

Article

Heavy Metals in Post-Exploitation Reservoirs—The Bagry Lake Case Study (Poland)

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Abstract: The paper presents the research study on the concentration of Fe, Mn, Cu, Pb, Zn, Cd and Ca in the sediment as well as in the supernatant (layer of water just above the sediment) of the Bagry Lake, Cracow (Poland); Ca was not included in the supernatant analysis. There are a number of works in the literature on the concentrations of metals in the water environment of flow-through dam reservoirs and factors influencing their distribution. These reservoirs were created for various purposes, e.g., water supply, flood protection, leveling the flows in the rivers and recreational purposes. Since it is difficult to find information on metals and factors influencing their distribution in the aquatic environment of post-exploitation reservoirs, this work aims to fill this gap. The additional purpose of the work was to assess the potential influence of metals' presence in the sediment of Bagry Lake on benthic organisms. Correlations between metals in the sediment and their volatile and mineral fractions as well as in particle size fractions of ≥ 0.06 mm and < 0.06 mm were determined. Except for cadmium, metals showed a positive correlation with the sediment volatile fraction of granulometry < 0.06 mm (a clay-silty fraction). It has been shown that metals, in both supernatant and sediment, are of an anthropogenic origin related to previous on-lake operations, as well as a nearby modern technical infrastructure. Statistical models were used to measure the strength of relationships between the concentration of various metals in the sediments. A cluster analysis was used to study interactions between the concentration of metals in supernatant, in sediment and in its volatile and mineral fractions as well as in fractions with different granulation. It was found that individual metals and sediment fractions form pairs of quite strong clusters, e.g., Fe sediments and Mn sediments, Fe supernatant and Mn supernatant, Cu supernatant and Pb supernatant, volatile fraction and mass fraction of particles < 0.06 mm and mineral fraction and mass fraction of particles ≥ 0.06 mm. The equilibrium model "supernatant—sediment mineral fraction—sediment volatile fraction" was developed for metals in various granulometric fractions of the sediment as well as in the supernatant. The model estimated a metal concentration in both fractions of the sediment (separately) as well as an impact they had on the metal concentration in the supernatant. It also showed how changes in a metal's concentration in both fractions are reflected in concentrations of metals in the aquatic environment.

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1. Introduction

The presence of heavy metals in lakes is related to chemical characteristics of anthropogenic substances and minerals found in sediments and the lake surroundings. Nearly every metal, if present at sufficiently high concentrations, may be toxic for plants and organisms living in the lake as well as for humans. Particularly dangerous are heavy metals since they persist in the environment and tend to accumulate in organisms; some of them may be very toxic [1]. If they are present in high concentrations, heavy metals can disturb life functions both in individual organisms and the entire ecosystem. In the

aquatic environment, they may affect the number and structure of aquatic invertebrate communities [2–4] and cause morphological [5], physiological, neurological and genetic changes [6–9]. At the same time, some metals such as iron, copper, zinc, calcium and magnesium are a common and necessary component of plants and animals. Some others such as, e.g., arsenic, chromium, cobalt, manganese, molybdenum, nickel, selenium and vanadium may be vital for organisms in the environment, but their levels should be kept very low. On the other hand, metals such as mercury, lead and cadmium are not essential for organisms and are classified as highly toxic [10].

There are many different methods for assessing heavy metal toxicity. These may be indicators of the impact of metal on health, e.g., Average Daily Intake from Soil Ingestion, Inhalation and Dermal Absorption [11]. Toxicity indexes are also used to describe toxicity [12].

In order to analytically determine the metal concentration in the fractions of sediments with rose geochemical properties, metals are extracted using solutions containing various acids and, if it is necessary, other substances such as reducers, hydrogen peroxide and acetic acid salts (Tessier method) [13] or using BCR extraction [14]. None of these methods guarantees identical results of the metal concentration in four fractions: F-1—an exchangeable fraction in which metals are adsorbed mainly by clay or exist as carbonate compounds, F-2—related to Fe-Mn oxyhydroxides, F-3—related to metals associated with organic matter and sulfides and F-4—residual part. The work abandoned the analytical determination of metal concentration in individual fractions. A new physical model for determining metal concentration in two fractions, mineral and organic, was proposed. Tessier and BCR methods allow chemical classification of the presence of metals in the settlement. However, they do not explain the relationships between metals and live organic matter. For example, iron or manganese bacteria can oxidize these metals. Oxidized and unoxidized forms of these metals accumulate in a biofilm produced by bacteria. Oxidation products can accumulate in biofilm as well as in intracellular organelles. Substances can penetrate the cell wall, followed by the bacterial cell membrane, and accumulate in cytoplasm. Biofilm [15,16] is a structure produced by microorganisms consisting of proteins, polysaccharides, nucleic acids, lipid substances and other produced by these microorganisms. Biofilm has adsorption properties in relating to mineral matter, for example, metal [16]. Metals in the form of minerals can be associated with organic matter and occur in a biofilm, in the interior of the cell or on the surface of the cell wall or cell membrane which can bind metals using with specific polysaccharides, proteins and lipids.

In the case of plants, metal transport to the interior of the cell can occur through diffusion, endocytosis or reaction with protein conveyors.

Interestingly, some metals commonly considered toxic may be necessary in cellular metabolism. For example, in the marine diatoma of *Thalassiosira weissflogii*, cadmium is necessary in the activation of the enzyme carbonate anhydrase participating in photosynthetic processes. Additionally, for other algae it can be an essential element in photosynthetic processes [17].

The metals reviewed in the paper include lead and cadmium; lead ranks second while cadmium seventh on the list of priority hazardous substances prepared by the Agency for Toxic Substances and Disease Registry [18]. Zinc and copper are particularly toxic to the aquatic environment [19] while iron and manganese play an important role in migration and accumulation of other metals in the aquatic environment [20].

Monitoring of heavy metals in the aquatic environment is important not only because of their toxicity but also because too low levels of some metals in the environment may disrupt life functions of plants and animals.

The occurrence of metals in sediments can be treated as a random phenomenon in a situation of anthropogenic impact on the aquatic environment. Therefore, the presence of metals in sediments does not result from the main feature of minerals found in sediments. It is external sources of metal that shape their concentration in sediments. For a

description of the mutual relations between the metal concentration in sediments, statistical models may be used, for example linear, but the designation of the parameters of the model is not sufficient to state, with sufficient certainty, mutual relationships between metals. A statistical assessment of the quality of the received model is necessary, which can be carried out by testing the hypothesis about the significance of the model. In addition, the parameters of the received model require checking of their importance because it is not certain whether the presence of all tested metals is correlated with each other. The development of a statistical model and testing the appropriate statistical hypotheses was the subject of analyzes and calculations carried out by the authors.

Mutual links between the metal concentration in water and sediments with other components of the aquatic environment (various types of sediment fraction, granulometric composition and calcium concentration in sediments) is usually difficult in a mathematical description. The authors decided to determine these connections using a modified cluster analysis [21] using their own method of determining the distance of connections between elements of the aquatic environment.

Determining the interphase balance describing the relationship between metal concentrations in various sediment fractions and the concentration of a particular metal in water requires the development of a model for adsorption, absorption and chemical balances related to metal reactions with other mineral or organic substances (e.g., organic ligands) present in the aquatic environment. For a description of the balance between metals and the matter of natural origin, various types of izoterm equations are used [22–24]. The authors have developed their own original model of interphase balance which was used to assess the impact of sediments on the aquatic environment and vice versa. This model describes the state of equilibrium with respect to the metal concentrations contained in the three phases. One of the first models describing interfacial equilibria in the aquatic environment was the equilibrium partitioning model (EqP). It described the relationship between the concentration of a substance in water and its concentration in the sediment using a linear relationship [25]. The model (EqP) was improved. An example is the equilibrium partitioning sediment benchmarks model (ESBs) developed for the interstitial water–sediment system. This model is a combination of the linear equilibrium model and the Freundlich isotherm [26]. Equilibrium models can be created based on various equilibrium equations (e.g., isotherm equations for pure adsorption: Langmuir, Freundlich, BET, Hery and others).

2. Data, Methods and Techniques

2.1. Lake Description

Bagry Lake has an irregular shoreline with numerous bays and peninsulas. The shoreline becomes more regular only in the southeastern and eastern parts of the lake; it extends more or less latitudinally for about 1 km. The width of the lake varies from 160 to 380 m while its area ranges from 29.27 ha to 31.4 ha [27,28]. The bottom of the lake is irregular as a result of uncontrolled flooding of post-mining excavations of natural aggregates and clay. Some wrecked tracks, railways and floating equipment can be spotted at the bottom, as well as a sunken barge (western part of the lake). The railway tracks are located near the southeastern shore of the lake. The average depth of the lake is 6 m, while its maximum depth is 11 m. Bagry Lake is the second largest water reservoir in the Cracow agglomeration and the largest within the city limits [27].

In the past, this area was covered with forest and the Drwienia (Drwina Długa) River passed across fields and meadows. Around the year 1934, extraction of aggregates in this area began and lasted until 1971, forming the current shape of the lake (except for a triangular bay, which was constructed in 1977). The history of Bagry Lake comprises almost 30 years [29].

Nowadays, the lake is used for recreation purposes, with several sailing clubs and two beaches (the eastern beach and the northeastern one), both opened around the year

2000. The eastern beach remains unguarded, while the northeastern bathing beach has lifeguards.

2.2. Materials and Methods

The study focused on the presence of Fe, Mn, Cu, Pb, Zn, Cd and Ca in the sediment and in the supernatant (layer of water just above the sediment) of the lake; Ca was not analyzed in the supernatant. In addition, a granulometric analysis of the sediment and its volatile (organic) fraction were determined. Samples of the sediment and the supernatant were collected at 18 sampling points, along the transects in 2021; the transects were located along the northern and southern shores of Bagry Lake and the central part of the lake (Figure 1a). The lake is an artificial water reservoir resulting from the extraction of sand and gravel. It is a place of rest of the inhabitants of Cracow. For this reason, water quality control is very important. It is located near residential buildings. There are swimming pools on its banks. It is a place for water sports and fishing. Extreme points of the lake have coordinates $50^{\circ}02'06.83''$ N, $19^{\circ}58'59.08''$ E and $50^{\circ}01'49.11''$ N, $19^{\circ}59'51.69''$ E; it is located at an altitude of 195 m above sea level. All sediment samples were taken with the Ekman scoop (Figure 1c); the thickness of the series was about 5 cm. The supernatant samples were collected with a scoop (Figure 1b).

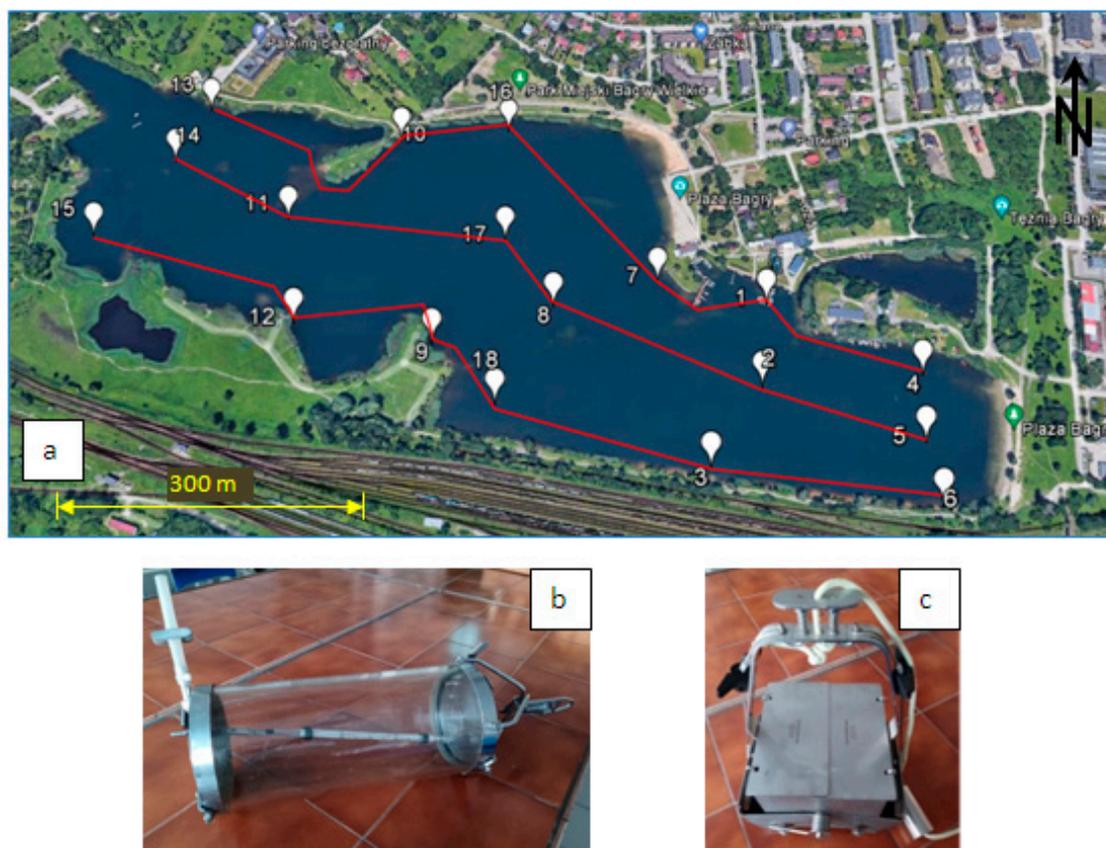


Figure 1. (a)—Map of Bagry Lake with the measuring points and transects (red lines), (b)—Scoop, (c)—Ekman scoop.

