in the reservoir, caused mainly by high precipitation totals in that period and the damming structure being jammed by vegetation debris, resulting in a threat of water overspill over the dam crest and flooding of buildings located nearby. Such actions, after Nachlik (2006), may be classified as the so-called flood prevention measure, which promotes restoration or preservation of natural outflow conditions from the catchment. These are actions facilitating limitation of flood damage in a given area and as such they are frequently applied in flood control retention facilities.

The adverse course of weather conditions observed in the second and third decades of September, particularly low precipitation total (12 mm) in that period, caused further subsidence of the water pool in the reservoir and groundwater levels in the adjacent area. The lowest water elevation in the analysed half-year was recorded on 1 October. The water elevation in the reservoir on that day was 72.16 m a.s.l., while the level of groundwaters in the analysed wells ranged from 70.71 m a.s.l. (well P-21) to 72.65 m a.s.l. (well 5').

Precipitation total of 59 mm, observed in the first decade of October caused an intensive rise in the water pool in the reservoir and the analysed wells. At the end of that half-year the water pool in the reservoir was found at 72.67 m a.s.l., while the groundwater levels reached elevations from 70.89 m a.s.l. (well P-21) to 73.29 m a.s.l. (well 5').

In the analysed summer half-year groundwaters fed reservoir waters from wells nos. 1' and 2', where the supply time amounted to 21 and 35days, respectively. Supplying the reservoir waters with groundwaters from adjacent areas was also reported from wells nos. 4', 5' and 6', while the water inflow time ranged from 49 days (well 6') to 184 days (well 5').

It may be stated that for a greater part of the analysed water years waters retained in the investigated reservoir fed groundwaters in adjacent areas, with the longest supply time ranging from 282 up to 366 days recorded for wells from P-2 to P-21 located within a close distance from the dam (Table 4).

Table 4. The numbers of days when reservoir waters were supplied by ground waters in adjacent area and ground waters in adjacent area were supplied by reservoir waters in 2015, 2016 and 2017 hydrological years

Well no.	Number of days					
	Groundwaters supplying reservoir waters			Reservoir waters supplying groundwaters		
	2015	2016	2017	2015	2016	2017
P-2	7	0	0	282	366	365
P-3	7	0	0	282	366	365
P-16	7	0	0	282	366	365
P-17	7	0	0	282	366	365
P-18	7	0	0	282	366	365
P-20	7	0	0	282	366	365
P-21	0	0	0	289	366	365
1’	-	0	42	-	366	323
2’	-	7	105	-	359	260
3’	-	0	56	-	366	309
4’	-	70	259	-	296	106
5’	-	184	365	-	182	0
6’	-	35	147	-	331	218

In turn, in the case of wells nos. 1’to 6’ located in the central area of the reservoir the waters were found to flow in both of these opposite directions. According to Radecki-Pawlik and Kapusta (2006), surface retention may not only be supplied by precipitation, but also by the soil itself, if in a porous medium such hydraulic gradients are formed, which may counter the gradient of the gravitational potential directed downward. In the analysed years groundwaters fed the reservoir waters for a period ranging from 7 days (well 2’) up to 365 days (well 5’). Recorded results are confirmed e.g. by studies conducted by Bem and Kacy (2003) in the Stawy Raszyńskie Nature Reserve, in which those authors stressed in the case of groundwaters the possible occurrence of a draining or alimentary effect of reservoirs on adjacent areas.

It needs to be observed here that the longer supply time of reservoir waters with groundwaters was recorded for wells nos. 4’, 5’ and 6’ located east of the reservoir, which may be explained by the greater supply area and influx of waters from outside the immediate catchment.

Calculations of relationships between elevations of water pools in the reservoir and elevations of groundwater tables in the investigated wells conducted for the analysed winter and summer half-years of the investigated water years in most cases showed strong dependencies. In the winter half-years of the first two years the calculated correlation coefficients ranged from 0.58 for well P-16 to 0.96 for wells P-2 and P-18 (Table 5). In turn, for the summer half-years these values ranged from 0.34 for well 3' to 0.99 in wells P-2 and P-3. It needs to be observed here that in most cases, except for the correlation for well 3', the obtained dependencies were significant at $\alpha = 0.01$. As it was reported by Kala (2002), for the phenomena analysed in life sciences objective inference on strong dependencies is sufficient already at the significance level $\alpha = 0.05$. In turn, in the winter half-year of the last year of the study the weakest dependencies were found between the discussed parameters. Statistically significant relationships were obtained for only six out of all the discussed wells, in which correlation coefficients ranged from 0.48 (well 2') to 0.85 (well P-20).

