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Assessment of Concentrations of Selected Metals in the Groundwater in the Wielkopolska National Park

Michał Fiedler, Adam Zydroń, Mariusz Korytowski*
Poznan University of Life Sciences, Poland
**corresponding author email: michal.fiedler@up.poznan.pl*

1. Introduction

Contamination of groundwater may become a major problem reducing availability of water (Gu et al. 2020, Luczaj 2016, Umar et al. 2009). Increasing pollution of these waters also decreases in the groundwater resources, constituting not only the source of potable water, but also water used in agriculture, while also affecting the condition of vegetation and welfare of animals in areas covered by nature protection measures (Vitale et al. 2017, Aniszewski 2020).

Groundwater quality is determined by many factors, primarily human activity, the distribution of precipitation, the impact of surface waters and subsurface geochemical processes. Both natural hydrological processes and anthropogenic factors may lead to periodical changes in groundwater quality (Luczaj & Masarik 2015, Vasnthavigar et al. 2010). Groundwater susceptibility to contamination may be defined as sensitivity of such waters to an introduced pollutant load, resulting from specific properties of the aquifer (Van Duijvenbooden & Waegningh 1987). The actual groundwater susceptibility, difficult to determine using quantitative standardised methods, needs to include properties of the hydrogeological system, in which the water cycle takes place both in the unsaturated zone and in the aquifer. Thus it needs to consider the potential release of contaminants to groundwater (Wachniew et al. 2016, Krogulec 2016). Groundwater susceptibility to pollution may be assessed using methods based on the Geographic Information Systems (GIS), the process approach and statistical methods (Duarte et al. 2019, Kong et al. 2019, Mozejko 2012, Wachniew et al. 2016).

The process of cations mobility in the soils depend on various parametres such as rain pH and soil properties. The significant leaching of potassium, sodium, calcium and magnesium from the plant root zone could couse groundwater pollution and on nutrient imbalance (Małecki et al. 2017, Nawaz et al. 2012, Walna et al. 2000). The investigations of the chemical characteristics of the precipitation in the Wielkopolski National Park has shown its high acidity, which can drop below pH 3.0. Effect of such rains was washing out of large amounts of Ca and Mg from sandy and naturally very acid soils (Walna & Siepak 2012).

A frequently stressed aspect is connected with the advantageous effect of afforestation on the improvement of groundwater quality (Allen & Chapman 2001, He et al. 2019, Lowrance et al. 1997). In forested areas a considerable role in the circulation of contaminants is played by forest management measures, resulting among other things in leaching of nitrates and heavy metals from clear-cutting areas (Buttle 2011, Mannerkoski et al. 2005, McHale et al. 2007, Rusanen et al. 2004).

2. Materials and methods

This study is based on data concerning metal concentrations in groundwater, provided by the Wielkopolska National Park. Water samples were collected in February, May, August and November 2017 from 15 wells located in the Park (Fig. 1) varying in their position in the relief, as presented in the hill-shading map below (Fig. 2).