Before analyzation for heavy metals (Fe, Mn, Cd, Cu, Ni, Pb and Zn), the sediment samples were dried at 105°C , crushed and sieved through a sieve mesh size of 0.2 mm.

The heavy metals in both supernatant and sediment samples was determined (in duplicate) at the accredited laboratory of Cracow Water.

In the water sample, the concentration of iron was determined using the Hach PB-W-02 cuvette test, of manganese using the ICP-OES method (PN-EN ISO 11885:2009), of zinc using the AAS flame method (PN-ISO 8288:2002, contrAA 800 analyzer) and of lead, copper and cadmium using the AAS method with graphite tube furnace (PN-EN ISO 1115586:2002, contrAA 800 analyzer).

Metals in sediments were determined after mineralization of sediments. In the obtained liquid samples, the concentration of iron was determined using the Hach PB-W-02 cuvette test, of manganese using the AAS method with the graphite tube furnace (PN-EN ISO 1115586:2002, contrAA 800 analyzer), of zinc, lead, copper and cadmium using the AAS method in a flame (PN-ISO 8288:2002, contrAA 800 analyzer) and of calcium by ion chromatography (PN-EN ISO 14911:2002).

In the case of water samples, the mean relative errors of cadmium, copper, lead and zinc concentration measurements were, respectively, 12.4%, 3.4%, 11.2% and 4.6%.

To check granulometric composition and volatile fractions, the samples were dried at 105 °C and sieved through a sieve mesh size of 1.0 mm. Then, particles smaller than 1.0 mm were sieved through a 0.06 mm sieve. This way, two fractions were obtained: sandy (diameter 1.0–0.06 mm) and fine, comprising silty clay (0.06–0.002 mm) and clay (<0.002 mm) fractions. The volatile fraction was separated by burning the sample in a muffle furnace at 550 °C until a constant weight was obtained [30]. The granulometric composition of the sediments and both fractions were then determined with the gravimetric method.

Sediment samples contained salts of carbonic acid, mainly calcium carbonate; it originates from limestone rocks and mollusks (mussels, snails) currently residing in Bagry Lake. The high burning temperature results in calcination (decarbonization) of calcium carbonate and other carbonates and a loss of carbon dioxide. To correct for the weight losses, the samples were treated with water saturated with carbon dioxide, dried at 105 °C and then weighed again [30].

The determination of the granulometric composition and the concentration of mineral and organic substances, as well as the statistical analysis of the obtained results, was carried out at the Department of Water Supply, Sewerage and Environmental Monitoring of the Faculty of Environmental Engineering and Energy of the Cracow University of Technology.

The ecotoxicological criterion was used to assess a potential threat to benthic organisms associated with a presence of metals in the lake's sediment. The criterion is based on two threshold values—LEL (lowest effect level) and SEL (severe effect level). According to this criterion, when metal concentrations are kept below the LEL their toxic effect on benthic organisms is not observed, while when the SEL is exceeded, the toxic effect is evident, and the sediment is considered as highly polluted. LEL/SEL values for Cd, Cu, Pb, Zn, Mn and Fe are, respectively, [mg/kg d.m.] 0.6/10, 16/110, 31/250, 120/820, 460/1100 and 20,000/40,000 [31].

2.3. Model of Relationships between Metals in Sediment

Each aquatic environment has its characteristic features regarding the relationship between elements of this environment. The article presents a statistical description of the relationship between metals found in sediments. This is an original way to demonstrate connections between metals, which additionally take into account the analysis of the statistical significance of these connections.

Relationships between different metals in the lake sediment were examined with a linear model:

$$[Me_s] = Constant + a_1 [Fe_s] + a_2 [Mn_s] + a_3 [Cu_s] + a_4 [Pb_s] + a_5 [Zn_s] + a_6 [Cd_s] \quad (1)$$

Me—metal

[...]—metal concentration

s—sediment

Constant —model constant

$a_1 \div a_6$ —model parameters

The significance of coefficients $a_1 \div a_6$ was determined by Student's *t*-test at the significance level of 0.05. The hypothesis of the significance of Equation (1), also at the significance level of 0.05, was examined using the F-Fisher-Snedecor test.

2.4. Method of Determining Mutual Relationships between Metals in Water and Sediments

In the case of complex relationships between the aquatic environment components (metals, sediment fractions and sizes of sediment particles), being difficult to describe using mathematical models applies a bunch of connections used in Cluster Analysis. This type of method requires a preliminary determination of the relationship between pairs of aquatic environment components. The tangent distance was used for this purpose, calculated on the basis of correlation coefficients. Since synergistic connections were analyzed, it was necessary to modify the traditional method of cluster analysis consisting in omitting negative tangent distances. Usually, the smaller the tangent (and therefore also negative), the stronger the connections. Such behavior in this analysis would lead to erroneous conclusions. As a result of such an analysis, synergistic and antagonistic connections would be mixed. In the cluster analysis used, the smaller negative tangent distances were replaced by greater negative or positive resulting from the beam method. The selection of focus was made only on the basis of positive tangent distances. The procedure corresponded to the Ward method [21].

To study the presence of metals in the supernatant and the sediment, a correlation matrix was created for the following features: six metals present in the supernatant, seven metals present in the sediment, mass fractions of the sediment with granulometry ≥ 0.06 mm and <0.06 mm and mineral and volatile fractions in the sample (17 features in total). To determine the sequence of closest features and clusters of feature sequences, tangential distances between 17 features were calculated from the Pearson's *R* correlation coefficients. The tangent distance was

$$w = \sqrt{(1 - R^2)} / R \quad (2)$$

2.5. Model of Equilibrium between the Metal Concentration in Supernatant and in Sediment

Assume that the equilibrium between an aqueous phase and mineral and volatile sediment phases for metals can be described by:

$$[Me_m] = k_1 [Me_w]^{\alpha_1} \quad (3)$$

$$[Me_v] = k_2 [Me_w]^{\alpha_2} \quad (4)$$

$[Me_w]$ —metal concentration in a supernatant phase [mg/L]

$[Me_m]$ —metal concentration in a mineral fraction of a sediment phase [g/kg d.m.

m] or [mg/kg d.m. m]

$[Me_v]$ —metal concentration in a volatile fraction of a sediment phase [g/kg d.m. v]

or [mg/kg d.m. v]

indices:

w—supernatant phase

m—mineral fraction of sediment

v—volatile fraction of sediment

d.m.—dry matter

$k_1, k_2, \alpha_1, \alpha_2$ —isotherm constants

Equations (3) and (4) are frequently used as metal adsorption isotherms (Freundlich isotherm) [23,24]. In the case of lake sediment studies, the concept of adsorption should be extended to accumulation of substances (absorption). For both concepts, the concentration equilibrium constant can be defined, but interactions specific for adsorption, e.g., van der Waals forces between a molecule and a solid, do not have to occur; it may also be chemical interactions, e.g., between metal and an organic ligand.

The mass balance for the sediment phase shows that:

$$[Me_m]m_m + [Me_v]m_v = [Me_s](m_m + m_v) \tag{5}$$

So based on (3), (4):

$$k_1 [Me_w]^{\alpha_1} y + k_2 [Me_w]^{\alpha_2} (1 - y) = [Me_s] \tag{6}$$

and

$$y = m_m / (m_m + m_v) \tag{7}$$

$[Me_s]$ —metal concentration in a sediment phase [g/kg s, or [mg/kg d.m. s]

m_m —mass of the mineral fraction [kg d.m. m]

m_v —mass of a volatile fraction [kg d.m. v]

y —mass of a sediment mineral fraction [kg m/kg d.m. s]

index:

s—sediment

Model (6) describes the equilibrium state of metals concentrations contained in three phases, i.e., overlying water, mineral fraction of sediments and organic fraction of sediments.

The unknown in Equation (6) are constants k_1, k_2, α_1 and α_2 , which can be determined by measuring $[Me_w], [Me_s]$ and y .

Derivatives of Equations (3) and (4) in relation to the metal concentration in the supernatant describe how changes in a metal concentration in the mineral $d[Me_m]$ and volatile $d[Me_v]$ fractions impact the metal concentration in the supernatant $d[Me_w]$. To compare the derivatives (the same units), the mineral fraction derivative must be multiplied by its mass fraction (y) in the sediment, and the volatile fraction derivative must be multiplied by its mass fraction ($1 - y$):

$$\frac{d[Me_m]}{d[Me_w]} \cdot y = k_1 \alpha_1 [Me_w]^{\alpha_1 - 1} \cdot y \left[\frac{l}{kg \text{ d.m. s}} \right] \tag{8}$$

$$\frac{d[Me_v]}{d[Me_w]} \cdot (1 - y) = k_2 \alpha_2 [Me_w]^{\alpha_2 - 1} \cdot (1 - y) \left[\frac{l}{kg \text{ d.m. s}} \right] \tag{9}$$

The metal concentration in the sediment can be related to its concentration in sediment fractions as follows:

$$[Me_s] = [Me_m]y + [Me_v](1 - y) \tag{10}$$

The differential of the metal concentration $[Me_s]$ in the sediment is described as:

$$d[Me_s] = \frac{\partial [Me_m]}{\partial [Me_w]} \cdot y \cdot d[Me_w] + \frac{\partial [Me_v]}{\partial [Me_w]} \cdot (1 - y) \cdot d[Me_w] \tag{11}$$

Changes in metal concentrations in the supernatant, relative to their change in sludge $\frac{d[Me_w]}{d[Me_s]}$ are described as:

$$1 = \frac{\partial[Me_m]}{\partial[Me_w]} \cdot y \cdot \frac{d[Me_w]}{d[Me_s]} + \frac{\partial[Me_v]}{\partial[Me_w]} \cdot (1-y) \cdot \frac{d[Me_w]}{d[Me_s]} \quad (12)$$

The impact of the metal concentration in the mineral fraction P_m or the volatile one P_v of the sediment on its concentration in the supernatant can be described as normalized shares:

$$P_m = \frac{\frac{\partial[Me_m]}{\partial[Me_w]} \cdot y \cdot \frac{d[Me_w]}{d[Me_s]}}{\frac{\partial[Me_m]}{\partial[Me_w]} \cdot y \cdot \frac{d[Me_w]}{d[Me_s]} + \frac{\partial[Me_v]}{\partial[Me_w]} \cdot (1-y) \cdot \frac{d[Me_w]}{d[Me_s]}} = \frac{\frac{\partial[Me_m]}{\partial[Me_w]} \cdot y}{\frac{\partial[Me_m]}{\partial[Me_w]} \cdot y + \frac{\partial[Me_v]}{\partial[Me_w]} \cdot (1-y)} \quad (13)$$

$$P_v = \frac{\frac{\partial[Me_v]}{\partial[Me_w]} \cdot (1-y) \cdot \frac{d[Me_w]}{d[Me_s]}}{\frac{\partial[Me_m]}{\partial[Me_w]} \cdot y \cdot \frac{d[Me_w]}{d[Me_s]} + \frac{\partial[Me_v]}{\partial[Me_w]} \cdot (1-y) \cdot \frac{d[Me_w]}{d[Me_s]}} = \frac{\frac{\partial[Me_v]}{\partial[Me_w]} \cdot (1-y)}{\frac{\partial[Me_m]}{\partial[Me_w]} \cdot y + \frac{\partial[Me_v]}{\partial[Me_w]} \cdot (1-y)} = 1 - P_m \quad (14)$$

The sensitivity of the aquatic environment to a varying metal concentration in both (mineral and volatile) sediment fractions can be described using derivatives: $\frac{d[Me_w]}{d[Me_m]}$,

$\frac{d[Me_w]}{d[Me_v]}$. Sensitivity of the aquatic environment, expressed as relative changes in metal

concentrations in the aquatic environment in relation to these changes in both sediment fractions, i.e., mineral (Q_m) and volatile (Q_v) ones, can be expressed as:

$$Q_m = \frac{d[Me_w]}{d[Me_m]} \cdot \frac{[Me_m]}{[Me_w]} = \frac{1}{\alpha_1} \quad (15)$$

$$Q_v = \frac{d[Me_w]}{d[Me_v]} \cdot \frac{[Me_v]}{[Me_w]} = \frac{1}{\alpha_2} \quad (16)$$

3. Results

3.1. Sediment

A mineral fraction in the sediment ranges from 0.812 to 0.987 g/g dry matter (d.m.) (0.9142 ± 0.0456 g/g d.m.) with an average of 91.4% d.m. while the volatile organic fraction is definitely lower and varies from 0.013 to 0.188 g/g d.m. (0.0858 ± 0.456 g/g d.m.), with an average of 8.58% d.m.

Moreover, the fractions with a diameter ≥ 0.06 mm (sand fraction) and <0.06 mm (fine fraction with silty clay and clay fractions) were analyzed in the sediment. Particles with a diameter ≥ 0.06 mm predominate in the dry mass of the sample; they vary from 60.64 to 94.60% (79.38 ± 9.39%). The mass fraction of particles with a diameter < 0.06 mm is smaller and ranges from 5.40 to 39.36% (20.62 ± 9.39%).

