

# Identification of processes controlling chemical composition of pit lakes waters located in the eastern part of Muskau Arch (Polish-German borderland)

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**Abstract:** Exploitation of lignite within the area of Muskau Arch, carried out from the mid-nineteenth century, contributed to the transformation of the natural environment and changes in water regime. In the post-mining subsidences pit lakes were formed. The chemical composition of waters is a consequence of the intensive weathering of pyrite ( $\text{FeS}_2$ ), which is present in Miocene lignite-bearing rock forming the embankments of the lakes. This process leads to the formation of Acid Mine Drainage (AMD) and finally acidification of lake waters.

This paper presents results of the identification of hydrogeochemical processes affecting the chemistry of waters from these reservoirs carried out using the speciation and statistical (cluster and factor) analyses. Cluster analysis allowed to separate from the analyzed group of anthropogenic reservoirs 7 subgroups characterized by a similar chemical composition of waters. The major processes affecting the chemistry of waters were identified and interpreted with help of factor and speciation analysis of two major parameters (iron and sulfur).

## Introduction

Exploitation of lignite in the area of Muskau Arch caused the formation of the biggest in Poland group of artificial post-mining reservoirs, called also the “anthropogenic lake district” (Jędrzák 1997, Wróbel, 1997). Waters of these reservoirs are characterized by significantly different composition from the average chemistry of surface waters in Poland. The main distinguishing feature is acidic reaction of water, accompanied by elevated concentrations of sulfates and metals. Chemistry of these waters is formed as a result of the Acid Mine Drainage (AMD) – intensive weathering of pyrite ( $\text{FeS}_2$ ) occurring in miocene lignite-bearing rocks forming the embankments of reservoirs (Skoczyńska-Gajda and Labus 2011, Skoczyńska-Gajda and Labus 2011, Labus and Skoczyńska 2013). Acid Mine Drainage is one of the main hydrogeochemical problems associated with mining activity. The generation of AMD is likely to cause serious environmental pollution. It could lead to ecological destruction of water environment (impoverishment of flora and fauna) and the contamination of drinking water resources.

Within the analyzed reservoirs numerous hydrogeochemical processes occur affecting the final chemical composition of waters. Transformation of iron and sulfur is of major importance amongst them. To identify the processes

forming the chemistry of the waters, speciation analysis of those elements was carried out.

With aid of statistical techniques, despite significant differences among the waters chemistry, the subgroups were characterized by similar properties of the chemical composition, and the main processes determining their chemistry were identified.

The results of work may have practical application in the area of environmental protection and engineering. Particular identification and interpretation of hydrogeochemical processes occurring in the analyzed reservoirs can be the basis for the development of appropriate methods of acidic water remediation.

## Study area

The area under consideration is localized in the border zone between Poland and Germany, in the eastern part of the Muskau Arch (known also as Muskauer Faltenbogen and Łuk Mużakowa) (Fig. 1). It covers about 100 reservoirs of the total area over 150 ha, which originated about 30–100 years ago. The origin of the lakes is connected with mining of Miocene lignites conducted in the region since the second half of the 19<sup>th</sup> century until 1974. The lignite exploitation was largely conditioned by geological structure of the region. Lignite, deposited in Miocene sediments in depths of 100–200 m, has been uplifted to the

surface because of glaciectonical disturbances connected with a lobe of Elsterian glaciation. The sediments were compressed and pushed up, what made the lignite exploitation in open pits possible (Kožma and Kupetz 2008). Exploitation of lignite caused the destruction of a vegetation cover, geomorphology changes and water conditions disturbances. The long and usually narrow subsidence basins, gradually filled with water, were created as a result of open-pit and underground exploitation.

The area studied encloses 27 reservoirs situated NW to the town of Łęknica (Fig. 1). They are featured by higher acidity and concentrations of sulfates and metals compared to other lakes located in the entire region.

## Materials and methods

Basic physicochemical parameters (pH, Eh, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Fe<sub>og</sub>, Mn<sup>2+</sup>, Al<sup>3+</sup>) were determined in water samples collected from 27 reservoirs. In addition, in reservoir No. 24, located in the Chwaliszówka river basin, analysis in the vertical profile was carried out.

In the analyzed samples the oxidation – reduction potential (Eh) and pH were measured *in situ* using the multifunction meter – Elmetron CX-742. The major ions were determined using standard methods in the laboratory of the Institute of Applied Geology, Silesian University of Technology in Gliwice. In the depth profile of the reservoir No. 24, the temperature and oxygen content were measured.

To determine the forms (speciation) of iron and sulfur compounds at various depth zones of the reservoir No. 24, mathematical modeling with use of PHREEQC II software (Parkhurst and Appelo 1999) was carried out.

Cluster analysis was applied for grouping the reservoirs characterized by similar physicochemical parameters of waters. The major processes affecting the chemistry of waters were identified and interpreted with help of factor analysis using the Statsoft 8 software (Statsoft 2005).

### Cluster analysis

In order to separate groups of reservoirs characterized by similar properties of the physicochemical composition of

water (pH, Eh, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Fe<sub>og</sub>, Mn<sup>2+</sup>, Al<sup>3+</sup>) statistical techniques of cluster analysis (CA) were used.

Cluster analysis is associated with the extraction of certain groups (clusters) from the data sets (objects, observations). This method can be used to test water quality data and determine whether samples can be grouped into a distinct population (hydrochemical groups). There are two basic types of data clustering algorithms: hierarchical and non-hierarchical. Hierarchical clustering is a method which aims to build a binary tree (dendrogram) of the data that successively merge similar groups of points. The commonly used non-hierarchical algorithm is k-means clustering. In general, the *k*-means method is based on minimizing the variation within clusters and maximizing variability between them. This method will produce *k* different clusters of greatest possible distinction (Guller et al. 2002, Statsoft 2005).