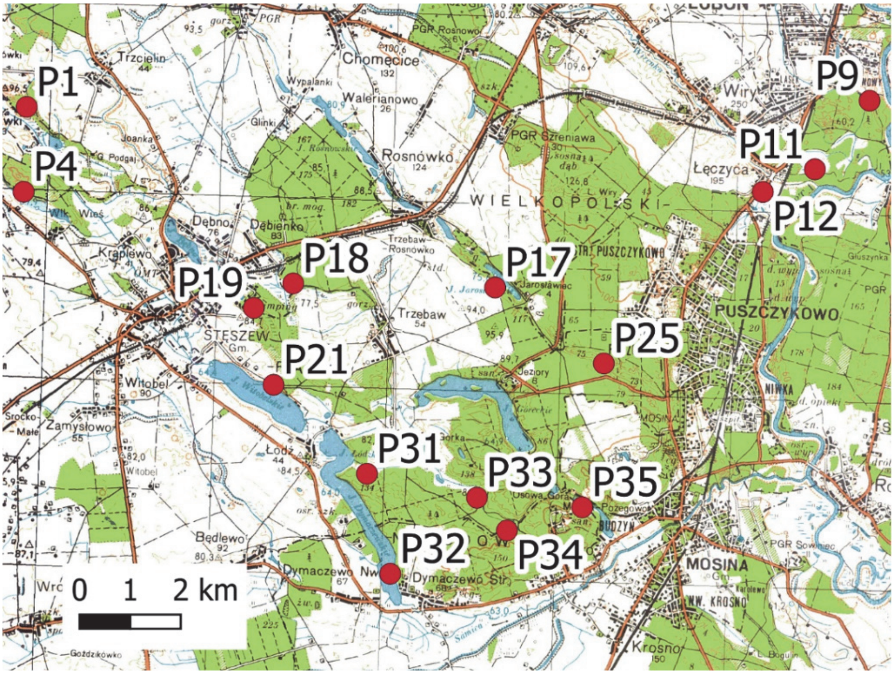

Fig. 1. Location of groundwater sampling sites

The Wielkopolska National Park is situated 15 km south of Poznań (western Poland) an covers area of 76 km^2. The soils originated from loamy and sandy postglacial material of the last glaciation. The dominating soils are grey brown podzolic (47%) and brown podzolic soils (30%), while the other soils are podzols (7%), proper brown soils (6%), alluvial soils (3%), deluvial soils (2%) and anthropogenic soils, arenosols, muck soils, turf soils, brown acid soils (Nowak 1999). The average annual sum of precipitation is 550 mm and does not show significant changes during long period (Miler 2018).

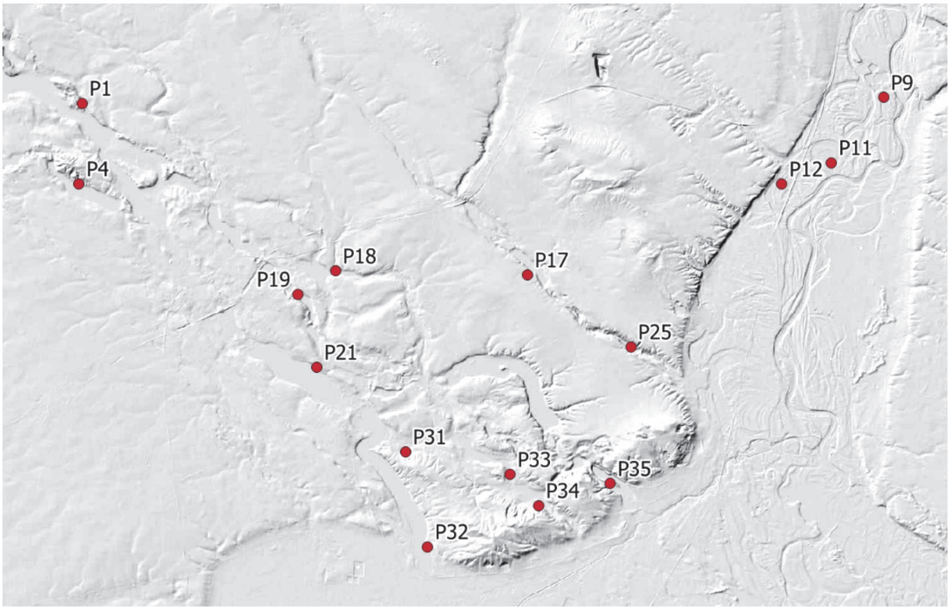

Fig. 2. Hillshading map of analyzed area

Groundwater was sampled after at least three exchanges of the water column in a borehole, using a suction-and-force combustion pump. Earlier, the water level in the piezometer and water temperature were measured. Analyzed elements were barium, boron, calcium, iron, potassium, magnesium, manganese, sodium and zinc. The concentrations of dissolved elements (B, Ba, Ca, Fe, K, Mg, Mn, Na, Zn) in the water samples were determined using the technique of atomic absorption spectrometry, according to method W-METAXFL1.

Variability of investigated parameters was assessed using the analysis of variance (ANOVA). Values outside 1.5·IQR (Inter Quartile Range) were considered to be outliers. The outliers were replaced by the values calculated according to the following equations:

$$Up = Q_3 + 1.5IQR \tag{1}$$

$$Low = Q_1 - 1.5IQR \tag{2}$$

where:

Up – concentrations for values outside the 75-th quartile (Q_3),

Low – concentrations for values below the 25-th quartile (Q_1).