It was noticed that the volatile fraction ($1 - y$) decreases with a higher concentration U_d of particles ≥ 0.06 mm and increases along with U_d for particles < 0.06 mm (Figure 2). Additionally, a mineral fraction y gets smaller when the fine fraction U_d (< 0.06 mm) increases; it increases along with U_d for particles ≥ 0.06 mm (Figure 2). The above observations indicate that the mineral fraction is mainly associated with a sand fraction while the volatile fraction is mainly associated with a fine silty clay and clay fractions.

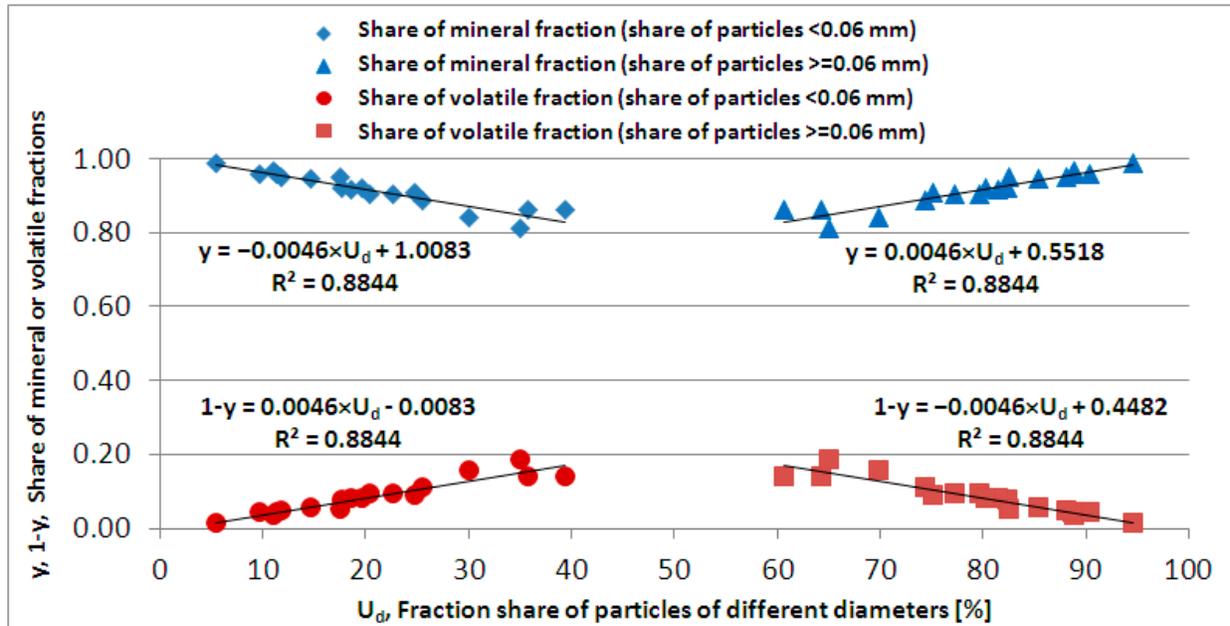


Figure 2. Mineral and volatile fractions vs. particles of different diameters in the sediment.

Table 1 summarizes the average metal concentration in the dry sediment mass, standard deviations and the minimum and maximum values calculated on the basis of the analysis results for the whole lake.

A negative correlation between the sediment mineral fraction and its metals concentration is observed for Fe, Mn, Cu, Pb, Zn and Ca (—◆— Figure 3); such correlation is not true in case of Cd (positive correlation). Therefore, a high mineral fraction will be followed by a generally lower concentration of Fe, Mn, Cu, Pb, Zn and Ca in the sediment, except for Cd (—◆— Figure 3). Mostly, it means that metals tend to accumulate in the volatile fraction while cadmium, on the other hand, will accumulate in mineral matter.

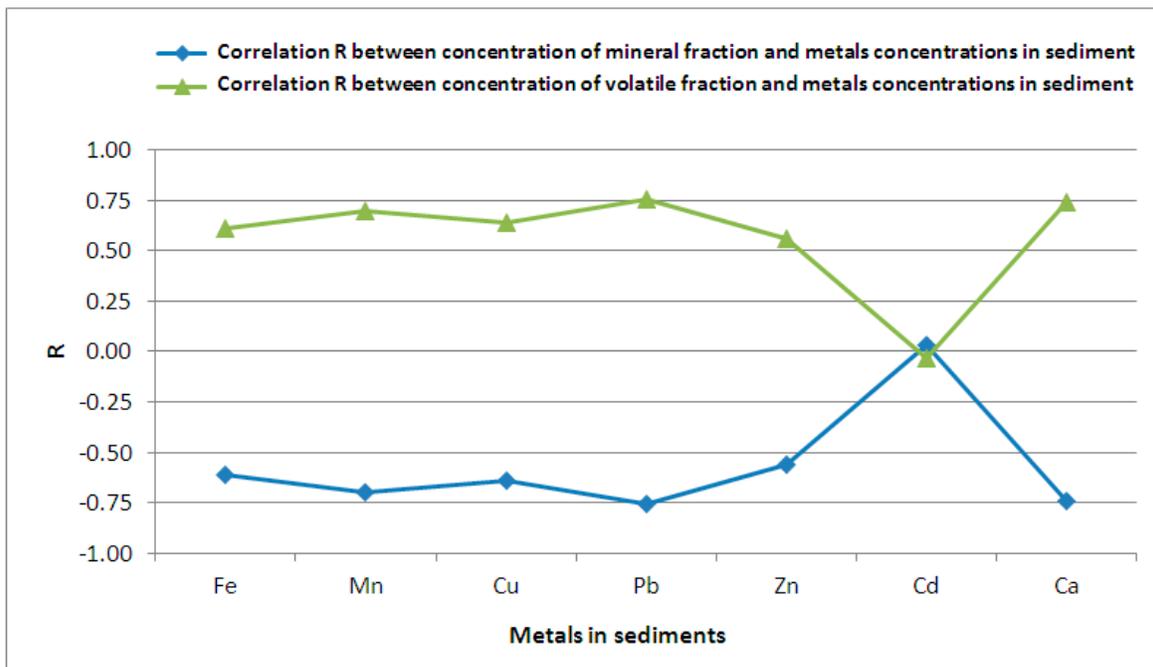


Figure 3. Correlation R between different fraction of the sediment and a metal’s concentrations.

A positive correlation between the fine particles (<0.06 mm ) and the metals in the sediment is observed for Fe, Mn, Cu, Pb, Zn and Ca (Figure 4); only for Cd the correlation is negative. Since the fine fraction (<0.06 mm) comprises both mineral and organic matter it means that fine particles predominate in accumulation of metals, except for Cd. An increase in the fine fraction <0.06 mm () is followed by higher metal concentration in the sediment, again except for Cd. For the fraction ≥ 0.06 mm (), the opposite is true: its higher concentration in the sediment results in a lower metal concentration, except for Cd (Figure 4). Therefore, looking at the line () in Figure 3, it can be assumed that metals accumulate in the fine volatile fraction (<0.06 mm,  Figure 4) of the sediment but not in the fine mineral fraction (see a blue line  in Figure 3). In the case of Cd, the opposite it true: Cd accumulates mainly in the mineral fraction ( Figure 3) with particles ≥ 0.06 mm ( Figure 4).

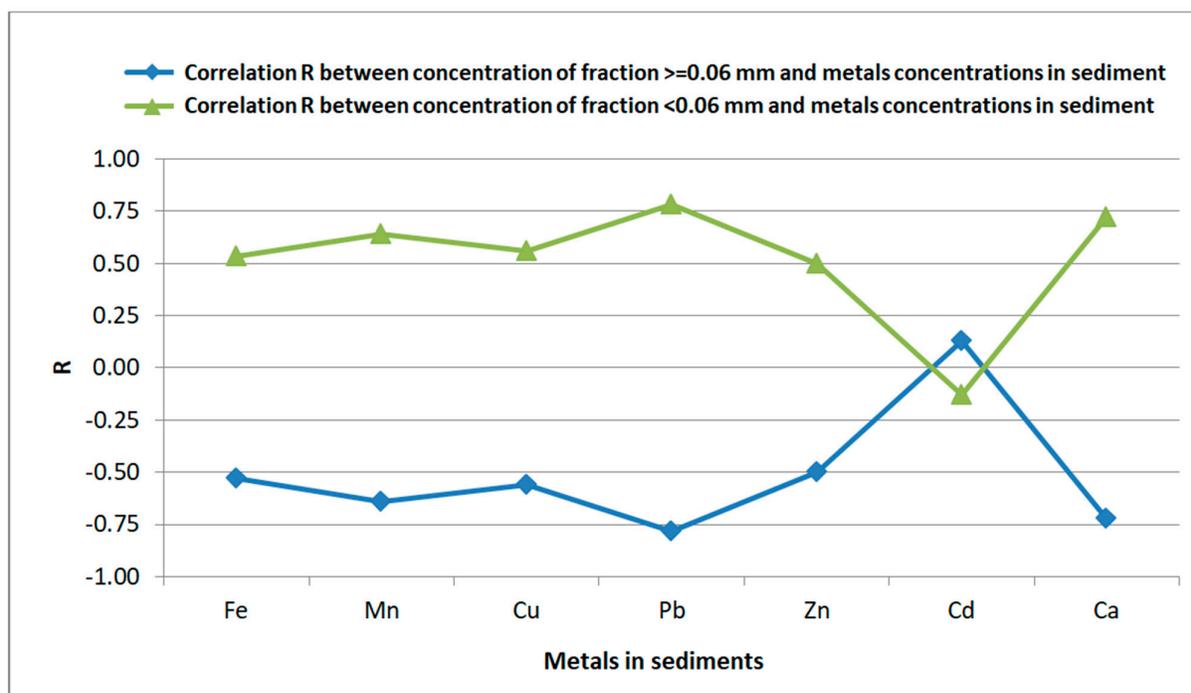


Figure 4. Correlations R between different particle fractions in the dry mass of the sediment and metals concentrations.

Table 1. Metals concentrations in the sediment (d.m.—dry matter).

	Fe [g Fe/kg d.m.]	Mn [mg Mn/kg d.m.]	Cu [mg Cu/kg d.m.]	Pb [mg Pb/kg d.m.]	Zn [mg Zn/kg d.m.]	Cd [mg Cd/kg d.m.]	Ca [g Ca/kg d.m.]
Average=	16.04	292.7	65.53	24.33	122.9	0.7709	64.45
Standard deviation=	9.803	159.4	42.06	13.65	84.48	0.5845	32.27
Min=	3.162	61.60	2.113	1.962	25.35	0.1592	28.70
Max=	36.03	566.4	161.0	54.11	321.0	1.831	144.8

Figures 5–10 show the metal concentration maps for Fe, Mn, Cu, Pb, Zn and Cd in the lake sediment. Due to sunken scrap metal from World Wars I and II, a distribution of metals in the sediment is determined mainly by an anthropogenic pressure. There are two main parts of the lake with substantial metal levels: the southeastern region (sunken tracks, elements of the narrow-gauge railway, etc. [32]) and the northwestern region (sunken barge at a depth of 6 m [33]). In these areas, the highest concentrations of all analyzed metals are observed in the sediment. There is also one more specific place, located near the B1 site, where high concentrations of Fe, Mn and Zn are detected. This is the marina, where sailing equipment made of iron alloys with manganese and/or with anti-corrosive zinc coatings contributes to higher metal concentrations in the sediment. The higher concentrations of metals Cu, Pb, Zn and Cd in the southeastern part of the lake are associated with pieces of various alloys used in construction of sunken railway elements (copper wires, lead sheaths of cables and slide-bearing alloys containing Sn, Pb, Sb, Cu, Al, Ni, As and Cd) and other recently sunken objects.

Other sources of Cd could be protective cadmium coating of iron surfaces, cadmium sulfide used in production of protective yellow-orange paint or its alloys with copper in traction wires [34].

Water of low hardness and with some carbon dioxide may initiate corrosion of lead-containing materials [34], such as, e.g., battery parts, anti-corrosive paint coatings with minium and copper wire sheaths. Higher concentrations of zinc in water may also be

attributed to corrosion of galvanized ferrous materials and the presence of dissolved carbon dioxide [34].

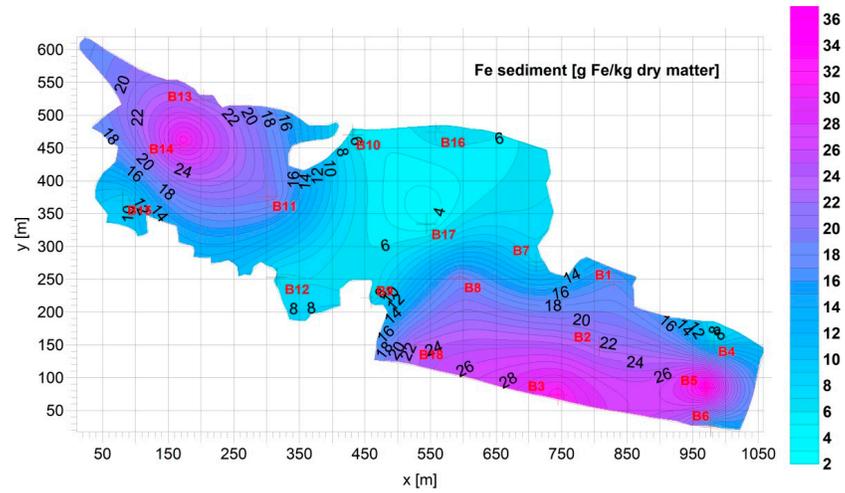


Figure 5. Fe in the sediment [g Fe/g dry matter].