In this paper the hierarchical agglomeration method was carried out to determine the number of groups to which the reservoirs can be classified. In order to decide which clusters should be aggregated a measure of dissimilarity between sets of observations is required. This was achieved by use of an appropriate metric (a measure of distance between pairs of observations) – the Euclidean distance, and a linkage criterion which specifies the dissimilarity of set – the Ward's method.

### Factor analysis

Factor analysis (FA) was used as an aid in identification of the main processes determining the chemistry of water from the reservoirs and to define their effect on the parameters of water (Labus and Siwek 2003). FA consists of a group of methods and statistical procedures for examining the interactions among a large number of variables and the detection of a hidden pattern of relationships between them.

The most commonly used methods of factor analysis are:

- Principal Component Analysis (PCA),
- Principal Factor Analysis (PFA).

The PCA is preferred as a method of data reduction.

The PFA, used often for detection of structures and relationships (Paradysz 2005), in this paper was used to discover the relationships

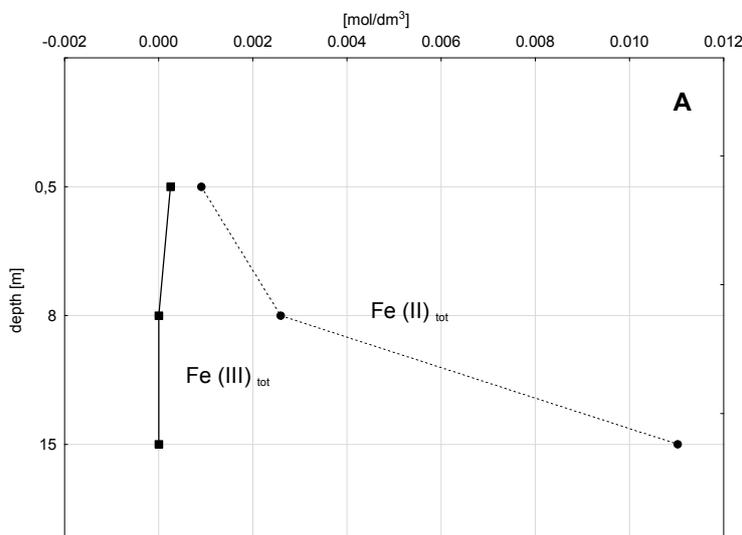


Fig. 1. ?

between the parameters of waters from reservoirs (variables) and the processes that determine their chemical composition.

To determine the number of principal factors the Cattell's scree test was used. The factors are ordered along the X axis according to the decreasing eigenvalues which are plotted against the Y axis. Cattell (Paradysz 2005) suggests finding the place where the smooth decrease of eigenvalues appears to level off to the right of the plot. To the right of this point only irrelevant "factorial scree" is found. Therefore, it should not be separated more factors other than these located on the left side of the point.

It often happens that the same variables are highly correlated with various factors, which leads to unambiguous interpretation. In this case making the rotation of factors (rotation the axes relative to the coordinate origin) is necessary. The purpose of this rotation is to obtain a clear pattern of loadings, i.e. factors that are clearly marked by high loadings for some variables and low loadings for the others (Zeliaś 2000).

In this paper PFA was carried out using a rotation that maximizes the variance (varimax). The purpose was to obtain a simple structure of factor loadings, allowing for the relatively easy interpretation of factors.

## Results

### Physicochemical and speciation analysis

The results of physicochemical analysis are presented in Tab. 1 and 2, and speciation analysis in Tab. 3 and 4.

Reservoir No. 24, in which physicochemical analysis was conducted in the profile, belongs to the meromictic type. In the case of meromictic lakes waters from particular depth zones do not mix in the whole profile. There are 3 depth zones in these lakes: a subsurface zone (mixolimnion) which is mixed, a bottom zone (monimolimnion), in which no mixing occurs and (between them) a transition zone (chemocline) where the temperature and chemical composition of water change rapidly (Chełmicki 2002).

In the analyzed reservoir: mixolimnion is at the depth of about 5–6 m, chemocline at 6–9 m and monimolimnion at 9–15 m.

In the subsurface zone of the analyzed reservoir iron occurs in both forms: di- and trivalent, and with depth an increase of the concentration of divalent iron form is observed (Fig. 2A). In all zones of the reservoir the dominant form of divalent iron are  $\text{Fe}^{2+}$  and  $\text{FeSO}_4$  (Tab. 3). In the case of the