In order to determine whether different metals exhibit a similar variability, respective analyses were conducted for the relationships using Pearson's correlation coefficients. The Principal Component Analysis (PCA) and cluster analysis made it possible to include various factors influencing variance. A factorial analysis applying normalised varimax rotation was performed in order to reduce related environmental variables and identify a small set of variables clearly explaining a considerable proportion of variance for the variables. Cluster analysis was conducted applying Ward's method, assuming Euclidean distances as a measure of similarity between clusters. Prior to PCA the Kaiser-Meyer-Olkin (KMO) tests and Bartlett's tests of sphericity were performed to assess applicability of original data. KMO<0.5 was assumed as a condition satisfying Bartlett's test of sphericity. Data which failed to meet the conditions for the normal distribution were transformed using logarithms. The number of clusters was determined applying the silhouette method.

In the case of metal concentrations in groundwater below the limit of detection, values corresponding to the limit for a given element were assumed for the analyses.

All statistical analyses and graphs were made using the R 3.6.2 statistical software package. Spatial data are presented with the use of the QGIS 3.12 programme.

3. Results and discussion

Characteristic concentrations of analysed metals (B, Ba, Ca, Fe, K, Mg, Mn, Na and Zn) in groundwater samples collected from 15 wells located in the Wielkopolska National Park are presented in Table 1 and in Fig. 1.

Concentrations of these metals showed high variability. Levels of the analysed metals in 2017 fell within the following ranges: B from 0.05 to 0.156 $mg \cdot dm^{-3}$, Ba from 0.022 to 0.150 $mg \cdot dm^{-3}$, Ca from 52.6 to 260 $mg \cdot dm^{-3}$, Fe from 0.001 to 5.40 $mg \cdot dm^{-3}$, K from 0.664 to 13.1 $mg \cdot dm^{-3}$, Mg from 7.95 to 38.1 $mg \cdot dm^{-3}$, Mn from 0.002 to 1.61 $mg \cdot dm^{-3}$, Na from 7.02 to 97.4 $mg \cdot dm^{-3}$ and Zn from 0.001 to 0.009 $mg \cdot dm^{-3}$. Mean concentrations of tested metals fell within the order: Ca (127 $mg \cdot dm^{-3}$) > Na (27.8 $mg \cdot dm^{-3}$) > Mg (16.9 $mg \cdot dm^{-3}$) > K (3.52 $mg \cdot dm^{-3}$) > Fe (0.464 $mg \cdot dm^{-3}$) > Mn (0.298 $mg \cdot dm^{-3}$) > Ba (0.073 $mg \cdot dm^{-3}$) > B (0.044 $mg \cdot dm^{-3}$) > Zn (0.002 $mg \cdot dm^{-3}$).

The comparison of metal concentrations presented by Walna & Siepak (2012) and Walna (2013) shows decrease of concentration of zinc, calcium and magnesium. Present average content of Zn is 0.004 mg·dm^{-3}, whreas in 2010 year was 0.007 mg·dm^{-3} and in 1994 0.040 mg·dm^{-3}. Average concentrations of Mg decreased from 31.4 mg·dm^{-3} in 2010 year to 16.9 mg·dm^{-3} in 2017 and average calcium concentration decreased in the same period from 198 mg·dm^{-3} to 127 mg·dm^{-3}. Concentrations of K and Na are at similar level as measured in 2010 (Walna 2013).

Median values of concentrations for most parameters correspond to quality class I in relation to boundary values for the physico-chemical condition of groundwater (Rozporządzenie 2015). Only the median of Mn concentrations corresponds to quality class 2, while that of Ca – to quality class 3. However, these values fall within the ranges for the geochemical background (Table 1). Low levels of heavy metal contamination for forested areas were also confirmed by Chrzan et al. (2013).

As shown in Table 1 and Fig. 3, the distribution of groundwater concentrations of analysed metals to a considerable extent deviates from normal distribution for most analysed elements. Figure 3 also presents a considerable number of outliers, particularly for higher concentration values.