Table 5. Correlation coefficients (r) and significance levels (α) for relations of water levels in the reservoir with groundwater depths, in analysed wells in the adjacent area in winter and summer half-years of the 2015, 2016 and 2017 hydrological years

Well no.	P-2	P-3	P-16	P-17	P-18	P-20	P-21	1'	2'	3'	4'	5'	6'
Winter half-year of 2015													
r	0.94	0.94	0.88	0.91	0.96	0.93	0.91	-	-	-	-	-	-
α	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	-	-	-	-	-
Summer half-year of 2015													
r	0.9	0.9	0.89	0.89	0.95	0.92	0.92	-	-	-	-	-	-
α	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	-	-	-	-	-
Winter half-year of 2016													
r	0.96	0.95	0.58	0.75	0.75	0.62	0.88	-	-	-	-	-	-
α	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	-	-	-	-	-
Summer half-year of 2016													
r	0.99	0.99	0.75	0.89	0.97	0.78	0.97	0.79	0.8	0.34	0.75	0.62	0.85
α	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	0.01	0.01	0.01
Winter half-year of 2017													
r	0.6	0.6	0.24	0.33	0.34	0.85	0.61	0.1	0.48	0.1	0.45	0.1	0.62
α	0.01	0.01	-	-	-	0.01	0.01	-	0.01	-	-	-	0.01
Summer half-year of 2017													
r	0.74	0.74	0.61	0.64	0.73	0.9	0.74	0.79	0.94	0.89	0.94	0.81	0.97
α	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

A considerable effect on such a situation in that half-year was exerted by the below zero temperatures maintained from mid-December to the third decade of February, which could have considerably disturbed the mutual relationships between waters retained in the reservoir and groundwaters in the adjacent areas. In turn, for the summer half-year of the discussed year, similarly as in the earlier analysed summer half-years, strong dependencies were obtained, since the correlation coefficients ranged from 0.61 for well P-16 to 0.97 for well 6'(Table 5, Fig. 7) and these values were also significant at $\alpha = 0.01$.

It may be stated that apart from the course of weather conditions and relief in the immediate vicinity of the reservoir, the strong dependencies resulted also from the properties of the deposits lying in the area adjacent to the reservoir. According to Halfen and Czamary (2007) and Michalak and Nowicki (2009), hydrogeological parameters of deposits found in the escarpments and bottom of a given reservoir and its immediate vicinity, particularly porosity, to a considerable degree determine mutual dependencies between reservoir waters and groundwaters.

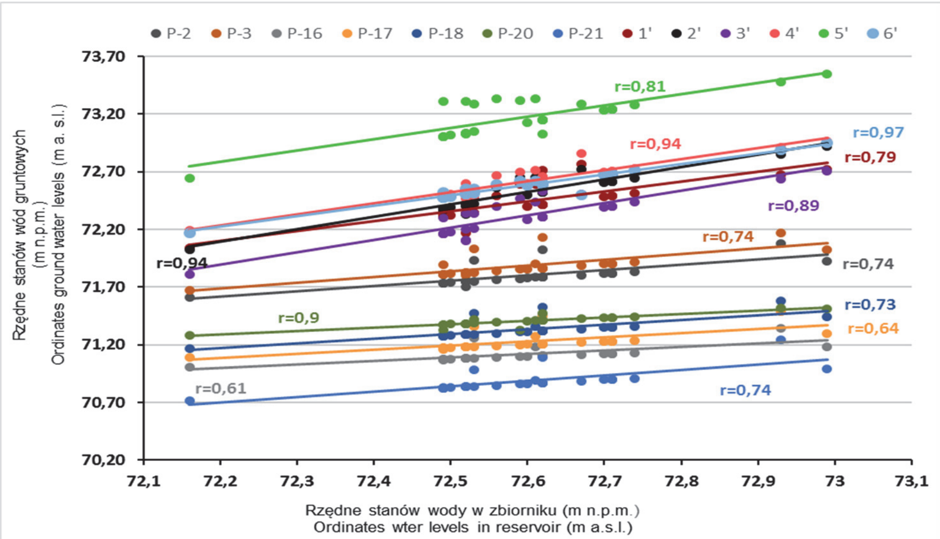

Fig. 7. Correlations between elevations of water levels in the Przebędowo reservoir and elevations of groundwater levels in analysed wells in the 2017 summer half-year