**Table 1.** Physicochemical parameters of waters from analyzed reservoirs

Parameter No. of reservoir	pH	Eh [mV]	Cl <sup>-</sup> [mg/l]	SO <sub>4</sub> <sup>2-</sup> [mg/l]	Ca <sup>2+</sup> [mg/l]	Mg <sup>2+</sup> [mg/l]	Na <sup>+</sup> [mg/l]	K <sup>+</sup> [mg/l]	Fe <sub>og</sub> [mg/l]	Mn <sup>2+</sup> [mg/l]	Al <sup>3+</sup> [mg/l]
1	3.3	613	13.1	522	86.5	20.1	13.2	8	1	0.9	2.2
2	3.6	590	11.1	469	82.5	18.5	9.3	6.5	0.3	0.9	0.3
3	2.8	700	10.2	1970	361.6	49.7	7.4	8.6	47.4	4.2	25.3
4	2.7	725	8.1	1942	319.3	47.3	7.2	7.8	80.8	3.9	16.3
5	2.7	727	8.5	1887	206	37.9	7.6	6.4	80.2	4.1	34.8
6	2.8	701	4.2	647	50.6	17.3	4.2	6.2	29.4	0.9	30.3
7	2.6	735	9.4	2024	255.5	41	8.5	8.2	186.4	4.4	4.8
8	2.2	760	6.1	1934	103.6	24.8	6.4	4.8	144.7	3.2	31.5
9	2.9	690	10.7	1582	270.3	43.2	9.4	8.9	26.3	2.9	3.6
10	2.9	693	4.2	605	43.4	10.6	5.4	7.1	17.5	1.0	5.3
11	2.9	691	5.8	591	43.2	8.9	3.3	4.4	14.1	2.8	3.1
12	2	782	12.3	524	200.9	31.2	3.9	6.7	26.1	2.7	4.5
13	3.2	675	11.1	689	87.6	18.9	5.3	4.2	8.9	0.8	1.1
14	2.8	705	7.2	524	96.5	22.8	1.7	3.4	145	3.1	24.7
15	2.8	780	6.9	768	111.8	35.1	9.2	6.5	76	2.5	15.8
16	2.7	734	9.3	498	32.5	23.4	6	10.1	26	1.5	11.7
17	2.6	765	6.1	476	150.2	12.9	2.9	4.5	11	0.9	1.5
18	2.9	728	16.3	354	44.7	26.1	3.1	3.8	100	3.7	22.7
19	3.1	690	13.8	635	265.8	29.9	9	8.3	26.7	2.3	0.9
20	3.2	687	12.7	510	225.3	21.2	7	6	16.8	2.1	1.7
21	3.2	680	11.8	623	290.1	31.2	9.1	7.2	20	1.7	3.4
22	3.1	701	14.5	756	310.7	33.4	5.5	3.1	17.8	3.6	11.2
23	3.2	692	14.8	596	276.3	36.7	8.3	7.1	8.9	1.5	2.9
24	3	654	17.1	698	116.7	22.1	3.7	2.9	64.7	3.5	2.7
25	3	725	10.1	402	61.3	11.5	5.4	3.8	4.5	2.1	1
26	6.5	350	11	120	52.1	9.2	1.9	4.3	1	0.2	0.9
27	3.2	620	9.6	345	49.8	16.3	2.7	3.5	2.7	1.0	1.1

**Table 2.** Changes of physicochemical and chemical parameters in a vertical profile of the analyzed reservoir No. 24

H [m]	T [°C]	pH	Eh [mV]	O <sub>2</sub> [mg/l]	Cl <sup>-</sup> [mg/l]	SO <sub>4</sub> <sup>2-</sup> [mg/l]	Ca <sup>2+</sup> [mg/l]	Mg <sup>2+</sup> [mg/l]	Na <sup>+</sup> [mg/l]	K <sup>+</sup> [mg/l]	Fe <sub>og</sub> [mg/l]
0.5	25.6	3	654	7.5	17.1	662	116.7	22.1	3.7	2.9	64.7
2	24	3	667	7.6	19.1	711	109.5	24.1	4.1	3.3	60.3
5	16.4	4	623	7.5	23.1	701	121.3	26	4.3	3.2	78.5
8	10.1	4	488	7.5	22.3	923	169.8	38.9	4.9	6.7	145
10	8.9	4	446	0	23.5	1218	179.1	44.5	4.8	8.4	557
12	8.7	4	419	0	22	1311	193.1	51.5	4.9	8.5	584
15	8.7	3.9	435	0	22	1530	209	55.4	5.1	8.7	616

**Table 3.** Forms of iron [mol/dm<sup>3</sup>] dominant in water of the analyzed reservoir No. 24

	Fe(II) <sub>tot</sub> [mol/dm <sup>3</sup> ]	Fe <sup>2+</sup> [mol/dm <sup>3</sup> ]	FeSO <sub>4</sub> [mol/dm <sup>3</sup> ]	FeHSO <sub>4</sub> <sup>+</sup> [mol/dm <sup>3</sup> ]	FeOH <sup>+</sup> [mol/dm <sup>3</sup> ]
mixolimnion	9.079·10 <sup>-4</sup>	6.860·10 <sup>-4</sup>	2.199·10 <sup>-4</sup>	1.664·10 <sup>-4</sup>	1.567·10 <sup>-10</sup>
chemocline	2.593·10 <sup>-3</sup>	1.999·10 <sup>-3</sup>	5.926·10 <sup>-4</sup>	4.497·10 <sup>-7</sup>	1.283·10 <sup>-9</sup>
monimolimnion	1.103·10 <sup>-2</sup>	8.336·10 <sup>-3</sup>	2.686·10 <sup>-3</sup>	2.684·10 <sup>-6</sup>	3.430·10 <sup>-9</sup>
	Fe(III) <sub>tot</sub> [mol/dm <sup>3</sup> ]	FeSO <sub>4</sub> <sup>+</sup> [mol/dm <sup>3</sup> ]	Fe(OH) <sup>2+</sup> [mol/dm <sup>3</sup> ]	Fe <sup>3+</sup> [mol/dm <sup>3</sup> ]	Fe(OH) <sub>2</sub> <sup>+</sup> [mol/dm <sup>3</sup> ]
mixolimnion	2.506·10 <sup>-4</sup>	1.651·10 <sup>-4</sup>	5.011·10 <sup>-5</sup>	1.222·10 <sup>-5</sup>	1.135·10 <sup>-5</sup>
chemocline	3.137·10 <sup>-6</sup>	7.820·10 <sup>-7</sup>	1.033·10 <sup>-6</sup>	6.905·10 <sup>-8</sup>	1.187·10 <sup>-6</sup>
monimolimnion	1.128·10 <sup>-6</sup>	4.153·10 <sup>-7</sup>	3.579·10 <sup>-7</sup>	3.592·10 <sup>-8</sup>	2.750·10 <sup>-7</sup>