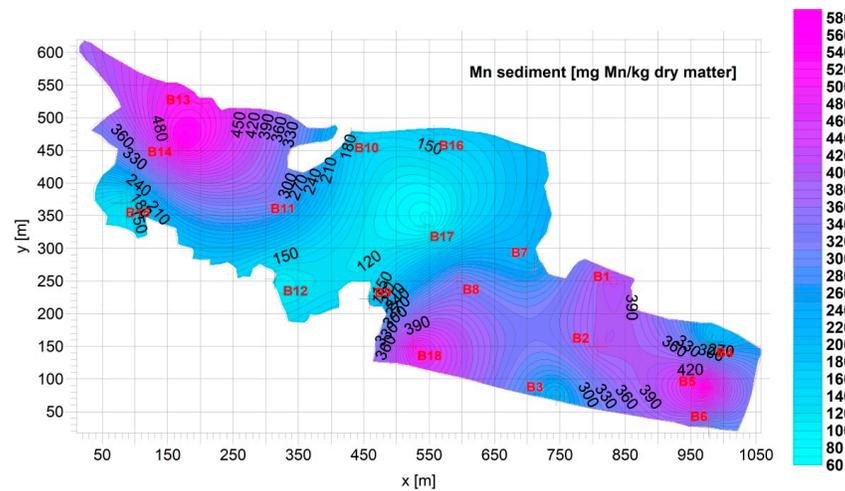


Figure 6. Mn in the sediment [mg Mn/kg dry matter].

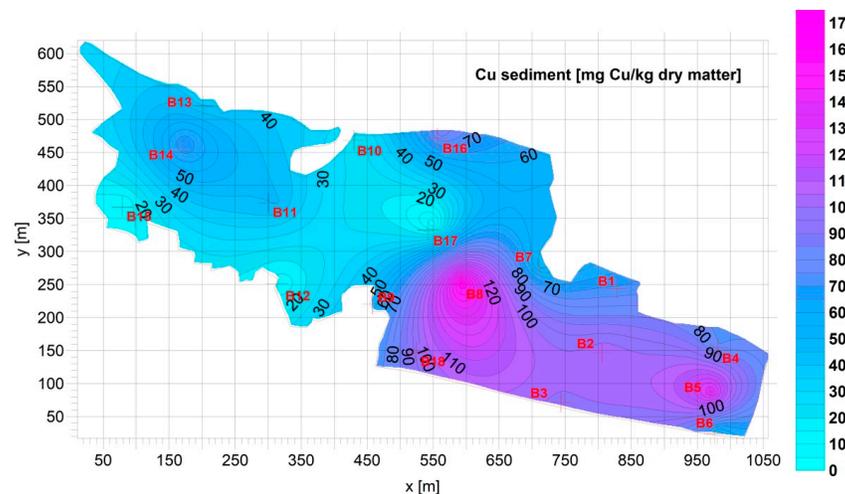


Figure 7. Cu in the sediment [mg Cu/kg dry matter].

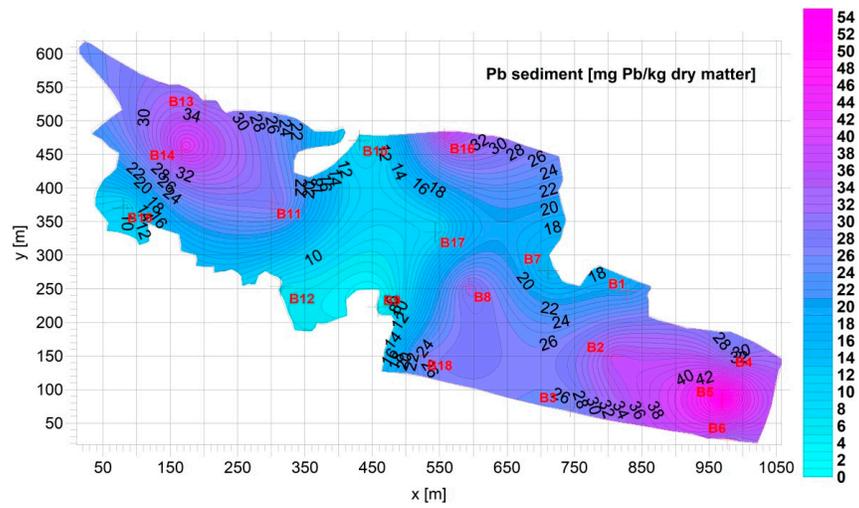


Figure 8. Pb in the sediment [mg Pb/kg dry matter].

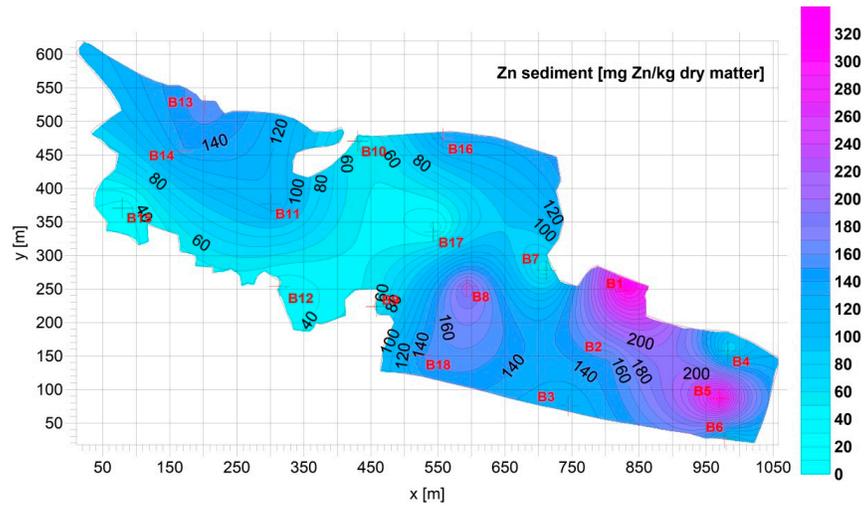


Figure 9. Zn in the sediment [mg Zn/kg dry matter].

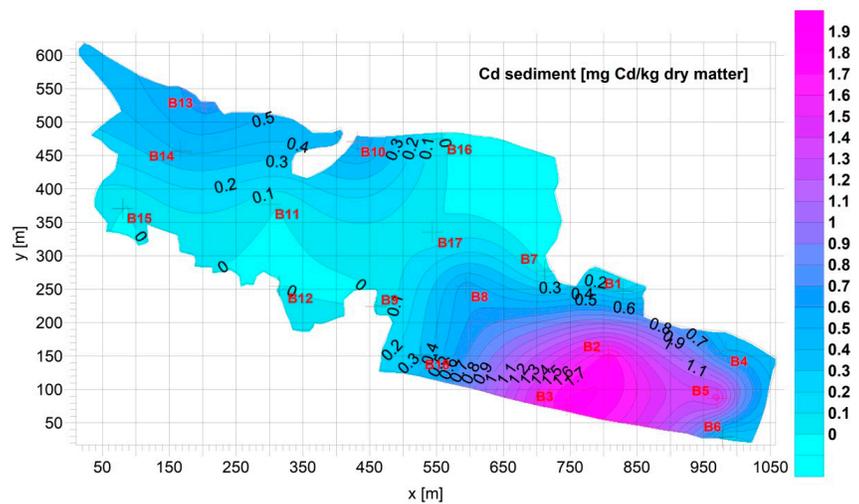


Figure 10. Cd in the sediment [mg Cd/kg dry matter].

The ecotoxicological criteria showed that the SEL threshold value for Cu was exceeded at two measurement sites, while the LEL values for Cd, Cu, Pb, Zn, Mn and Fe were exceeded at 4, 13, 5, 9, 3 and 5 measurement sites, respectively.

3.2. Supernatant

Table 2 presents the average concentrations of metals in the supernatant (layer of water just above the sediment) of Bagry Lake as well as the standard deviations and the minimum and maximum concentrations which have been calculated based on the results of analyzes for the entire lake. Only lead concentrations exceeded the acceptable level of 0.014 mg Pb/L (see the Ordinance, [35]); its concentration at B6 was 2.2 times higher.

Table 2. Metals concentrations in the supernatant.

	Fe [mg Fe/L]	Mn [mg Mn/L]	Cu [mg Cu/L]	Pb [mg Pb/L]	Zn [mg Zn/L]	Cd [mg Cd/L]
Average	0.8928	0.09733	0.01261	0.005663	0.04165	4.172×10^{-5}
Standard deviation=	1.044	0.07402	0.02157	0.007396	0.03117	3.060×10^{-5}
Min=	0.05300	0.03000	0.0005274	3.330×10^{-5}	0.007400	7.200×10^{-6}
Max=	3.690	0.3010	0.09659	0.03081	0.1065	0.0001200

In water, iron at the +2 oxidation state is present in a dissolved form as Fe^{2+} ion or as one ($[\text{FeOH}]^+$) or di-hydroxy ($[\text{Fe}(\text{OH})_2]^-$) ion or as dissolved carbonate and sulphate aqua complexes ($\text{FeCO}_3(\text{aq})$, $(\text{FeSO}_4(\text{aq}))$) and as FeHCO_3^+ cation. Oxidized iron is present as Fe^{3+} , $[\text{FeOH}]^{2+}$, $[\text{Fe}(\text{OH})_2]^+$, $[\text{Fe}(\text{OH})_4]^-$, $[\text{FeSO}_4]^+$, $[\text{Fe}(\text{SO}_4)_2]^-$, $[\text{FeHSO}_4]^{2+}$, $[\text{FeCl}_2]^{2+}$, $[\text{FeCl}_2]^+$, $[\text{FeHPO}_4]^+$ and $[\text{FeH}_2\text{PO}_4]^{2+}$ [36]. These Fe^{3+} forms are pH-dependeent. In natural water, iron can be present in dissolved, suspended or colloidal forms, depending on pH and the presence of organic substances, oxygen and carbon dioxide. Iron may be assimilated by aquatic organisms and released from sediments to water, under reducing conditions. Insoluble forms of iron include mainly iron di- and tetraoxide and iron III hydroxide, carbonate and sulfide.

Manganese in natural surface water is present mainly as Mn^{2+} , Mn^{3+} and Mn^{4+} [36]. It is easily oxidized by dissolved oxygen and by manganese bacteria. Its forms are similar to iron compounds and ions (see above). In the presence of oxygen, manganese is oxidized to insoluble forms of manganese oxides MnO_x while in anoxic zones it is reduced to soluble compounds. In its insoluble form, manganese occurs mainly as manganese di-, tri- and tetraoxide and is usually accompanied by iron compounds. Studies show that soluble manganese transfers between sediment and water more easily than a soluble iron [37].

Copper in water is present as Cu^+ , Cu^{2+} and Cu^{3+} but most often at the +2 oxidation state [36]. In a dissolved form, Cu forms a copper carbonate aqua complex and various complex ions combining carbonate and hydroxy ions (similar to Fe); $\text{Cu}(\text{OH})_2$ dissolves better at $\text{pH} > 7$, while $\text{Cu}_2(\text{OH})_2\text{CO}_3$ at $\text{pH} < 7$. Copper is adsorbed in sediments; the process depends on pH, ligands, iron and manganese oxides and sediments characteristic. Copper occurs in the free state and mainly as an insoluble sulfide mixed with iron sulfide, hydroxide or carbonate and as a hydroxide mixed with its carbonate.

Lead in natural water is present at +2 and +4 oxidation states [36]. The Pb^{2+} ion forms soluble aqua complexes with carbonate, sulfate and OH group in the form of hydroxide. In addition, it can form a series of complex positive and negative ions comprising carbonate and hydroxyl group—similar to the elements listed above. Pb reacts with organic ligands containing sulfur, nitrogen and oxygen. Currently, tetramethyllead is not emitted with exhaust gases, but in anaerobic conditions, biological synthesis of tetramethyllead is possible. Lead can be adsorbed on mineral deposits and humic compounds; its insoluble form is sulfide.

Zinc in water is present at the +2 oxidation state [36]. It forms complex positive and negative ions with OH groups as well as soluble aqua complexes with carbonate and sulfate. Zinc forms inorganic and organic complexes and adsorbs onto suspensions and sediments. In sediments, it may react with iron and manganese oxides, carbonates and organic substances. Zinc occurs in an insoluble form as hydrated silicate, carbonate, sulfide or oxide.

Cadmium in water is present at the +2 oxidation state [36]. It forms soluble aqua complexes with carbonate and sulphate as well as complex positive and negative ions with the OH⁻ group and a complex cation [CdCl]⁺. Cadmium is easily adsorbed into suspensions. It forms inorganic and organic complexes and reacts with humic compounds; its insoluble forms include sulfides or carbonates.

In natural waters, these metals form similar soluble compounds, mostly complex positive and negative ions containing OH groups, carbonates, sulfates and chlorides; aqua complexes based on carbonates; sulphates, oxides and hydroxides. They can be oxidized or reduced as well as adsorbed or absorbed in mineral and organic matter. The mass balance between the aqueous and sediment phase may vary depending on the actual amount of a particular element.