The highest Ba concentrations in groundwater were observed in profiles P34, P35 and P9 throughout the entire year of 2017 (Fig. 4) and they were over 2-fold greater than in the other wells. Elevated Ba concentrations were recorded in well P12, Ca in P18, Fe in P11 and P33, K in P19, Mg in P19, Mn in P35, while Na – in wells P34 and P9. No significant variation in concentrations was observed in the successive measurement periods (Fig. 4).

Correlations in metal concentrations may indicate that contamination originates from the same source, and that they have the same circulation routes (Ke et al. 2017). On the other hand, a lack of significant relationships means that metals may originate from various sources and may be influenced by various factors (Xu et al. 2018). The matrix of correlations for Pearson's coefficients for the concentrations of analysed metals is presented in Table 2. A significant correlation was found between concentrations of the following metals at $p < 0.01$: B-Mn (r = 0.46), B-Na (r = 0.57), Ba-Mg (r = 0.47), Ba-Mn (r = 0.35), Ba-Na (r = 0.49), Ca-K (r = 0.39), Ca-Mg (r = 0.67), K-Mg (r = 0.58), Mg-Na (r = 0.49) and additionally at $p < 0.05$ for B-Zn, Ba-K, Ca-Na, Fe-Mn and K-Na. As can be seen here, elements showing the lowest correlation of concentrations with the other metals include Zn (only with B) and Fe (with Ba and Mn), whereas Ba shows correlation with the highest number of metals (Fe, Mg, Mn, Na and K).

Table 1. Concentrations of selected metals in groundwater, limits for water classes and geochemical background for soils of analyzed area

Metal	Samples	Median	Mean	Min	Max	Std. deviation	Skew	Kurtosis	Limits for water class[1]			Geochemical background[2]
									1	2	3	
	No	mg·dm^{-3}										mg·kg^{-1}
B	60	0.027	0.044	0.005	0.156	0.043	1.243	0.169	0.5	1	1	0.01-0.06
Ba	60	0.072	0.073	0.022	0.150	0.028	0.464	-0.336	0.3	0.5	0.7	4-39
Ca	60	121.5	126.8	52.6	260	47.9	0.818	0.615	50	100	200	40-130
Fe	60	0.007	0.464	0.001	5.40	0.957	10.063	0.124	0.2	1	5	90-620
K	60	2.50	3.518	0.664	13.1	2.898	2.978	0.374	10	10	15	0.1-26
Mg	60	16.65	16.88	7.95	38.1	6.639	0.970	0.857	30	50	100	10-90
Mn	60	0.153	0.298	0.002	1.61	0.379	3.331	0.049	0.4	1	1	5-271
Na	60	23.15	27.80	7.02	97.4	19.5	2.467	2.515	60	200	200	0.5-39
Zn	45	0.001	0.002	0.001	0.009	0.002	1.582	1.484	0.5	1	2	7-67

[1] – Rozporządzenie … (2015)

[2] – Lis & Pasieczna (2005)