**Table 4.** Forms of sulfur [mol/dm<sup>3</sup>] dominant in water of the analyzed reservoir No. 24

	S(VI) <sub>tot</sub> [mol/dm <sup>3</sup> ]	SO <sub>4</sub> <sup>2-</sup> [mol/dm <sup>3</sup> ]	CaSO <sub>4</sub> [mol/dm <sup>3</sup> ]	HSO <sub>4</sub> <sup>-</sup> [mol/dm <sup>3</sup> ]	FeSO <sub>4</sub> [mol/dm <sup>3</sup> ]
mixolimnion	6.891·10 <sup>-3</sup>	5.006·10 <sup>-3</sup>	7.595·10 <sup>-4</sup>	3.339·10 <sup>-4</sup>	2.199·10 <sup>-4</sup>
	S(VI) <sub>tot</sub> [mol/dm <sup>3</sup> ]	SO <sub>4</sub> <sup>2-</sup> [mol/dm <sup>3</sup> ]	CaSO <sub>4</sub> [mol/dm <sup>3</sup> ]	FeSO <sub>4</sub> [mol/dm <sup>3</sup> ]	MgSO <sub>4</sub> [mol/dm <sup>3</sup> ]
chemocline	9.608·10 <sup>-3</sup>	7.286·10 <sup>-3</sup>	1.160·10 <sup>-3</sup>	5.926·10 <sup>-4</sup>	4.129·10 <sup>-4</sup>
monimolimnion	1.593·10 <sup>-2</sup>	1.090·10 <sup>-2</sup>	1.526·10 <sup>-3</sup>	2.686·10 <sup>-3</sup>	6.216·10 <sup>-4</sup>

trivalent iron, FeSO<sub>4</sub><sup>+</sup>, Fe(OH)<sup>2+</sup>, Fe(OH)<sub>2</sub><sup>+</sup> complexes and Fe<sup>3+</sup> are predominate. With depth a decrease of the concentration of Fe<sup>3+</sup> in favor of Fe<sup>2+</sup> ions is noticeable (Fig. 2B).

The dominant forms of sulfur in mixolimnion are: SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> ions, and compounds: CaSO<sub>4</sub> and FeSO<sub>4</sub> (Tab. 4). In chemocline and monimolimnion SO<sub>4</sub><sup>2-</sup>, FeSO<sub>4</sub>, CaSO<sub>4</sub> and MgSO<sub>4</sub> occur.

Main hydrogeochemical processes occurring in the analyzed reservoir were identified based on the speciation analysis of iron and sulfur forms (reaction 1–9) (Fig. 3). Fe<sup>2+</sup> ions, which are the product of pyrite weathering, according to the AMD reaction (1), are transported to the analyzed reservoir with leachate from Miocene lignite-bearing rock forming the embankments of the reservoir. In the subsurface zone (mixolimnion) oxidation of ferrous to ferric ions may occur according to the reaction (2) and formation of their hydro-complexes (reaction 3) may take place. Due to the elevated concentration of sulphates, their complexes with Fe<sup>3+</sup> are formed according to the reaction (4). Fe<sup>2+</sup> remaining in the water can migrate in the simple

form or form compounds, mostly with sulphates (reaction 5), identified in the water using the speciation analysis (Tabs 3 and 4). Jarosite – hydrous sulfate of potassium and iron – can precipitate from acid water rich in sulphates and ferric ions (reaction 6). To determine the possibility of crystallization of jarosite and Fe(OH)<sub>3</sub>, the relevant saturation indexes (SI) were calculated by means of PHREEQC II software. The results are presented in Tab. 5. Saturation state of water with respect to a particular mineral is defined by the SI. When SI > 0, water is supersaturated relative to a particular mineral, when SI < 0, water is undersaturated and when SI = 0, a thermodynamic equilibrium occurs. On the basis of calculations it was found that the subsurface and transition zones are supersaturated with respect to jarosite, and so is a high probability of its precipitation.

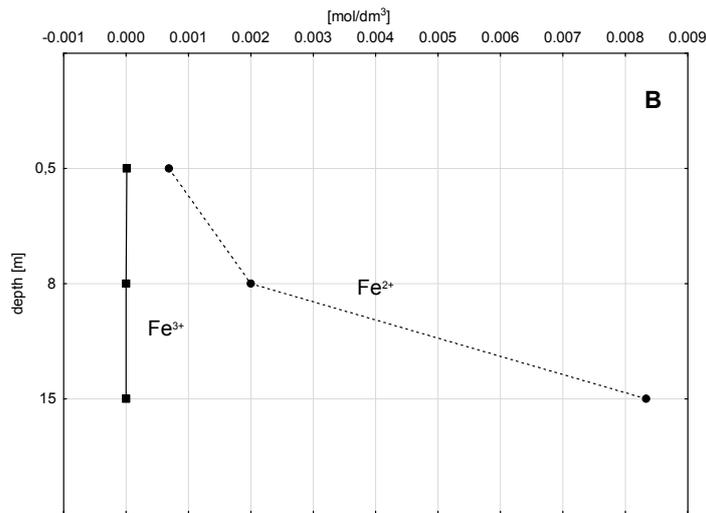
In the transition zone (chemocline) of the reservoir ferric ions can be bound in the form of iron hydroxide (III) (reaction 7), present in the form of characteristic brownish-orange sediments. The SI value (Tab. 5), although not exceeding the thermodynamic equilibrium (SI = 0), indicates

a tendency to water saturation with respect to Fe(OH)<sub>3</sub> within this zone.