Maps (Figures 11–16) show concentrations of Fe, Mn, Cu, Pb, Zn and Cd in the supernatant. The highest concentrations of the metals are observed in the southern part of the lake. Not all high metal concentrations correspond exactly to the locations where the sediments with a high metal concentration were spotted because the lake is relatively shallow and polymictic, so mixing of water is probably initiated mainly by wind. However, supernatant motion is definitely lower due to a bottom drag caused by the water column. Apart from sunken metal elements, the water quality in the southeastern part of the lake is additionally affected by a run off from railway tracks located near the southern shore.

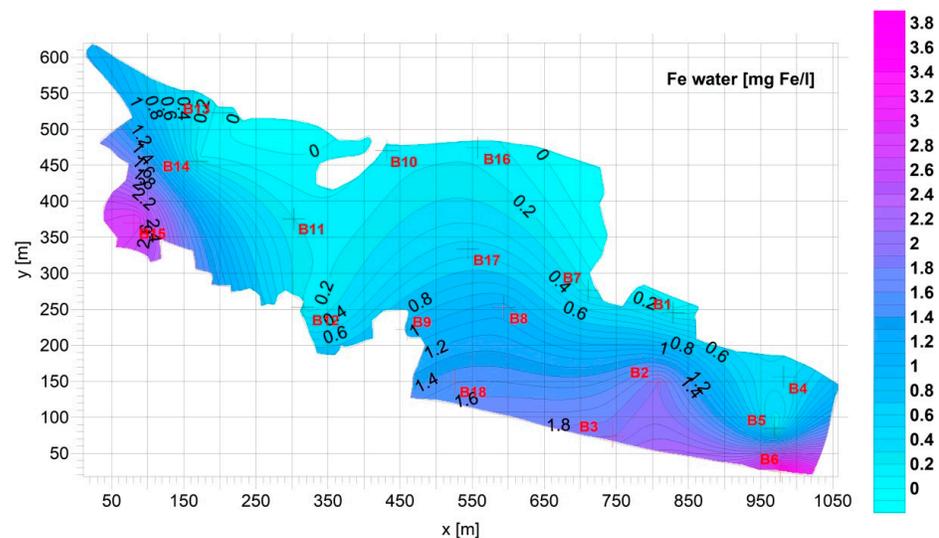


Figure 11. Fe in the supernatant [mg Fe/L].

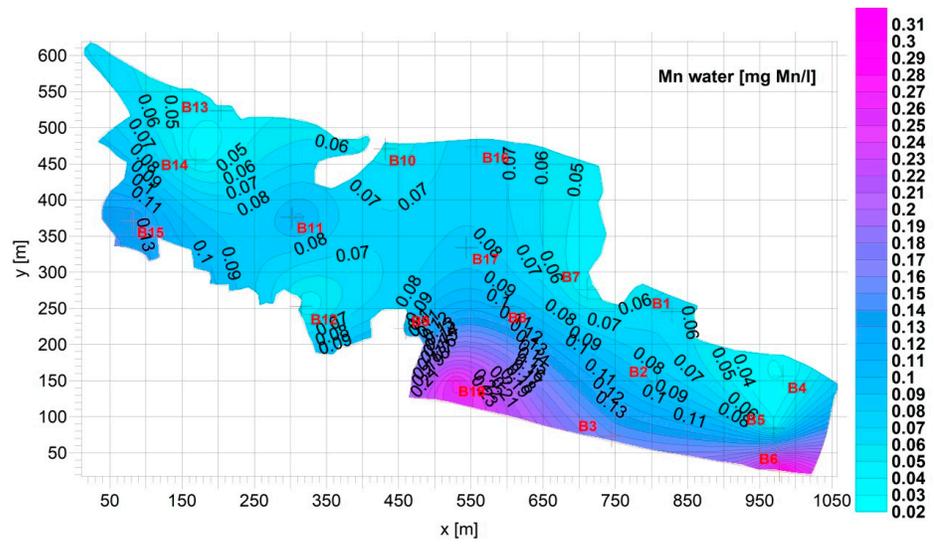


Figure 12. Mn in the supernatant [mg Mn/L].

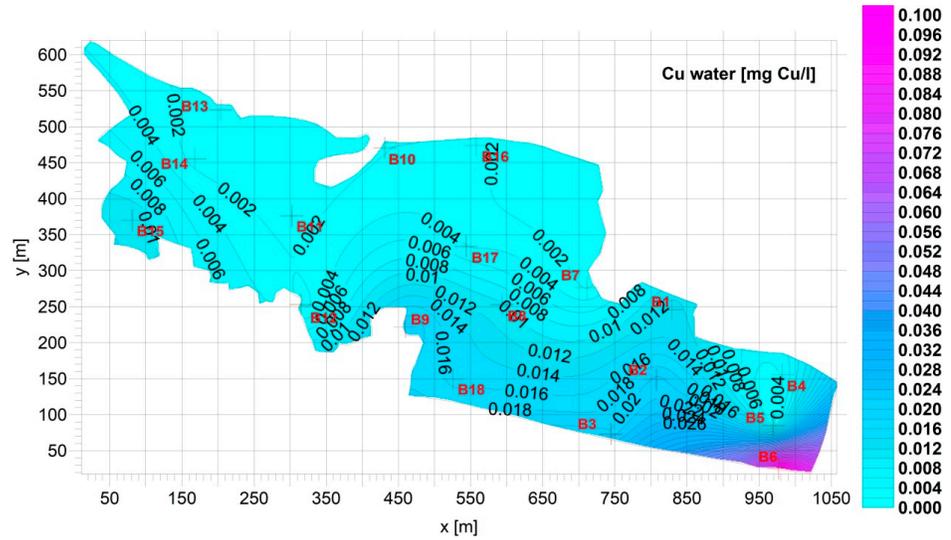


Figure 13. Cu in the supernatant [mg Cu/L].

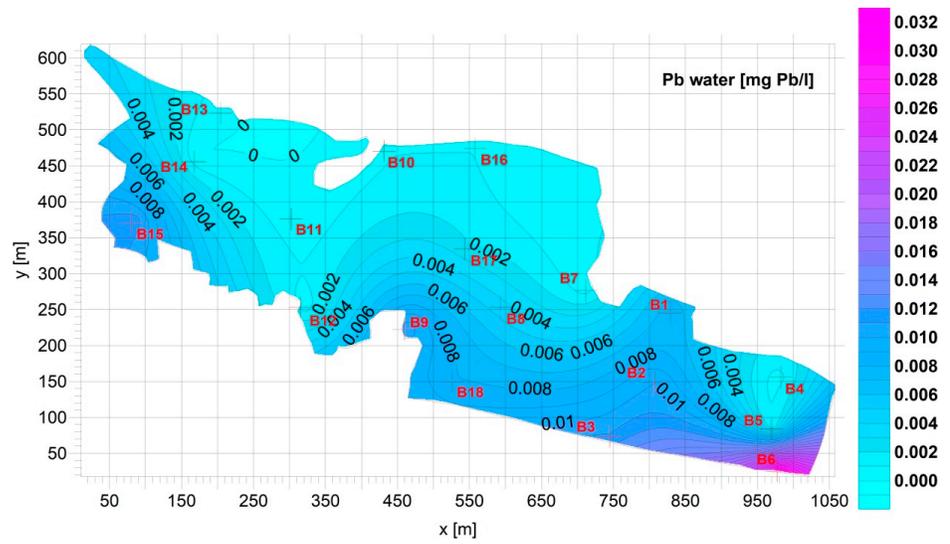


Figure 14. Pb in the supernatant [mg Pb/L].

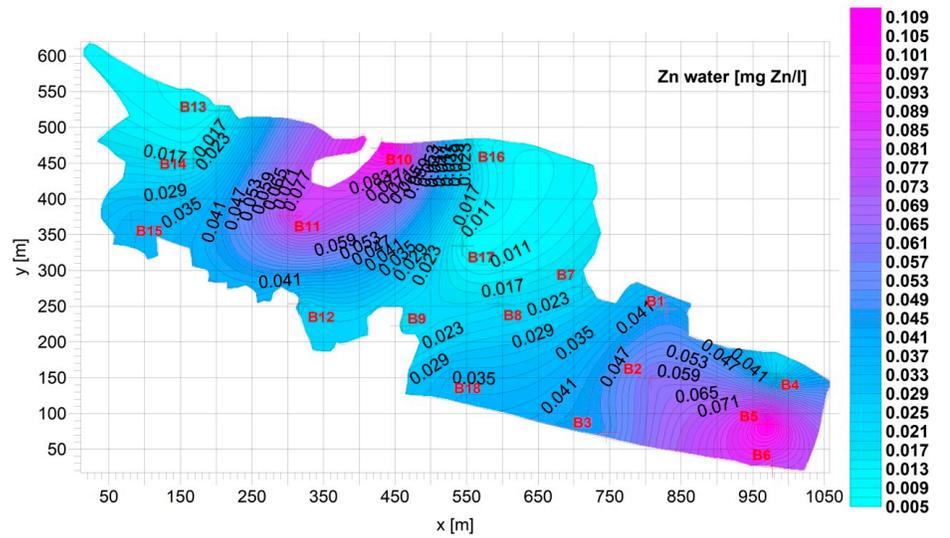


Figure 15. Zn in the supernatant [mg Zn/L].

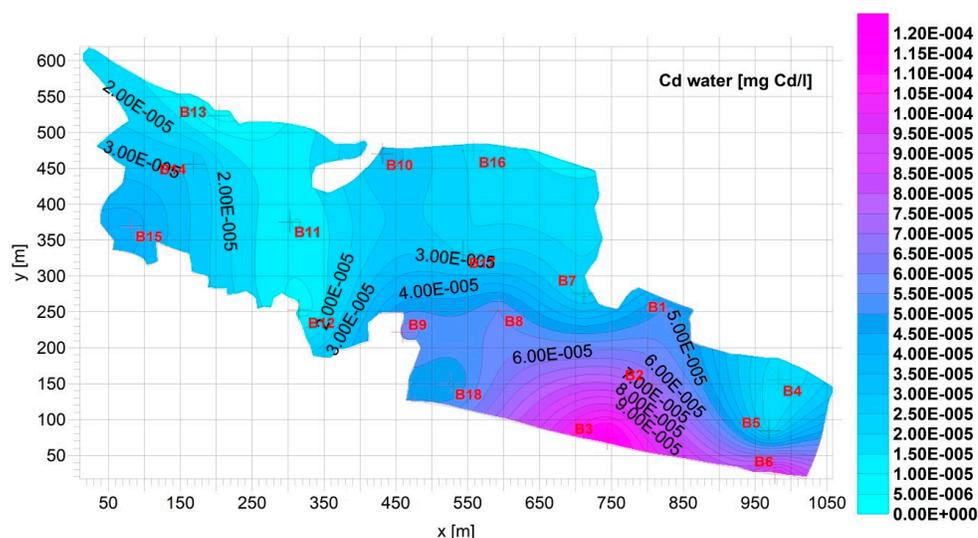


Figure 16. Cd in the supernatant [mg Cd/L].

4. Relationships between Metals in Sediment

Table 3 lists the parameters of the model (1), significance factor (F) and the correlation coefficient R. All models in Table 3 are significant ($F \leq 0.05$) with high correlation coefficients R. Figure 17a–f shows the fit of the model (1) to the measured metals concentrations $[Me_s]$.

Table 3 confirms a correlation of iron and manganese co-occurrence. It can be explained by the presence of manganese in iron alloys and co-occurrence of these metals in the environment. In addition, iron and manganese correlate with lead; its presence may be associated with slide bearing alloys used in internal combustion engines and railway electric traction motors [38]. The sunken equipment makes such a correlation reasonable.

The co-occurrence of copper, lead and zinc (Table 3) is also related to the presence of sunken copper alloys [38].

Cadmium correlates only with iron and manganese, although it can also be found in sliding bearing alloys (together with tin and lead) or copper alloys [38]. Cadmium does not correlate with either lead or copper. Its association with iron results from the recent use of cadmium for steel surfaces as corrosion protection plating or as decorative plating. Currently, cadmium plating is banned as highly toxic.