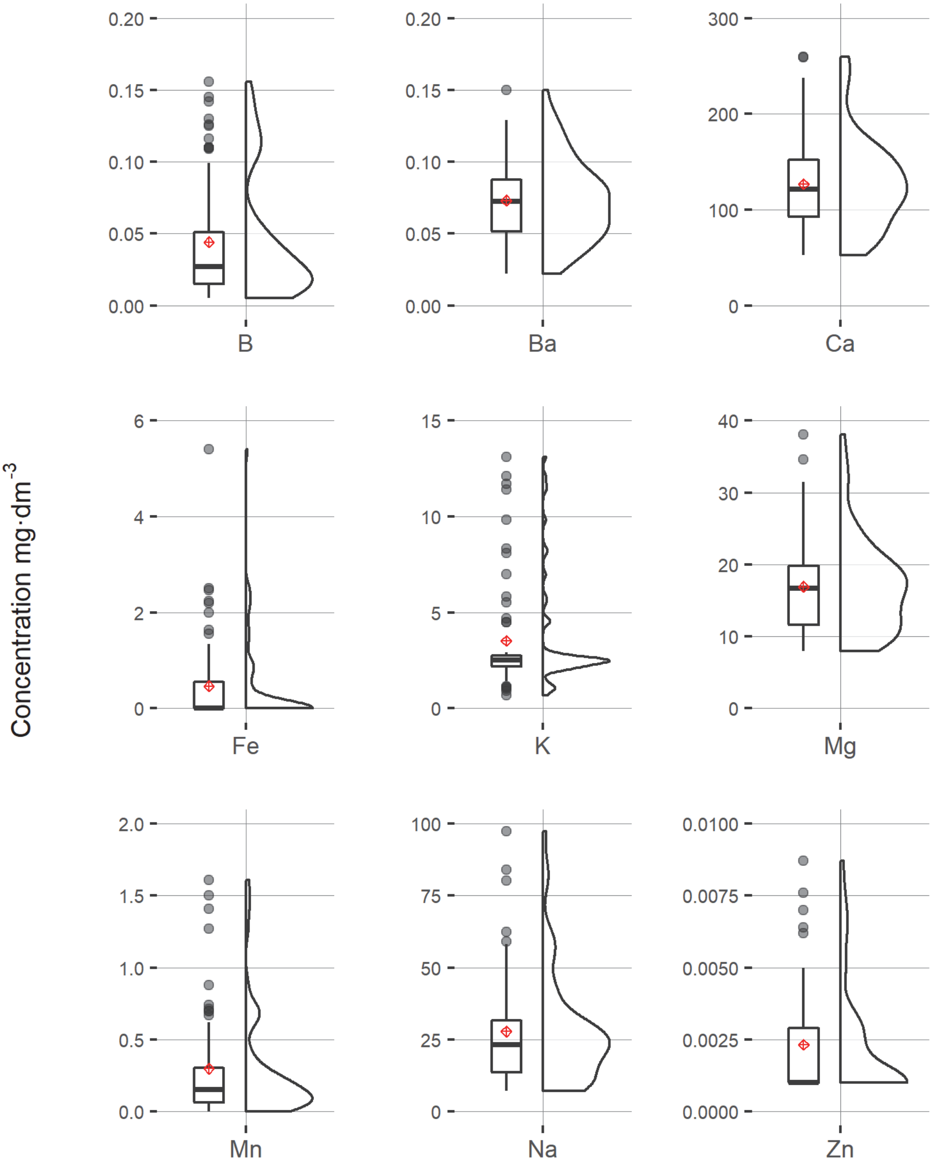

Fig. 3. Characteristic values, distribution and outliers of analysed metal concentrations in groundwater of the Wielkopolska National Park