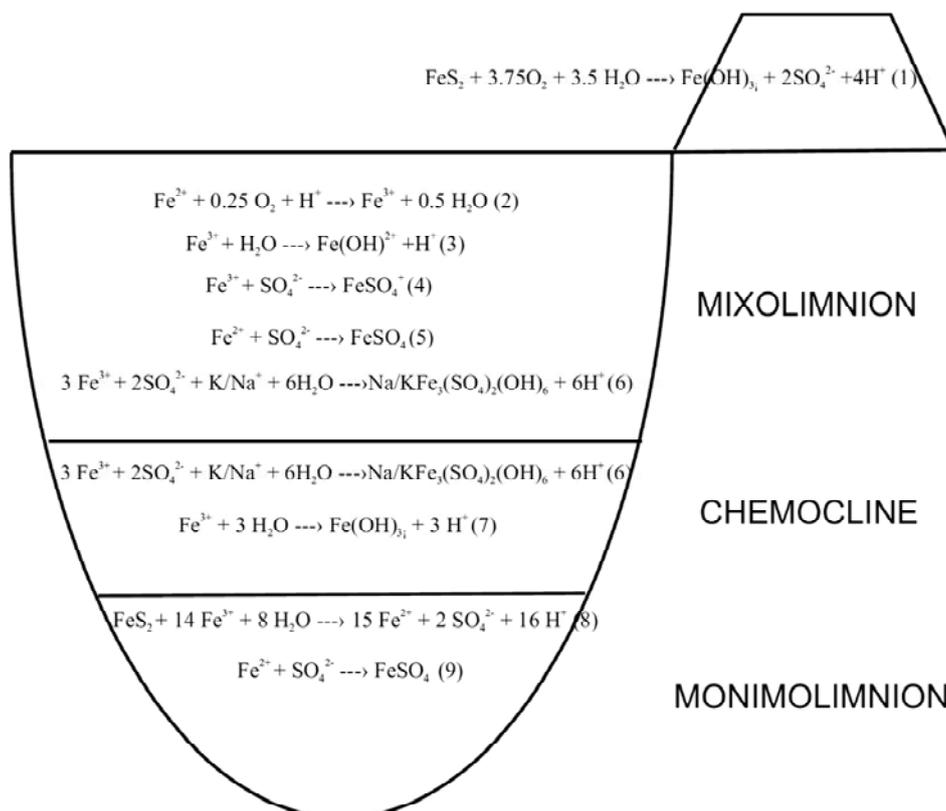
**Table 5.** Saturation indexes of Fe(OH)<sub>3(a)</sub> and jarosite in depth zones of reservoir No. 24

	Fe(OH) <sub>3</sub>	Jarosite
mixolimnion	-1.25	1.93
chemocline	-0.55	0.37
monimolimnion	-1.24	-1.2

In the bottom zone (monimolimnion) lower Fe<sup>3+</sup> concentrations are observed in the contrary to significantly increased Fe<sup>2+</sup> (Fig. 2B). This can be explained by the consumption of ferric ions due to oxidation of pyrite (reaction 8), which is (as suggested in (Jędrzak, 1997)) present in bottom sediments of the reservoir. The products of this process, besides of ferrous ions, are also sulphates at concentrations higher than in mixolimnion (Tab. 4). Ferrous ions remain in the bottom zone mainly as Fe<sup>2+</sup>. They may also form complexes with sulphates as it was the case in mixolimnion (reaction 9).



**Fig. 2.** Concentrations vs. depth: A – divalent and trivalent forms of iron; B – Fe<sup>2+</sup> i Fe<sup>3+</sup> ions in the vertical profile of the analyzed reservoir No. 24



**Fig. 3.** Primary processes connected with the transformation of iron and sulfur forms to occur in the analyzed reservoir No. 24

**Cluster and factor analysis**

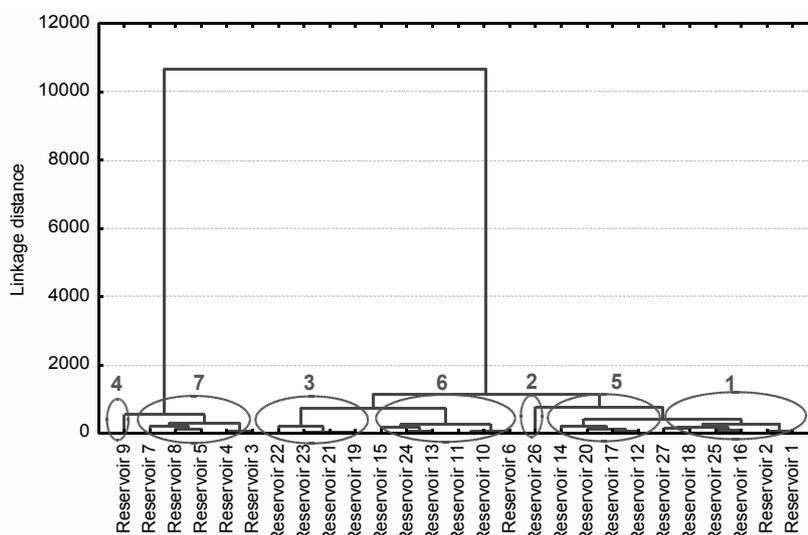
As a result of the agglomeration 7 clusters (groups of reservoirs) were finally formed (Figs 4 and 5).

The reservoirs of the cluster No. 3 (reservoirs: No. 19, 21–23) form a group located in the upper part of the Chwaliszówka river. A similar situation is observed in the case of cluster No. 7 (reservoirs: No. 3–5, 7, 8) – the reservoirs form a closed group located to the east of Łeknica village. Reservoirs belonging to the remaining clusters are scattered throughout the investigated area.

In order to clarify which features determine the membership of each reservoir to the cluster obtained through the hierarchical agglomeration method, k-means clustering was applied. It additionally allowed to check how the results of this method are consistent with these of the agglomeration analysis. The number of clusters (k-means) was selected based on the results of the previously conducted agglomeration. The average values of the measured parameters from selected clusters, which were compared, are shown in Tab. 6.