Table 3. Model parameters for metals concentrations in the sediment (s.—sediment, d.m.—dry matter): $[Me_s] = Constant + a_1 [Fe_s.] + a_2 [Mn_s.] + a_3 [Cu_s.] + a_4 [Pb_s.] + a_5 [Zn_s.] + a_6 [Cd_s.]$

	Constant	Multiplier for Concentration [g Fe/kg d.m.] Others [mg/kg d.m.]						Significance F	R
		Fe Sediment	Mn Sediment	Cu Sediment	Pb Sediment	Zn Sediment	Cd Sediment		
Fe sediment	-1.185		0.03727		0.2328			2.653×10^{-8}	0.9652
Mn sediment	47.02	17.85			-0.9139			4.524×10^{-7}	0.9457
Cu sediment	0.7386				1.718	0.1315		3.394×10^{-4}	0.8411
Pb sediment	3.087	1.551	-0.01271					3.030×10^{-5}	0.8934
Zn sediment	-15.68		0.1369	0.7184	1.658			2.088×10^{-6}	0.9415
Cd sediment	0.4990	0.06407	-0.003081					5.309×10^{-3}	0.8810

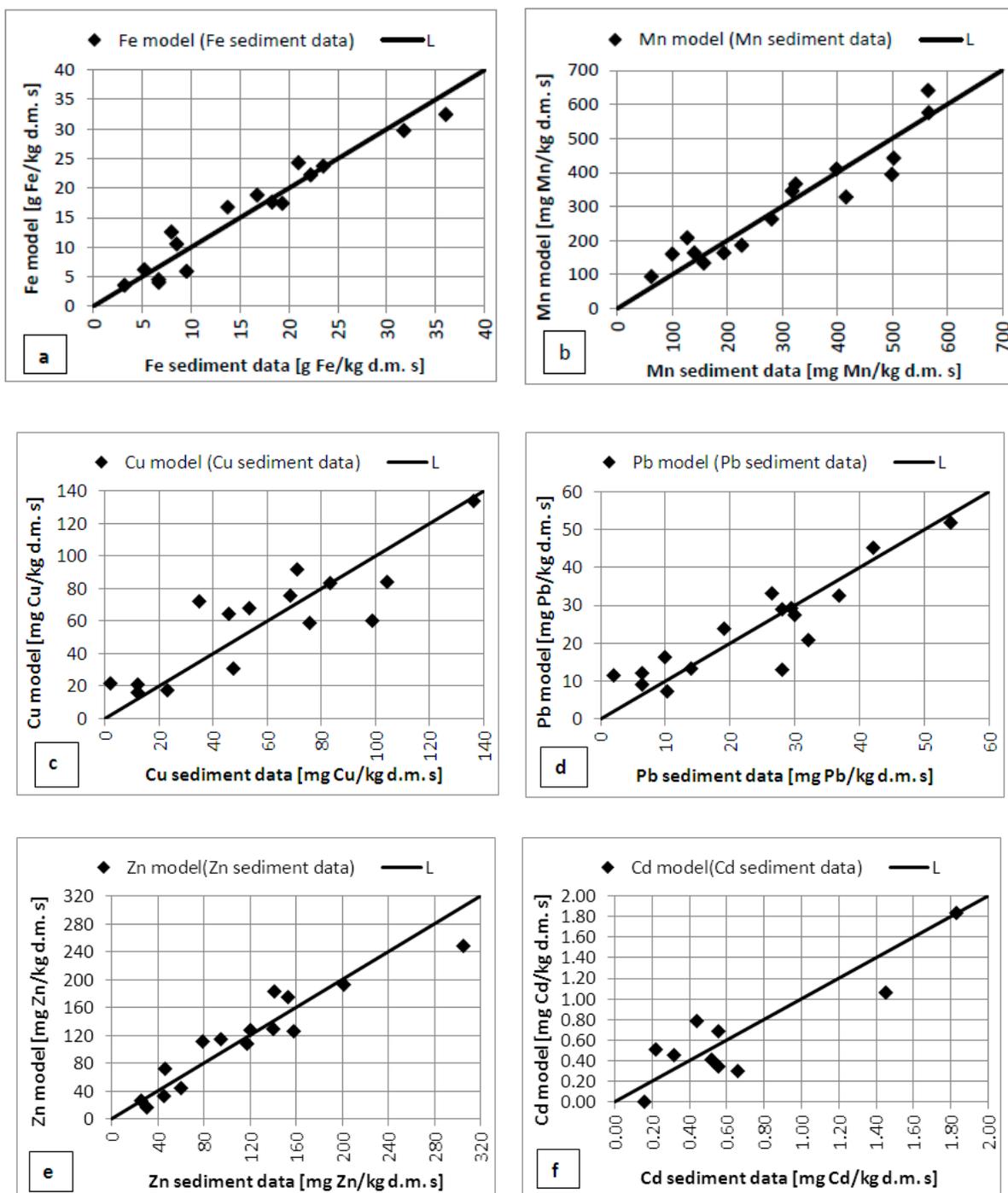


Figure 17. (a–f). Fit of the model (1) describing the relations between metals in the sediments.

5. Relationships between Metals in Supernatant and Sediments

The relationships between metals in the supernatant and the sediment can be very complex. Formation of similar compounds, adsorption or absorption on suspensions and in the sediments result in numerous interactions that have an effect on metals concentrations in water.

Cluster analysis enables description of relationships and interaction between various features or factors. Only positive values w (Equation (2)) were used in the cluster

analysis, although non-positive values were also present in the cluster transformation tables. Clustering was performed by beam analysis. This way it was possible to find common features, treated as tendencies of quantitative changes, to explain certain links (relationships), e.g., whether a higher concentration of one metal in the supernatant is accompanied by a higher concentration of another one in the sediment or whether a higher metal concentration in the sediment is associated with its higher concentrations in the mineral or the volatile fraction in the sediment, etc. Since the cluster analysis took into account only positive tangential distances, the resulting clusters refer to the increase or decrease of both values of the features, i.e., concentrations in supernatant, sediment or shares of different fractions in the sediment.

The dendrogram of links between features and sequences of clusters is shown in Figure 18. The distances between features and clusters in Figure 19 correspond to the distances shown in Figure 18. The definitions of clusters are presented in Table 4.

Three lower-level clusters can be distinguished in the dendrogram (Figure 18):

- Clusters for metals in the sediment;
- Clusters for metals in the supernatant without zinc;
- Cluster for the sediment mineral fraction and the fraction of particles ≥ 0.06 mm.

A characteristic feature of the clusters are two sets of links for metals in sediments and in the supernatant, without zinc (Figure 18). The link between these clusters exists but is quite distant ($w = 3.109$), which means that the relations between the metals in the sediment and the supernatant are relatively weak. This may be due to a strong adsorption or absorption of metals in the sediments and/or their poor dissolution (whether they occur alone or in metal alloys).

Individual metals and sediment fractions form pairs of quite strong clusters, for example:

- Cluster D: Fe sediment, Mn sediment;
- Cluster E: Fe supernatant, Mn supernatant;
- Cluster A: Cu supernatant, Pb supernatant;
- Cluster B: a volatile mass fraction, a mass fraction of particles < 0.06 mm (silty and clay fractions);
- Cluster C: a mineral mass fraction, a mass fraction of particles ≥ 0.06 mm (sand fraction).

The presence of cadmium in the sediments is related to almost all other metals, except for calcium (Figure 18). This fact is confirmed by a small distance between cadmium and other metals clusters in the sediment (cluster L, $w = 1.599$). However, its presence is mainly statistically significant in connection with iron and manganese in the sediment (Table 3). However, the linear model (1) showed that a higher manganese concentration will be only slightly followed by a lower cadmium concentration in the sediment (Table 3).

The cluster for iron and manganese in the sediment (cluster D, $w = 0.680$) is only slightly stronger than the one for iron and manganese in the supernatant (cluster E, $w = 0.757$; Figure 18). Strong relationships between iron and manganese in the sediments have been also confirmed by statistical calculations (Table 3), which show that a linear relationship (1) between these metals, including lead, has a high correlation coefficient $R = 0.9652$ (Table 3).

Another strong link has been observed for zinc in the sediment. It has strong correlations with iron, manganese, lead and copper (clusters: D, I, J, K) and slightly weaker ones with cadmium (cluster L; Figure 18). The dendrogram (Figure 18) confirms the link between zinc and manganese and between copper and lead (Table 3, $R = 0.9415$). In the sediment, zinc shows the closest correlations with manganese, iron and lead and to a lesser extent with copper (Figure 18). However, statistical calculations (Table 3) did not confirm a significant link between zinc and iron in the sediment at the level of $F \leq 0.05$,

although the correlation coefficients for zinc and iron, manganese, copper and lead are quite similar (0.6578, 0.7506, 0.6905 and 0.6557, respectively; Table 5).

Copper in the sediments correlates weakly with cadmium ($R = 0.3951$) and more strongly with iron, manganese, lead and zinc: the coefficients R are equal to 0.6309, 0.5394, 0.6881 and 0.6905, respectively (Table 5). Such copper correlations are also confirmed by the clusters D, I, J and K and a weaker links with cadmium, represented by cluster L.

There is also a high correlation between lead and iron ($R = 0.7433$) and lead and manganese ($R = 0.7399$) in the sediment (Table 5). However, the linear model (1) showed that in the sediment, a higher iron concentration is accompanied by a higher lead concentration, while a higher manganese concentration will be only slightly followed by a lower lead concentration (Table 3); it happened despite the positive correlation coefficient for lead and manganese in the sediment. It can be explained by the fact that model (1) takes into account many different concentrations of metals simultaneously, while the correlation coefficients are calculated for pairs of metal concentrations only. The link between lead and iron and manganese results indirectly from the cluster J connected to the cluster D via the cluster I (zinc). However, statistical calculations did not confirm links between zinc and lead concentrations in the sediment (at the significance level of $F \leq 0.05$).

There is a strong cluster B between the sediment volatile fraction and the fraction of particles < 0.06 mm; see the trend line in Figure 2. Cluster B is strongly linked with clusters (D, I, J, H and K) associated with metals in the sediment (see correlations in Figures 3 and 4).

The link between metal clusters in the calcium-free sediment and the zinc-free supernatant is relatively weak (cluster M, $w = 3.109$).

Calcium in the sediment (cluster N) and indirectly zinc in the supernatant (cluster O) are related to all metals present in both sediment and supernatant. Calcium and zinc are also indirectly related (clusters: N, O) to the organic sediment fraction with particles < 0.06 mm. Such correlation can be also concluded from the correlation plots in Figures 3 and 4.

Correlation of metals in the supernatant and the sediment with the sediment mineral fraction with particles ≥ 0.06 mm is extremely weak and practically non-existent (cluster P, $w = 30.407$); see negative correlations in Figures 3 and 4 (only for cadmium, the correlation is slightly above zero).

In the presence of dissolved oxygen, iron and manganese form in water insoluble iron and manganese oxides, and therefore the correlation between their presence in the sediment and in the supernatant is weak (for Fe $R = 0.0452$ and for Mn $R = 0.0345$); the distance between iron and manganese in the sediment and in the supernatant is quite large (cluster M, $w = 3.109$). Zinc forms a number of soluble compounds, and the correlation between its presence in the sediment and in the supernatant is much higher ($R = 0.2600$) than for iron and manganese; however, the link distance between zinc in the supernatant and metals in the sediment and other metals in the supernatant is still weak (cluster O, $w = 3.570$).

Calcium in the sediment is mainly linked with the fine volatile fraction, particles < 0.06 mm (cluster N, $w = 3.566$; Figure 18). Therefore, it may be concluded that calcium originated from natural calcareous sediments with organic matter: these can be mollusk skeletons (a group of mussels, snails). The link is not strong but definitely stronger than between the mineral fraction with particles ≥ 0.06 mm (sand) (cluster P, $w = 30.407$). Formally, mollusk skeletons may be classified as mineral matter, as the organic concentration in exoskeletons is less than 5% [39]. However, mollusk skeletons are directly related to living matter; hence, cluster O ($w = 3.570$) is slightly stronger than cluster P ($w = 30.407$).

Cluster analysis shows that the metals concentration in the sediment and in the supernatant is indirectly related to a calcium concentration and the mineral fraction of the sediment as well as the fraction of particles < 0.06 mm in the sediment (cluster N, $w = 3.566$; Figure 18).

Looking at relationships between metals in the supernatant and in the sediment as well as different types of sediment, the strongest link was found between copper and lead in the supernatant (cluster A, $w = 0.312$, Figure 18; $R = 0.9547$, Table 5); it can be explained by copper alloys sunken in the lake or lead coatings of copper electrical wires found in the lake sediment.

Another strong cluster was found between iron and manganese in the sediment and in the supernatant (clusters: D, E, $w = \{0.680; 0.757\}$, $R = \{0.8271; 0.7974\}$, respectively, Table 5). Such a strong relationship may also be caused by sunken iron alloys as well as the natural co-existence of these metals in the sediments and in the supernatant.

The strong link between cadmium and Fe, Mn, Cu and Pb (cluster G, $w = 0.787$, Figure 18) in the supernatant and the high correlation coefficients $R \{0.7249, 0.6087, 0.6919$ and 0.7859 , respectively} (Table 5) result from the presence of cadmium in alloys with other metals or in metallic coatings of the sunken materials; there might be a common source of contamination with these metals.

The relationship between metals in the sediments or in the supernatant (cluster M, $w = 3.109$) is several times weaker than between metals within the sediment or supernatant phases (Figure 18). It may be explained by a poor migration of metals between the sediment and the supernatant, their poor solubility or corrosion resistant materials deposited at the bottom of Bagry Lake.