Mutual relationships between waters retained in reservoirs and groundwaters in adjacent areas have been investigated in many regions of Poland. Strong dependencies between these parameters have been stressed e.g. by Zubala (2005) and Przybyła and Kozdrój (2013) in their studies conducted on the Pakosław reservoir in the Orla river catchment. Many authors have also underlined the positive effect of waters retained in reservoirs on groundwaters in adjacent areas, manifested mainly in their supply in drought periods, as shown e.g. in studies by Szafrański and Stefanek (2008) carried out on the Mściwojów dam reservoir and by Sojka et al. (2010) in the Struga Dormowska catchment.

As it was reported by Operacz et al. (2012), an artificially raised water table by structures regulating damming height in relation e.g. to dam reservoirs considerably contributes to an increase in catchment retention. This phenomenon to a considerable extent prevents aridification of the area. According to those authors, from the point of view of water management increased underground retention, frequently close to total retention capacity of the catchment, is of paramount importance for the water cycle in the system.

For this reason it is crucial to conduct further studies on already existing facilities, which may serve as training grounds, particularly for the future new retention reservoirs and their assessed impact on the adjacent areas. According to Kanownik et al. (2011), at the accumulation of surface waters in reservoirs for their commercial or recreation use, monitoring studies are required especially in suburban areas under stronger anthropopressure. We also need to remember of the fact that the construction of dam reservoirs is considered to be particularly risky and requiring thorough analyses. Generally when assessing available water resources in catchments of watercourses located in river valleys we need to take into consideration infiltration or drainage effects of the main receiving waters on the adjacent area (Olszewska et al. 2012).

4. Conclusions

1. Conducted studies confirmed that a marked effect on the fluctuations in the water pool in the reservoir and groundwater levels in the adjacent area was exerted by the weather conditions, particularly daily precipitation totals in individual half-years of the analysed years. The maximum water levels in the reservoir and groundwaters in the analysed wells in the winter half-years was most frequently observed at the turn of March and April. In turn, in the summer half-years no definite trend was observed, as is frequently characteristic of drainless reservoirs. High water levels were most typically recorded at the turn of July and August and towards the end of those half-years.
2. Studies also showed that measures connected with water management in the flood control retention facilities, such as dam reservoirs, often significantly determine also changes in water levels both in the reservoir itself and groundwaters in the adjacent area. The measures classified as flood control prevention, e.g. opening of bottom outlets on damming structures in critical situations, contribute to the restoration or maintenance of natural outflow conditions from the catchment and limit flood damage in a given area.
3. The analysis of changes in the elevations of reservoir waters and groundwaters in the adjacent area indicated that for a greater part of the analysed hydrological years waters retained in the investigated reservoir fed groundwaters of adjacent areas, while the longest supply time, ranging from 282 days to 366 days, was found for wells P-2 to P-21 located in the vicinity of the dam. In turn, for wells from 1’to 6’ located in the area of the central part of the

reservoir the flow of waters in two opposite directions was observed, with the reservoir serving draining function next to the alimentary function.

4. Calculations for the relationships between elevations of waters in the reservoir and those of groundwater levels in the investigated wells, obtained for the analysed winter and summer half-years of the studied hydrological years in most cases showed strong dependencies. However, it needs to be stressed that stronger mutual dependencies between the above-mentioned parameters were found for the summer half-years, for which calculated correlation coefficients, statistically significant at $\alpha = 0.01$, ranged from 0.61 for well P-16 to 0.99 for wells P-2 and P-3, respectively.