**Table 6.** The average values and standard deviations of parameters of water from reservoirs belonging to the separated clusters

Parameters	Cluster No. 1 (reservoirs No.: 1, 2, 16, 18, 25, 27)		Cluster No. 2 (reservoir No. 26)		Cluster No. 3 (reservoirs No.: 19, 21, 22, 23)		Cluster No. 4 (reservoir No. 9)		Cluster No. 5 (reservoirs No.: 2, 14, 17, 20)		Cluster No. 6 (reservoirs No.: 6, 10, 11, 13, 15, 24)		Cluster No. 7 (reservoirs No.: 3, 4, 5, 7, 8)	
	Average value	Standard deviation	Average value	Standard deviation	Average value	Standard deviation	Average value	Standard deviation	Average value	Standard deviation	Average value	Standard deviation	Average value	Standard deviation
pH	3.11	0.31	6.5	–	3.15	0.05	2.9	–	2.65	0.5	2.93	0.16	2.60	0.08
Eh[mV]	668.3	67.25	350	–	690.7	8.61	690	–	734.7	45.8	699	41.34	729.4	15.12
Cl <sup>-</sup> [mg/l]	11.5	2.68	11	–	13.7	1.35	10.7	–	9.57	3.4	8.21	2.84	8.46	0.93
SO <sub>4</sub> <sup>2-</sup> [mg/l]	431.6	75.33	120	–	652.5	70.90	1582	–	508.5	22.6	666.3	71.51	1951.4	57.08
Ca <sup>2+</sup> [mg/l]	59.5	21.46	52	–	285.7	19.39	270.3	–	168.2	57.1	75.5	30.91	249.2	68.68
Mg <sup>2+</sup> [mg/l]	19.3	5.18	9.2	–	32.8	2.97	43.2	–	22.02	7.49	18.8	10.38	40.14	5.46
Na <sup>+</sup> [mg/l]	6.61	4.00	1.9	–	7.9	1.68	9.4	–	3.87	2.26	5.18	2.25	7.42	0.57
K <sup>+</sup> [mg/l]	5.95	2.71	4.3	–	6.4	2.28	8.9	–	5.15	1.48	5.21	1.30	7.16	0.95
Fe <sub>og</sub> [mg/l]	22.4	39.21	1	–	18.3	7.34	26.3	–	49.7	63.8	35.1	27.23	107.9	60.51
Mn <sup>2+</sup> [mg/l]	1.68	1.09	0.2	–	2.2	0.94	2.9	–	2.2	0.95	1.91	0.96	3.96	0.20
Al <sup>3+</sup> [mg/l]	6.5	9.0	0.9	–	4.6	4.53	3.6	–	8.1	11.1	9.7	12.12	22.5	12.79



**Fig. 4.** The results of agglomeration analysis – a dendrogram (hierarchical tree) with marked clusters (from 1 to 7)

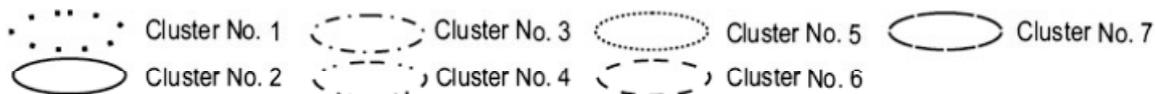
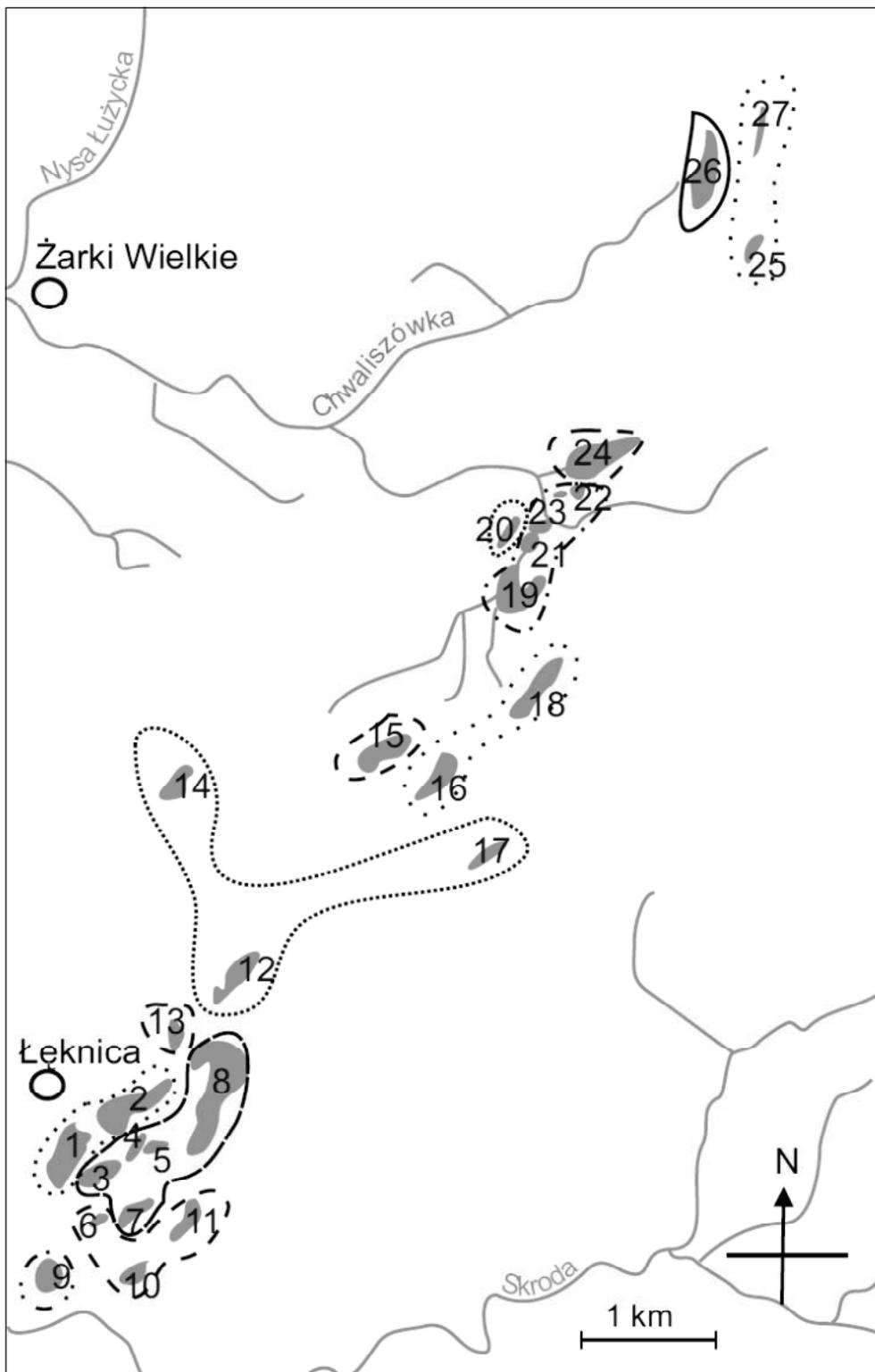