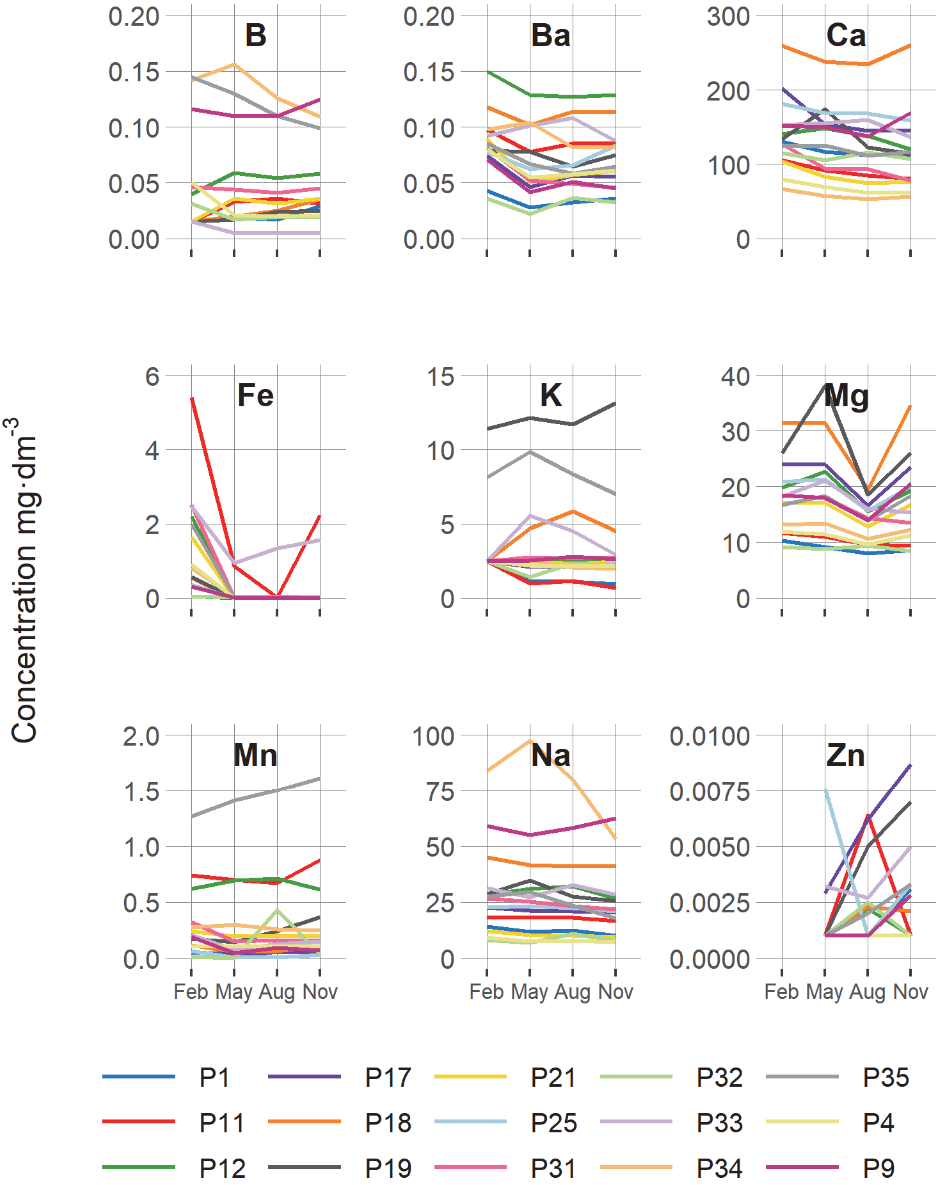

Fig. 4. Concentrations of metals in groundwater from sampling sites in the Wielkopolska National Park for the year 2017

Table 2. Correlation coefficient matrix for the analyzed elements and depth of groundwater (GWD)

	B	Ba	Ca	Fe	K	Mg	Mn	Na	Zn
Ba	0.04								
Ca	-0.28	0.25							
Fe	-0.10	0.44	0.07						
K	0.12	0.30	0.39	0.01					
Mg	-0.07	0.47	0.67	0.04	0.58				
Mn	0.42	0.35	-0.18	0.31	0.24	-0.05			
Na	0.57	0.49	0.27	0.08	0.31	0.49	0.09		
Zn	-0.31	0.04	0.29	0.05	0.13	0.25	-0.05	0.04	
GWD	-0.17	-0.26	0.08	-0.17	-0.17	0.17	-0.32	-0.04	0.40

🟨 – $p < 0.01$. 🟩 – $p < 0.05$

Concentration of dissolved elements could be correlated with depth from ground surface to groundwater (GWD). For 2017 year average depth of groundwater surface was from 0,74 m in site P33 to 17,86 m in site P17 (Table 3). The groundwater table fluctuations during the investigations were greatest in site P1 and equal 0.67 m, while average GWD for this site was 1.08 m. The smallest variation of GWD were observed in the site P18 and were only 0.03 m. There was no significant correlation of metal concentration between depth of groundwater (GWD) and B, Ca, Fe, K, Mg and Na (Table 2). A significant correlation was found between GWD and Zn ($p < 0.01$), Mn and Ba (both $p < 0.05$).