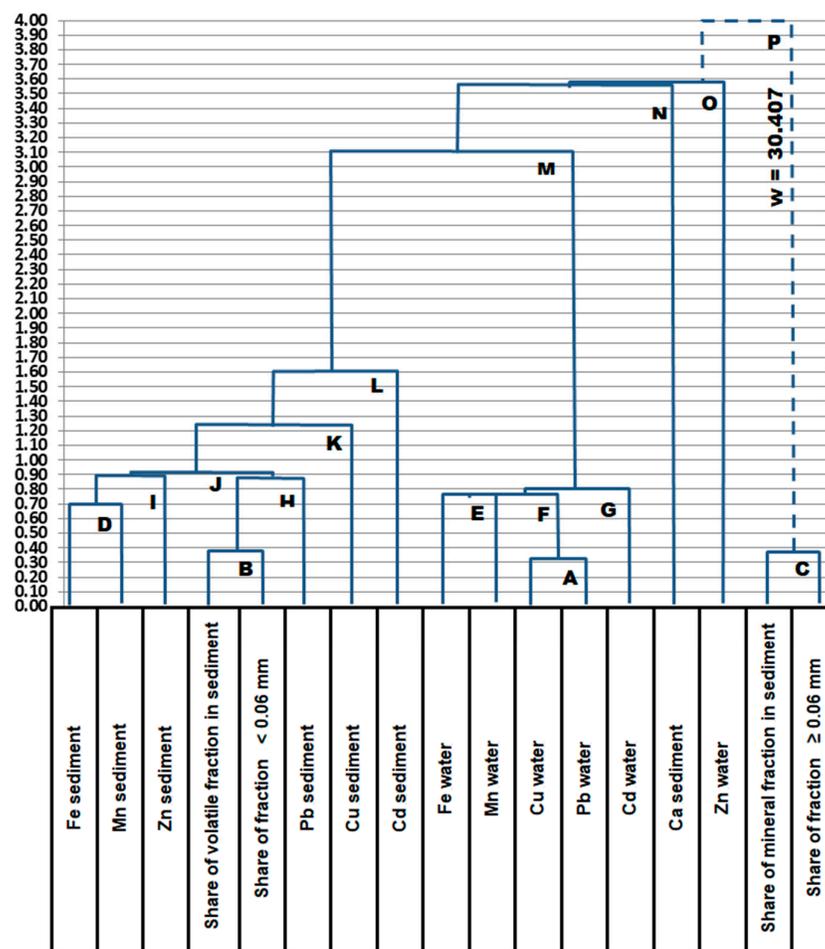


Figure 18. Dendrogram of the following features: presence of metals in the supernatant, in the sediment, mass of mineral and volatile fractions and mass fractions of particles larger or smaller than 0.06 mm.

Table 4. Definitions of clusters and distances in-between.

Clusters (Definitions):	Distances between Clusters w	Distances between Clusters [%]	Cluster
Cu supernatant + Pb supernatant = A	0.312	1.025	A
Volatile fraction + mass fraction < 0.06 mm = B	0.362	1.189	B
Mineral fraction + mass fraction >= 0.06 mm = C	0.362	1.189	C
Fe sediments + Mn sediments = D	0.680	2.235	D
Fe supernatant + Mn supernatant = E	0.757	2.489	E
E + A = F	0.758	2.492	F
F + Cd supernatant =G	0.787	2.588	G
Pb sediment +B = H	0.866	2.846	H
D + Zn sediment = I	0.880	2.895	I
I + H = J	0.900	2.960	J
J + Cu sediment = K	1.230	4.044	K
K + Cd sediment = L	1.599	5.259	L
G + L = M	3.109	10.224	M
M + Ca sediment = N	3.566	11.728	N
N + Zn supernatant = O	3.570	11.742	O
O + C = P	30.407	100.000	P

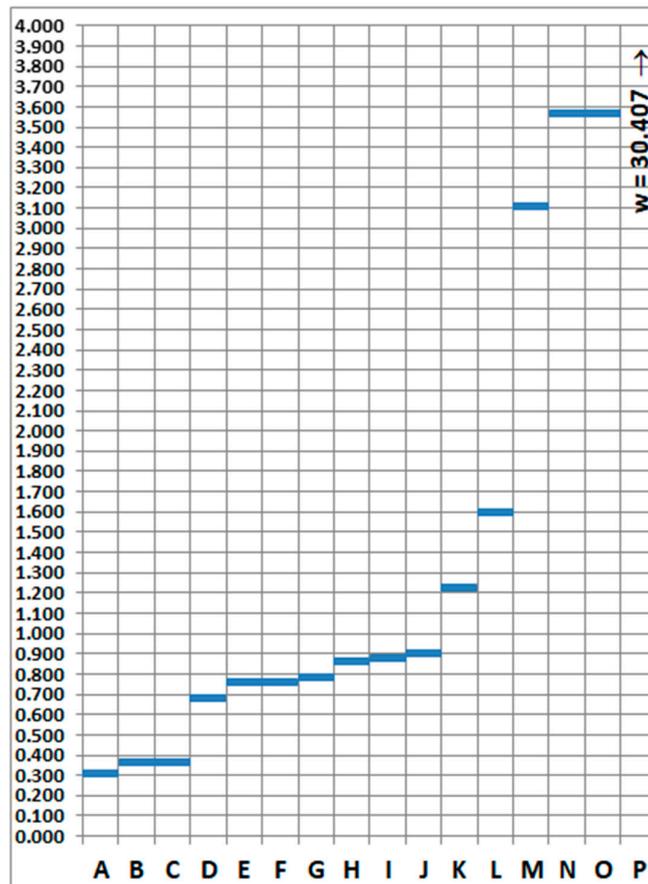


Figure 19. Distances between features and clusters.

Table 5. Table of correlations between various supernatant and sediment components.

	Fe	Mn	Cu	Pb	Zn	Cd	Fe	Mn	Cu	Pb	Zn	Cd	Ca	Mineral Fraction in Sample	Volatile Fraction in Sample	Mass Fraction ≥ 0.06 mm	Mass Fraction < 0.06 mm
Fe Supernatant	1.0000																
Mn Supernatant	0.7974	1.0000															
Cu Supernatant	0.7970	0.7740	1.0000														
Pb Supernatant	0.8981	0.8113	0.9547	1.0000													
Zn Supernatant	0.1762	0.1989	0.2697	0.2315	1.0000												
Cd Supernatant	0.7249	0.6087	0.6919	0.7859	0.1357	1.0000											
Fe Sediment	0.0452	0.0953	0.0010	0.0211	0.3009	0.3062	1.0000										
Mn Sediment	-0.1310	0.0345	-0.0262	-0.0639	0.2139	0.0490	0.8271	1.0000									
Cu Sediment	0.0531	0.1059	0.0428	0.0370	0.1587	0.2807	0.6309	0.5394	1.0000								
Pb Sediment	-0.0049	0.0378	0.0835	-0.0154	0.2552	0.0461	0.7433	0.7399	0.6881	1.0000							
Zn Sediment	-0.2014	-0.0579	-0.0410	-0.0420	0.2600	0.1051	0.6578	0.7506	0.6905	0.6557	1.0000						
Cd Sediment	0.1206	-0.1909	-0.1712	-0.0807	0.2827	0.3133	0.5302	-0.0162	0.3951	0.3597	0.0660	1.0000					
Ca Sediment	-0.0909	0.2224	-0.0007	-0.0359	-0.2303	-0.1693	0.0552	0.2700	0.1681	0.2637	0.2115	-0.4603	1.0000				
Mineral fraction in sample	-0.0354	-0.2514	-0.0679	-0.0362	-0.0839	-0.0503	-0.6104	-0.7007	-0.6412	0.5692	-0.5630	0.0329	-0.7407	1.0000			
Volatile fraction in sample	0.0354	0.2514	0.0679	0.0362	0.0839	0.0503	0.6104	0.7007	0.6412	-0.5692	0.5630	-0.0329	0.7407	-1.0000	1.0000		
Mass fraction ≥ 0.06 mm	0.0632	-0.1464	-0.0272	0.0411	0.0515	0.0237	-0.5320	-0.6423	-0.5601	-0.7837	-0.4968	0.1275	-0.7225	0.9404	-0.9404	1.0000	
Mass fraction < 0.06 mm	-0.0632	0.1464	0.0272	-0.0411	-0.0515	-0.0237	0.5320	0.6423	0.5601	0.7837	0.4968	-0.1275	0.7225	-0.9404	0.9007	-1.0000	1.0000

6. Equilibrium between the Metal Concentration in Supernatant and in Sediment

The coefficients in equation of adsorption and/or absorption (6) and the correlation coefficients R between the metal concentration found in the sediment $[Me_s]$ and calculated from the model (6) are summarized in Table 6. Figure 20a–f shows the model (6) fit to the measured metal concentration $[Me_s]$.

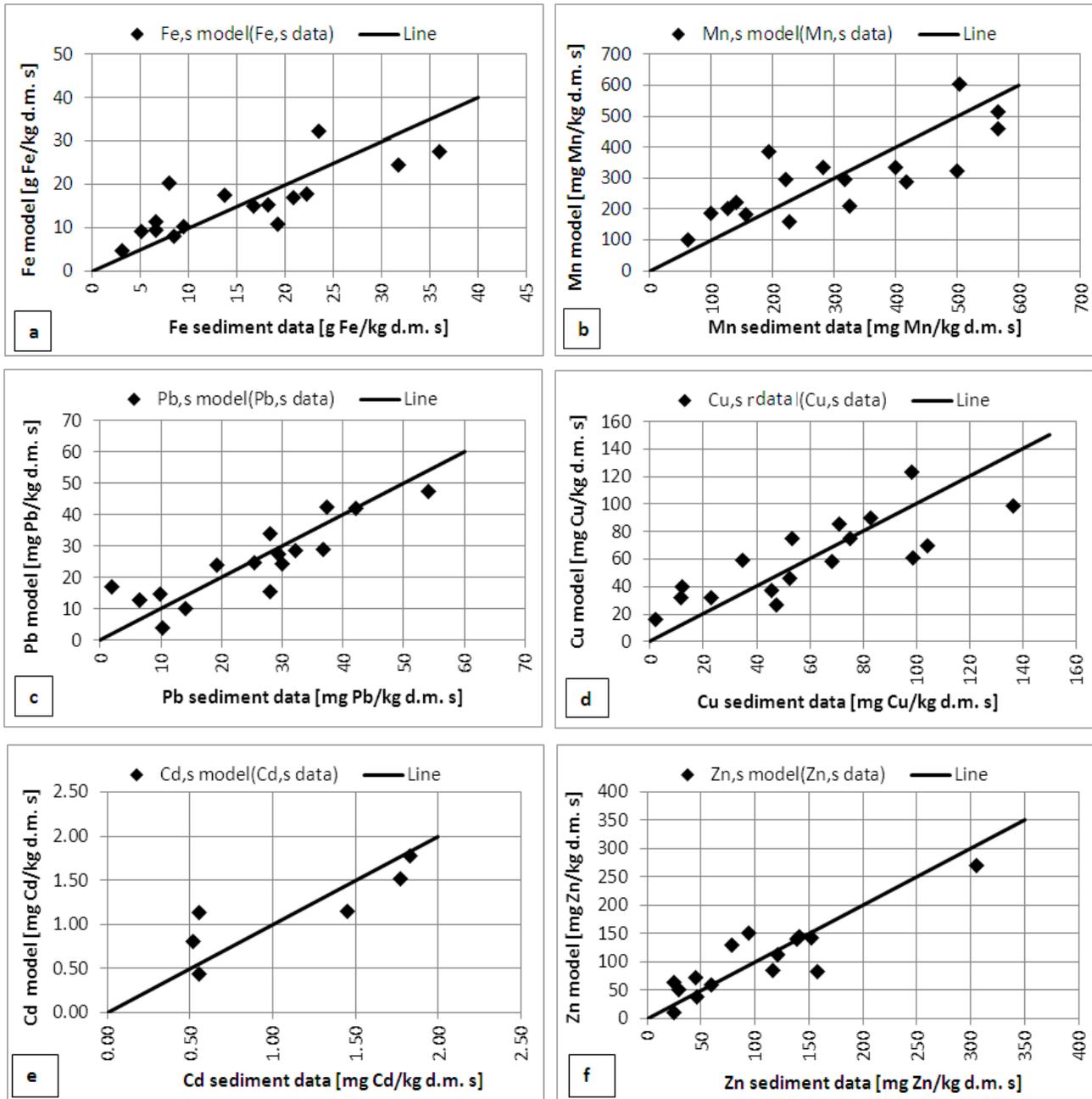


Figure 20. (a–f). Model (6) fit to the measured values of Fe, Mn, Pb, Cu, Cd and Zn.

Table 6. Coefficients for Equation (6).

Metal	k_1	α_1	k_2	α_2	R	Average Value	
						$[Me_m]$	$[Me_v]$
						[mg/kg d.m. m]	[mg/kg d.m. v]
Fe	2.510	0.000	1.611×10^2	0.000	0.783	2.510 g/kg d.m. m	161.1 g/kg d.m. v
Mn	62.57	0.000	2.931×10^3	0.000	0.799	62.57	2930.9
Cu	32.77	0.2410	6.290×10^2	9.552×10^{-3}	0.796	9.583	597.7
Pb	0.000	0.000	3.028×10^2	0.000	0.878	0.000	302.8
Zn	8.956×10^2	3.277	3.092×10^3	0.2610	0.884	0.1176	1279.3
Cd	1.144×10^4	4.938	3.509×10^3	0.5627	0.847	9.052×10^{-17}	12.788

R—correlation coefficient.