Fig. 5. Groups of analyzed reservoirs formed as a result of agglomeration

Waters of reservoirs from cluster No. 1 (reservoirs: No. 1, 2, 16, 18, 25, 27) are characterized by the lowest concentration of sulfates (average 431.6 mg/l) and low concentration of calcium (average 59.5 mg/l). Waters of reservoirs from cluster No. 3 (reservoirs No. 19, 21–23) have relatively low sulfates

(652.5 mg/l) and high (285.7 mg/l) average calcium contents. In waters from reservoirs belonging to cluster No. 5 (reservoirs: No. 12, 14, 17, 20) low concentrations of sulfates (average 508.5 mg/l) and relatively high of iron (average 49.7 mg/l) are observed. Waters from cluster No. 6 (reservoirs: No. 6, 10,

11, 13, 15, 24) are characterized by elevated concentrations of iron (average 35.1 mg/l) and aluminum (9.7 mg/l), and a relatively low content of calcium (75.5 mg/l). Waters from reservoirs in cluster No. 7 (reservoirs No. 3–5, 7, 8) have high average contents of sulfates (1951.4 mg/l), iron (107.9 mg/l) and aluminum (22.5 mg/l).

Furthermore, two individual reservoirs, clearly different in terms of water chemistry, were isolated. High water reaction (6.5 pH) was the parameter that determined the separation of reservoir No. 26 (cluster No. 2) as pH in the remaining lakes is in the range of 2.5–3.5. Waters of

the reservoir No. 9 (cluster No. 4) are characterized by high concentrations of sulfates (1582 mg/l) and relatively low of iron (26.3 mg/l) and aluminum (3.6 mg l).

For the interpretation of the main processes determining the reservoirs' water chemistry, and to define their effect on water parameters five main factors (F1–F5) extracted based on PFA with the highest eigenvalues were used. These factors, selected on the basis of the Cattell's scree test (Fig. 6), explain almost 90% of the total variance (Tab. 7). Factor loadings of each variable for separate factors are shown in Tab. 8, and the interpretation of the extracted factors is presented below.

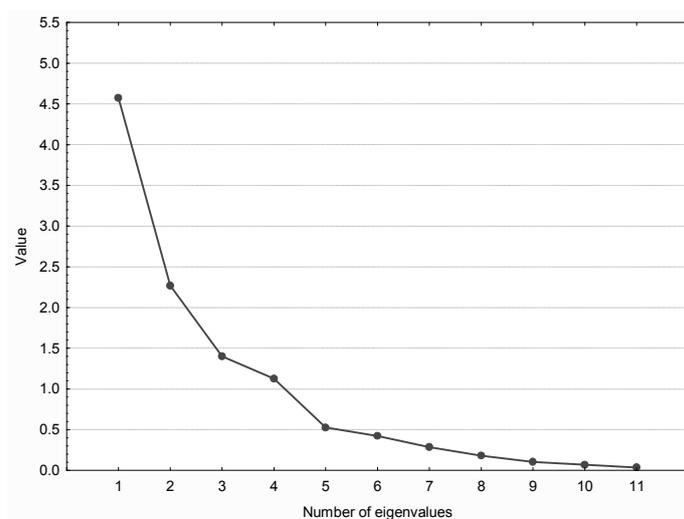


Fig. 6. The scree plot of eigenvalues

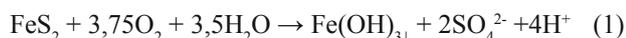
Table 7. The Principal Factor Analysis (PFA) and variance parameters

Factors	Eigenvalues	% of Total Variance	Cumulative Eigenvalues	Cumulative % of Total Variance
F1	4.6	41.6	4.6	41.6
F2	2.3	20.6	6.8	62.2
F3	1.4	12.7	8.2	74.9
F4	1.1	10.3	9.4	85.2
F5	0.5	4.8	9.9	90.0

Table 8. Values of factor loadings (the absolute values above 0,5 – bolded).

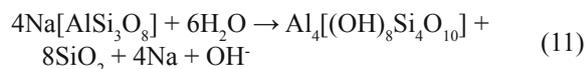
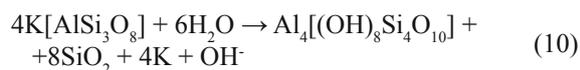
Variable \ Factor	F1	F2	F3	F4	F5
pH	-0.22	-0.10	0.09	<b>-0.95</b>	-0.11
Eh[mV]	0.21	0.06	-0.09	<b>0.95</b>	0.14
Cl <sup>-</sup> [mg/l]	-0.13	0.01	<b>0.94</b>	-0.13	0.18
SO <sub>4</sub> <sup>2-</sup> [mg/l]	<b>0.61</b>	0.31	-0.25	0.13	<b>0.57</b>
Ca <sup>2+</sup> [mg/l]	0.02	0.24	0.16	0.10	<b>0.93</b>
Mg <sup>2+</sup> [mg/l]	0.38	0.39	0.14	0.18	<b>0.76</b>
Na <sup>+</sup> [mg/l]	-0.02	<b>0.91</b>	0.18	0.06	0.17
K <sup>+</sup> [mg/l]	-0.04	<b>0.87</b>	-0.19	0.08	0.25
Feog[mg/l]	<b>0.91</b>	-0.02	0.02	0.20	0.05
Mn <sup>2+</sup> [mg/l]	<b>0.69</b>	-0.08	0.22	0.33	0.52
Al <sup>3+</sup> [mg/l]	<b>0.76</b>	-0.07	-0.35	0.15	0.08