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Abstract

The article presents the results of investigations carried out in the hydrological years of 2015, 2016 and 2017 in the Przebędowo reservoir basin (in areas adjacent to the reservoir). It is located in the Wielkopolskie province, 25 kilometres north of Poznań in the Murowana Goślina commune. The analysed catchment with an area of approx. 100 km^2 is mostly covered by forests, while in the immediate vicinity of the reservoir it also comprises arable land. The entire catchment is covered by postglacial deposits, such as sands and clays. Areas adjacent to the reservoir are composed of quaternary (Pleistocene) fluvial deposits. The analysis of layers contained within piezometers showed the predominance of medium sands, which were deposited up to a depth of about 3 m. The groundwaters in those layers formed a continuous aquifer horizon.

The analysed reservoir was constructed in the valley of the Trojanka river, from km 6 + 915 to km 8 + 371 of the river course, by the Greater Poland Provincial Land Drainage and Water Units Board in Poznań. It was put into operation in November 2014. The earth dam of the reservoir is class IV it is 334 meters long and 3.30 meters high. The reservoir with a length of 1450 m and a maximum bed-width of 120 m at a normal damming level has a flooded surface of 12.03 ha. The main purpose of the reservoir is to store water for agricultural purposes, improve climatic and water conditions in the adjacent agricultural areas, provide protect against flooding and fire for areas lying both below the dam and adjacent to the reservoir. Around the reservoir an ecological buffer zone was made in the form of tree and shrub plantings. It reduced runoff of biogenic compounds (nitrogen and phosphorus) and pesticides from adjacent agricultural areas.

The conducted analysis of precipitation data according to the criterion developed by Kędziora (1995) (following Kaczorowska, 1962) showed that the water year of 2015 was dry. The precipitation total in that year was 429 mm and was lower than the average of the multi-year period by 131 mm, while temperature was higher than average by 0.5°C. In contrast, the water year of 2016 was wet, as the precipitation total in that year was 682 mm, i.e. by 122 mm higher than the average of the multi-year period, with the air temperature higher than the average by 0.4°C. The last water year analysed (2017) was very wet, because the precipitation total exceeded the multi-year average by 244 mm, with the air temperature close to the average.

Results indicated that next to the character of the reservoir, also meteorological conditions had a considerable impact on changes in water levels in the analysed reservoir and groundwater levels in the adjacent area. Research showed a hydraulic connection between the water retained in the reservoir and groundwater in the adjacent areas. It was found that over a greater part of the water years analysed in this paper the water retained in the Przebędowo reservoir fed groundwaters of the adjacent areas. The longest supply time, which ranged from 282 days to 366 days, was recorded for wells P-2 to P-21. They are located within a short distance from the dam. In contrast, in the case of wells 1' to 6', located near the middle part of the reservoir, two-way water flow was found. In the analysed years the water in reservoir was fed by the groundwater from the wells for a period between 7 days (st. 2') to 365 days (st. 5').

The analyses carried out in the winter and summer half-years of the discussed water years indicated mostly strong relations between the elevation of water levels in the reservoir and groundwater elevation in the studied wells. However, it was found that the interrelationships between the discussed values were stronger in the summer half-years.The obtained research results generally showed that the waters accumulated in the Przebędowo reservoir have a positive impact on groundwaters in the adjacent areas and feed them during drought periods.

Keywords:
small-scale water retention, dammed reservoirs, groundwater

Ocena oddziaływania zbiornika zaporowego na zwierciadło wód gruntowych w terenach przyległych na przykładzie obiektu Przebędowo

Streszczenie

W pracy przedstawiono wyniki badań przeprowadzonych w latach hydrologicznych 2015, 2016 oraz 2017 w zlewni zbiornika Przebędowo (w terenach bezpośrednio przyległych do zbiornika), zlokalizowanej w województwie wielkopolskim, 25 km na północ od Poznania w gminie Murowana Goślina. W omawianej zlewni, o powierzchni około 100 km^2 przeważają lasy, a w mniejszym stopniu w terenie bezpośrednio przyległym do zbiornika występują grunty orne. Na całym obszarze zalegają utwory polodowcowe takie jak piaski i gliny. W ogólnym ujęciu tereny przyległe do zbiornika zbudowane są z osadów czwartorzędowych (plejstocen) fluwialnych, a analiza warstw objętych piezometrami wykazała przewagę piasków średnich zalegających do głębokości około 3m, w których wody gruntowe tworzą ciągły poziom wodonośny. W terenie bezpośrednio przyległym do zbiornika występują grunty orne.