Table 4 presents the matrix of principal components and variance of analysed heavy metal concentrations in groundwater identified at eigenvalues >1. These data for two principal components were additionally shown in Fig. 5. Three principal components given in Table 3 explain jointly 68.2% total variance, which does not meet the recommendation that principal components should explain min. 75% total variance (Loska & Wiechuła 2003). Principal component 1, responsible for the total load of metals in groundwater explains 31.6% variance and is correlated mainly with concentrations of Mg, Ba, Na, K and Ca. Principal components 2 and 3 explain 21.6% and 15.0% total variance, respectively. PC 2 is correlated mainly with B and Mn. In turn, PC 3 is correlated with Fe. The loading plot (Fig. 5) confirmed the results of the correlation analysis.

Table 3. Depth of groundwater at sampling sites (m)

Site	February	May	August	November
P1	2.97	2.86	2.88	2.74
P4	2.58	2.54	2.53	2.37
P9	4.78	4.60	4.86	4.49
P11	1.03	1.33	1.31	0.66
P12	1.27	0.98	1.13	0.72
P17	17.84	17.86	17.87	17.87
P18	0.82	0.90	0.85	0.49
P19	3.46	3.37	3.49	3.29
P21	7.27	7.17	7.75	7.32
P25	5.75	5.56	5.65	5.50
P31	2.24	2.21	2.21	2.02
P32	1.99	1.93	1.82	1.62
P33	0.81	0.63	0.75	0.78
P34	4.39	4.31	4.34	4.25
P35	0.80	0.78	0.84	0.68

Table 4. The first three principal components (PCs) obtained by PCA and percentage cumulative variance explained.

Metal	PC 1	PC 2	PC 3
B	0.02	0.66	0.21
Ba	0.53	0.05	0.15
Ca	0.42	0.31	0.00
Fe	0.08	0.04	0.65
K	0.48	0.00	0.03
Mg	0.71	0.10	0.03
Mn	0.06	0.46	0.12
Na	0.49	0.12	0.13
Zn	0.06	0.21	0.03
Eigenvalues	2.84	1.95	1.35
Cumulative explained variance	31.6	53.2	68.2

Performed correlation and PCA analysis identified two groups of elements. First group comprises Ba, Ca, K, Mg and Na. This group include elements that have high concentration levels and have natural sources. The second group is composed of B, Fe, Mn and Zn which usually are connected with anthropogenic sources. Additionally iron and manganese are widely found in soils and aquifers, which have similar geochemical behavior (Zhang 2020).

Cluster analysis also identified groups of sampling locations showing a similar variation in metal concentration in groundwater (Fig. 6). Three groups of sampling locations were identified. One includes wells P1, P4, P21, P1 and P32. This group represents sites located in the neighbourhood of open water bodies and there is possible temporary influence of lake or river water on groundwater in analysed sites. Sites P4, P21 and P32 are located nearby lakes and site P11 close to the Warta River (Fig. 1 and 2). The second one comprises wells P19, P18, P33 and P35 which are located in the lowest parts of area relief and are supplied by flows from surrounding areas. The third group is composed of wells P9, P12, P17, P25, P31 and P34 located on middle and upper parts of slope.