The first factor (F1) is characterized by the maximum value of factor loadings for sulfates and metals: iron, manganese and aluminum. The main processes associated with this factor are described by the reaction (1):



The products of this reaction are: colloidal form of iron (iron hydroxide) sulfate ions and hydrogen ions – responsible for acidification of the environment. With the decrease of pH (negative factor loadings) the redox potential (Eh) and concentrations of iron, aluminum, manganese and magnesium apparently increase. This is due to leaching and migration of metals to the water in the acidic environment. Only the contents of chlorides, sodium and potassium decrease, however, the values of the corresponding factor loadings are not statistically significant.

The second factor (F2) explains the presence of sodium and potassium in the analyzed waters (maximum factor loadings values). It is most likely related to the delivery of these elements due to decomposition of aluminosilicates (e.g. potassium and sodium feldspars present in Miocene lignite-bearing rock forming the embankments of the reservoirs) in the acidic environment (negative factor loadings for pH) according to the reactions (10 and 11):



Some reservoirs are located in the neighborhood of farmlands, thus fertilizers (K and Na nitrates) commonly used in these areas, are most probably an additional source of sodium and potassium.

The third factor (F3) is positively correlated with the chlorides, which probably reflects the delivery of these conservative ions with rainfall. Additionally, natural fertilizers used on nearby farmlands could be a source of this parameter.

The fourth factor (F4) is related to pH and redox potential (which are linked by an inversely proportional relationship). With the decrease of pH, the values of other parameters increase (except for the chlorides – already discussed), in connection with the higher mobility in acidic environments.

The fifth factor (F5) is related mostly to the presence of calcium and magnesium, which often occur concomitantly in nature. The source of these elements can be weathering of carbonate rock minerals (eg. calcite –  $\text{CaCO}_3$ ) or aluminosilicate (e.g. orthochlorite –  $(\text{Fe,Mg})_6(\text{OH})_2(\text{Si,Al})_4\text{O}_{10}$ ), whose presence were found in Miocene lignite-bearing rock forming the embankments of the lakes. Their concentration increases along with the decrease of pH, as in the case of other parameters, and (as previously described) is connected with dissolution of rocks and minerals, and migration of elements in acidic environments.

## Conclusions

Numerous hydrogeochemical processes related mainly to the transformations of iron and sulfur occur within the analyzed

reservoirs and affect the final waters chemistry. These have been identified based on the results of speciation analysis carried out for water from the selected reservoir No. 24. This example demonstrates that water chemistry is controlled by different hydrochemical processes in the particular depth zones. In the subsurface zone (mixolimnion) the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , and hydrocomplexes forming or jarosite precipitation are the main processes. In the transition zone (chemocline) jarosite crystallization may also occur and additionally,  $\text{Fe}(\text{OH})_3$  can precipitate, while in the bottom zone (monimolimnion) mainly oxidation of pyrite by the ferric iron is possible to occur.

The analyzed anthropogenic reservoirs are differentiated by acidic reaction and elevated concentrations of sulfates and metals. Moreover, there are some differences in water chemistry among them. On the basis of cluster analysis seven groups of reservoirs (clusters) characterized by the most similar properties of the chemical composition of waters were identified.

The Principal Factor Analysis allowed for the approximate identification of the basic processes controlling the chemical water composition of the reservoirs and detection of relationships between the physicochemical parameters. It was confirmed that the main effect on water chemistry has oxidation of sulfides, while the remaining processes are of minor importance i.e. dissolution of rock forming minerals leading to the enrichment of water in certain elements. Inversely proportional relationship between pH and other parameters (such as Eh,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}_{\text{og}}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ ) was noticed – in the case of most factors, the values of these parameters increase with the decrease of pH.

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### **Identyfikacja procesów kształtujących skład chemiczny wód zbiorników zlokalizowanych na obszarach pogórnicznych we wschodniej części Łuku Mużakowa (pogranicze polsko-niemieckie)**

**Streszczenie:** Eksploatacja węgla brunatnego prowadzona w rejonie Łuku Mużakowa od połowy XIX w. przyczyniła się do przeobrażenia środowiska naturalnego obszaru i zmian w stosunkach wodnych. W poeksploatacyjnych nieckach zapadliskowych formowały się zbiorniki wodne, tworząc tzw. „pojezierze antropogeniczne”. Skład chemiczny wód jest konsekwencją wietrzenia pirytu ( $\text{FeS}_2$ ), obecnego w mioceńskich utworach węglonośnych tworzących obwałowania zbiorników. Intensywny proces utleniania siarczku doprowadził do powstania kwaśnego drenażu – Acid Mine Drainage (AMD) i w efekcie do zakwaszenia wód jezior.

W artykule zaprezentowano rezultaty identyfikacji procesów hydrogeochemicznych wpływających na chemizm wód ww. zbiorników, przeprowadzonej z wykorzystaniem analizy statystycznej (analiza skupień i analiza czynnikowa) i specyjalnej. Analiza skupień pozwoliła na wydzielenie z rozpatrywanej grupy zbiorników antropogenicznych 7 podgrup cechujących się zbliżonym składem chemicznym wód. Dla zdefiniowania głównych procesów decydujących o chemizmie wód zbiorników zastosowano analizę czynnikową oraz analizę specyjalną dwóch głównych składników wód (żelaza i siarki).