Analizowany zbiornik został wykonany w dolinie rzeki Trojanki, od km 6+915 do km 8+371 jej biegu przez Wielkopolski Zarząd Melioracji i Urządzeń Wodnych w Poznaniu i został oddany do eksploatacji w listopadzie 2014 roku. Ziemna zapora czołowa na zbiorniku jest klasy IV, jej długość wynosi 334 m, przy wysokości 3,30 m. Zbiornik o długości 1450m i szerokości maksymalnej 120m, przy normalnym poziomie piętrzenia (NPP) ma powierzchnię zalewu 12,03ha. Głównym celem zbiornika jest magazynowanie wody dla celów rolniczych, poprawa warunków klimatycznych i wodnych na przyległych użytkach rolnych, oraz ochrona przeciwpowodziowa i przeciwpożarowa terenów leżących poniżej zapory, a także terenów przyległych do zbiornika. Wokół zbiornika wykonano ekologiczną strefę buforową w postaci nasadzeń z drzew i krzewów, redukującą spływy związków biogennych (azot, fosfor) i środków ochrony roślin z przyległych terenów użytkowanych rolniczo.

Przeprowadzona analiza wilgotnościowa omawianych w pracy lat według kryterium Kędziory 1995 (za Kaczorowska 1962) pozwoliła stwierdzić, że pierwszy analizowany w pracy rok hydrologiczny 2015 był rokiem suchym, w którym suma opadów wyniosła 429 mm i była niższa od średniej z wielolecia o 131 mm, przy temperaturze powietrza wyższej od średniej o 0,5°C. Natomiast rok hydrologiczny 2016 był rokiem wilgotnym, w którym suma opadów wyniosła 682 mm i była wyższa od średniej z wielolecia o 122 mm, przy temperaturze powietrza wyższej od średniej o 0,4°C. Ostatni analizowany w pracy rok hydrologiczny 2017 był bardzo wilgotny, gdyż suma opadów przekroczyła w tym roku średnią z wielolecia aż o 244 mm, przy zbliżonej do średniej temperaturze powietrza.

Uzyskane wyniki badań potwierdziły, że duży wpływ na zmiany stanów wody w analizowanym zbiorniku i wód gruntowych w terenie przyległym, poza charakterem zbiornika, miał przebieg warunków meteorologicznych. Badania wykazały, że pomiędzy wodami retencjonowanymi w zbiorniku a wodami gruntowymi w terenach przyległych istnieje więź hydrauliczna. Stwierdzono, że przez większą część analizowanych w pracy lat hydrologicznych retencjonowane w omawianym zbiorniku wody zasilały wody gruntowe terenów przyległych, przy czym najdłuższy czas zasilania, wynoszący od 282 dni

do 366 dni, stwierdzono dla studzienek od P-2 do P-21 zlokalizowanych w niedalekiej odległości od zapory. Natomiast w przypadku studzienek od 1'do 6' zlokalizowanych w okolicach środkowej części zbiornika stwierdzono dwukierunkowy przepływ wód. W analizowanych latach wody gruntowe zasilały od strony tych studzienek wody zbiornika przez okres od 7 dni (st. 2') do 365 dni (st. 5').

Przeprowadzone w analizowanych półroczach zimowych i letnich omawianych lat hydrologicznych obliczenia związków pomiędzy rzędnymi stanów wody w zbiorniku, a rzędnymi zwierciadła wód gruntowych w badanych studzienkach wykazały w większości silne zależności. Stwierdzono jednak, że wzajemne powiązania pomiędzy omawianymi wielkościami silniejsze były w półroczach letnich analizowanych lat.

W ogólnym ujęciu uzyskane wyniki badań wykazały, że zasoby wodne gromadzone w zbiorniku Przebędowo pozytywnie oddziaływają na wody gruntowe terenów przyległych, zasilając je w okresach posusznych.

Słowa kluczowe:
mała retencja, zbiorniki zaporowe, wody gruntowe