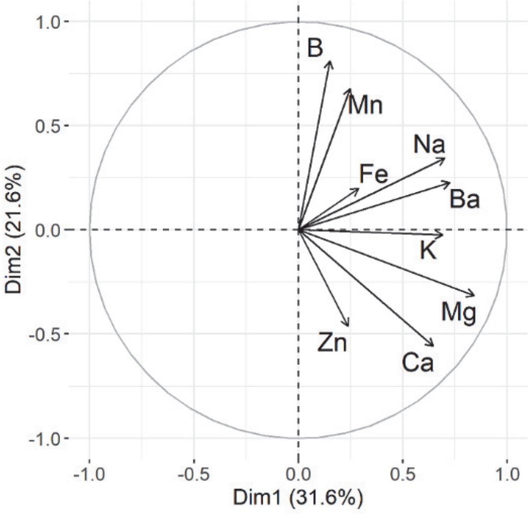

Fig. 5. Plot of loading of the first two principle components

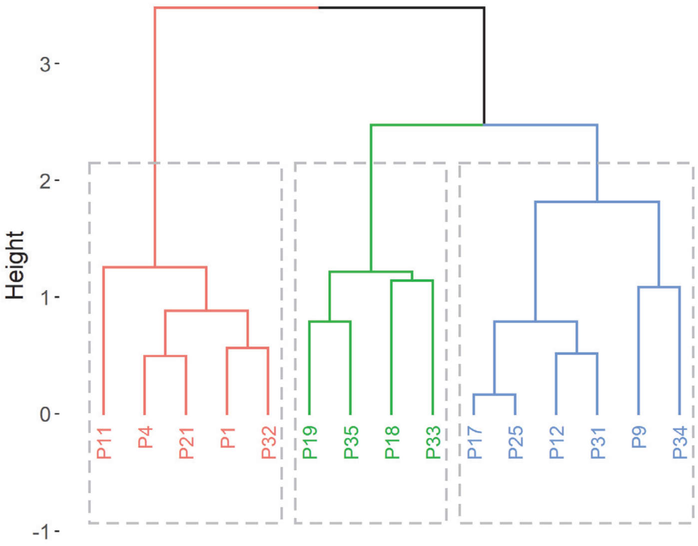

Fig. 6. Dendrogram of division of sampling sites

4. Conclusions

Heavy metals are some of the most hazardous contaminants of groundwater. This hazard is of particular importance in protected areas of nature value located near large industrial and urban centres. The impact of anthropopressure needs to be assessed on an on-going basis to ensure the earliest possible detection of threats.

Results of conducted studies indicate a relatively good condition of groundwater in the analysed area. Values of medians for concentrations in the case of most indexes correspond to quality class I in view of boundary values for physico-chemical parameters of groundwater. Only the median for Mn concentrations corresponded to quality class 2 and Ca for quality class 3. However, to ensure adequate assessment of water status it is necessary to determine proper values of the geochemical background under local conditions.

Performed statistical analyses identified two groups of elements. First group comprises Ba, Ca, K, Mg and Na. The second group is composed of B, Fe, Mn and Zn which usually are connected with anthropogenic sources.

The spatial analysis of variation in metal concentrations in groundwater may be facilitated by the application of cluster methods, combining areas with a similar variation in water quality parameters. Three groups of sampling locations showing a similar variation in metal concentration in groundwater were distinguished. The first one is located nearby open water bodies, the second in the lowest parts of relief and the third in the upper and middle parts of slopes.

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Abstract

This paper presents a statistical analysis of concentrations for selected metals in groundwater samples collected from 15 sites located in the Wielkopolska National Park in four periods of 2017. Concentrations of such metals as B, Ba, Ca, Fe, K, Mg, Mn, Na and Zn were analysed. Statistical analysis identified two groups of metals in terms of similarity in their concentrations in groundwater. One group is composed of Ba, Ca, K, Mg and Na, while the other comprises B, Fe, Mn and Zn. The analyses showed also considerable variation of investigated elements between various well locations. Three types of location were distinguished: situated nearby open water bodies, situated in the lowest parts of relief and located in the upper and middle parts of slopes.

Keywords:
groundwater quality, heavy metal, protected areas, Wielkopolska National Park

Ocena stężeń wybranych metali w wodzie gruntowej na terenie Wielkopolskiego Parku Narodowego

Streszczenie

W pracy przedstawiono statystyczną analizę stężeń wybranych metali w próbkach wody gruntowej pobieranych w roku 2017 w 15 miejscach na terenie Wielkopolskiego Parku Narodowego. Analizie poddano stężenia następujących metali: B, Ba, Ca, Fe, Mg, Mn, Na i Zn. Obliczenia statystyczne pozwoliły wydzielić dwie grupy pierwiastków wykazujące podobną zmienność stężeń. Do pierwszej zaliczono Ba, Ca, K, Mg i Na, podczas gdy do drugiej zaliczono B, Fe, Mn i Zn. Analizy wykazały również znaczącą zmienność stężeń badanych metali wynikającą z położenia miejsca poboru próbki w rzeźbie terenu. Wydzielone trzy typy lokalizacji to: położone w bezpośrednim sąsiedztwie wód powierzchniowych, położone w najniższych partiach terenu oraz położone w górnych i środkowych partiach zboczy.

Słowa kluczowe:
jakość wody gruntowej, metale ciężkie, obszary chronione,
Wielkopolski Park Narodowy