The analysis of the coefficients of the model (6) listed in Table 6 shows that:

1. Iron in the supernatant does not affect its concentration in mineral and volatile fractions of the sediment ($\alpha_1 = 0, \alpha_2 = 0$). At a substantial iron concentration in the sediments, model (6) did not detect its accumulation from the supernatant ($\alpha_1 = 0, \alpha_2 = 0$), or there was the maximum accumulation not dependent on the metal concentration in the supernatant. Iron is mostly accumulated in the volatile fraction, while its concentration in the mineral fraction is 2.510 g/kg d.m. (64 times lower).
2. Manganese in the supernatant does not affect its concentration in mineral and volatile fractions of the sediment ($\alpha_1 = 0, \alpha_2 = 0$). Model (6) did not detect any accumulation from the supernatant to the sediment ($\alpha_1 = 0, \alpha_2 = 0$), or the maximum accumulation was not dependent on the metal concentration in the supernatant. Manganese is present mainly in the volatile fraction; its concentration in the mineral fraction is 62.57 g/kg d.m. (47 times lower).
3. Copper in the supernatant correlates with copper in mineral and volatile fractions of the sediments. Model (6) showed the possibility of adsorption (general accumulation) from the supernatant to both sediment fractions. Copper is mainly present in the volatile fraction; in the mineral fraction its concentration is 9.583 mg/kg d.m. (62 times lower).
4. Lead in the supernatant does not correlate with its concentration in the mineral and volatile fractions of the sediment ($\alpha_1 = 0, \alpha_2 = 0$), or the maximum accumulation is not dependent on the metal concentration in the supernatant. Model (6) showed the possible adsorption (general accumulation) in the sediment volatile fraction. Lead is present mainly in the volatile fraction (302.8 mg/kg d.m. v.).
5. Zinc in the supernatant correlates with zinc in the mineral and volatile fractions of the sediment. Model (6) showed the possible adsorption (general accumulation) of zinc in both sediment fractions. Zinc is present mainly in the volatile fraction; in the mineral fraction its concentration is barely 0.1176 mg/kg d.m. m (10,878 times lower).
6. Model (6) showed that cadmium can be adsorbed (general accumulation) in both sediment fractions. However, its adsorption (general accumulation) in the mineral fraction is almost negligible. Cadmium is mainly adsorbed (general accumulation) in the volatile fraction. Its concentration in the mineral fraction is close to zero, while in the volatile one it reaches 12.788 mg/kg d.m. v.

Model (6) failed to demonstrate the influence of Fe and Mn accumulated in the sediments on their concentration in the supernatant (Table 7, $P_m = -, P_v = -$) and determine sensitivity of the aquatic environment to changes of Fe and Mn in the sediments (Table 7, $Q_m = -, Q_v = -$).

Copper present in the sediment mineral fraction affects 81% of the copper concentration in the supernatant while it affects only in 19% in the sediment volatile fraction. The aquatic environment is very sensitive to changes of Cu in the sediment volatile fraction (Table 7), $Q_m = 104.7 \%Me_w / \%Me_m$ and barely sensitive to changes of Cu in the mineral fraction (Table 7), $Q_v = 4.149 \%Me_w / \%Me_v$.

Lead present in the sediment volatile fraction affects 100% of the concentration of this metal in the supernatant (Table 7).

Zinc in the sediment volatile fraction affects about 99% of the concentration of this metal in the supernatant; the mineral fraction affects the aquatic environment only in 1%. The relative sensitivity of the aquatic environment to changes of the Zn concentration in the mineral and volatile fractions of the sediment remains low (Table 7, $Q_m = 0.3051 \%Me_w / \%Me_m$, $Q_v = 3.832 \%Me_w / \%Me_v$, respectively).

Cadmium in the sediment volatile fraction affects almost 100% of its concentration in the supernatant. The sensitivity of the aquatic environment to changes in the Cd concentration in the mineral and volatile fractions of the sediments remains low (Table 7, $Q_m = 0.2025 \%Me_w / \%Me_m$, $Q_v = 1.777 \%Me_w / \%Me_v$)

Table 7. Average share of mineral and volatile fractions in the sediment vs. metal concentrations in the supernatant.

Metal	P_m	P_v	Q_m [% Me_w / % Me_m]	Q_v [% Me_w / % Me_v]
Fe	–	–	–	–
Mn	–	–	–	–
Cu	0.8057	0.1943	4.149	104.7
Pb	0	1	–	–
Zn	0.01159	0.9884	0.3051	3.832
Cd	4.207×10^{-16}	~1	0.2025	1.777

where:

P_m – degree of the influence of the metal in the mineral fraction on its concentration in the supernatant (Equation (13));

P_v – degree of the influence of the metal in the volatile fraction on its concentration in the supernatant (Equation (14));

Q_m – relative sensitivity of the aquatic environment to relative changes in the metal concentration in the mineral fraction (Equation (15));

Q_v – relative sensitivity of the aquatic environment to relative changes in the metal concentration in the volatile fraction (Equation (16)).

7. Discussion

The concentrations of Fe and Mn in the Bagry Lake sediment stayed below the assumed geochemical background values, which were 47,200 and 850 mg/kg d.m., respectively [40]. The concentrations of Cd, Cu, Pb and Zn exceeded the background levels at 50%, 72%, 61% and 55.5% of the measurement points, respectively; the background values for these elements were 0.3 (Cd), 45 (Cu), 20 (Pb) and 95 (Zn) mg/kg d.m. [40]. Setting the geochemical background is difficult, especially for such specific ecosystems as artificial lakes. However, the higher metal concentrations in the sediment are most likely related to a large number of sunk construction materials, vehicles and boats, rails and narrow-gauge railway cars, cables, etc. [33]. Over time, the metals have been released from these objects to water and lake sediments due to dissolution, corrosion and adsorption (generally accumulation) in mineral or volatile material.

Lake sediments are an integral part of the aquatic environment and provide a habitat for many aquatic organisms; high concentrations of heavy metals may pose a threat to them. It should be noted, however, that the bioavailability of metals varies depending on many factors including both metals themselves and the characteristic of the aquatic environment [41]. The LEL and SEL ecotoxicological criteria indicate that copper can be toxic for benthic organisms at two locations while the potentially harmful effects of Cd, Cu, Pb, Zn, Mn and Fe have been noticed at 3 up to 18 measuring sites, located within Bagry Lake.

Due to the fact that no literature was found on the concentrations of metals in the water environment of post-exploitation reservoirs similar due to the exploited raw materials (natural aggregates and clay) and uncontrolled flooding, the concentrations of heavy metals contained in its water environment were compared to those of other dam reservoirs located in southern Poland. These reservoirs, unlike Bagry Lake, are flow reservoirs. They were created for flood protection, leveling the water levels in the rivers below the reservoir, supplying the population with water, the operation of hydropower plants and recreation.

Comparing Bagry Lake with other reservoirs (Table 8) the highest Cu concentration was noted in there; the concentration exceeds even the values observed in the Kozłowa Góra Reservoir, which strongly suffers from anthropopressure. The concentrations of Pb and Zn are slightly higher than in the Dobczycki or Czorsztyn Reservoirs but are definitely lower than in the Kozłowa Góra Reservoir. The Cd concentrations remain similar to those in the Czorsztyn Reservoir. The Fe concentrations are the lowest while the Mn concentrations are slightly higher than in the Czorsztyński Reservoir but are definitely lower than in the Dobczycki or Rożnów Reservoirs. It should be noted that a relatively high Cu concentration in the Bagry Lake sediment is site-specific. There was a rather weak relationship between the metal concentration in the sediment and in the supernatant in Bagry Lake.

Table 8. Concentrations of metals in sediments of the selected reservoirs.

Reservoir	Fe [g/kg]	Mn [mg/kg]	Cu [mg/kg]	Pb [mg/kg]	Zn [mg/kg]	Cd [mg/kg]
Bagry (currently analysed)	3.16–36.03	61.60–566.4	2.11–161.0	1.96–54.11	25.35–321.0	≤1.831
Dobczycki [20]	10.3–43.8	156–2355	9.3–44.2	11.5–40.7	16.5–264.4	0.33–2.4
Czorsztyński [20]	14.1–39.9	21.5–336	14.8–34.1	12–23.2	84.7–296.1	0.7–2.1
Rożnowski [20]	20.6–38.1	619–1381	27.5–38.4	16.9–26.3	78.5–189	1.4–2.6
Solina [42]	nd	nd	21.69–37.57	10.73–33.71	nd	0.12–1.4
Kozłowa Góra [43]	nd	109–784	6.8–112.5	105–1373	290–1875	2.8–22.7

nd—no data available.

It is difficult to set the geochemical background for iron and manganese in Bagry Lake since the lake stays in contact with groundwater, located southeast (about 1 m below the surface) and not insulated with impermeable layers.

The values 2×10^{-5} , 0.002, 2×10^{-4} and 0.01 mg/L were assumed as the geochemical background for Cd, Cu, Pb and Zn, respectively [1]. The geochemical background for Cu, Zn, Pb and Cd in Bagry lake supernatant was exceeded in 12, 16, 17 and 12 (out of 18) measuring sites, respectively.

Comparing the metals concentrations in the supernatant of Bagry Lake and water of other reservoirs (Table 9), it should be noted that the highest concentrations of Cu and Fe were found in Bagry Lake. The maximum concentration of Cu was about 5.8 times higher than the one in the Kozłowa Góra Reservoir; this reservoir is strongly influenced by anthropopressure. The highest concentrations of Fe, Mn and other metals in the supernatant water were observed in the southeastern part of Bagry Lake where surface runoff infiltrates close to the rail track. Zinc concentrations are slightly higher than those in the

Dobczyce Reservoir but definitely lower than the ones in the Czorsztyn Reservoir. Lead concentrations are much lower than in Kozłowa Góra Reservoir but definitely higher than in the other reservoirs; cadmium concentrations in Bagry Lake remain the lowest.

Table 9. Metal concentrations in reservoir waters.

Reservoir	Fe [mg/L]	Mn[mg/L]	Cu [mg/L]	Pb [mg/L]	Zn [mg/L]	Cd [mg/L]
Bagry (currently analysed)	0.053–3.690	0.030–0.301	0.000527–0.0966	3.33×10^{-5} –0.0308	0.00740–0.1065	7.2×10^{-6} –0.000120
Dobczycki [20]	0.003–0.970	0.0015–1.880	0.0007–0.0218	0.0001–0.0068	0.0010–0.0862	1×10^{-5} –0.00062
Czorsztyński [20]	0.0031–0.186	0.0033–0.050	0.0005–0.0079	0.0002–0.0030	0.0847–0.2961	2×10^{-5} –0.0002
Różnowski [20]	0.020–0.247	0.0083–0.1736	0.0013–0.0106	0.0001–0.0027	0.0040–0.0318	1×10^{-5} –0.00024
Solina [44]	0.020–0.030	0.0432–0.0441	0.00569–0.00626	nd	0.023–0.02325	Nd
Kozłowa Góra (Mn i Cu—[45], Zn, Pb, Cd—[46])	nd	0.0199–0.5936	0.0017–0.0167	0.002–0.074	0.012–0.190	0.0002–0.0080

nd—no data available.

Both the cluster analysis (Figure 18) and the analysis of the relationship between the metal concentrations in the supernatant and in the sediment confirmed that the relation is weak, e.g., a relatively low iron concentration in the sediment opposed to its high concentration in the supernatant. It may be explained by surface runoff and its infiltration into groundwater feeding Bagry Lake.

Since there are weak concentration equilibria between the supernatant and the sediments, it may be interesting to look into relations between metals concentrations in the supernatant and in the sediment fractions and vice versa. The interactions depend on a main direction of metal relocation between the phases, until the equilibrium is established. Due to the nature of sediments and materials submerged in Bagry Lake as well as rainwater infiltrating the area of the railway track, it is presumed that these are the key factors that determine metal concentrations in the supernatant.

Metal concentrations in the sediments and in the supernatant depend not only on the metal state but also on pH and redox conditions. Soluble compounds or those which undergo hydration or dissociation move freely between phases. On the other hand, insoluble forms are transported only by mechanical movements of supernatant and sediment particles or by density currents.

Many factors determine whether metals stay in soluble or insoluble forms. These factors contribute to migration of metals between phases and affect their adsorption or accumulation in sediments. The calculations of the model (6) refer to the average conditions that define the behavior of metals in the sediments and in the supernatant in Bagry Lake.

Since there is a strong correlation between the volatile fraction and the fraction with particles < 0.06 mm ($R = 0.9404$, Table 5), metal compounds might also be present in the silty clay and clay fractions; they do not have to be adsorbed or absorbed in organic matter but may constitute a separate fraction. The strong correlation between the volatile fraction and the fraction with particles < 0.06 mm suggests that there may be physical or chemical link between these fractions. Therefore, metal compounds may also be physically or chemically bound to the volatile fraction of the sediment.

Adsorption or absorption may occur between volatile matter and metal compounds, and the volatile fraction may contain combinations of metals with organic ligands.

Metals in the volatile fraction are mainly present in combination with the particle fraction < 0.06 mm (silty clay and clay fractions) (Table 6). Such conclusion is verified by the positive correlation coefficients (R) for Fe, Mn, Cu, Pb and Zn; it confirms a synergistic relationship between the volatile fraction and the metal concentration of the sediment (Figure 3, Table 5).

Calculations for cadmium are inconsistent. The coefficient R for cadmium in the sediment is positive for the mineral fraction and the fraction with particles ≥ 0.06 mm (Figures 3 and 4, Table 5), but calculations for adsorption or absorption showed mainly its link with the volatile fraction (Table 6); a cluster analysis showed also connections be-

tween the volatile fraction and fraction with particles < 0.06 mm. Very small positive correlation coefficients for cadmium in the sediment and in the mineral fraction ($R = 0.0329$, Table 5) as well as in the sediments and the fraction with particles ≥ 0.06 mm ($R = 0.1275$, Table 5) cannot explicitly exclude its presence in the volatile fraction, associated with the particle fraction < 0.06 mm.

It should be noted that correlation coefficients reflect only two features, while the cluster analysis the entire group; adsorption and absorption analysis considers four features (metal concentration in the supernatant, metal concentration in the sediment, mass of mineral and volatile fractions). Cadmium is indirectly associated with the volatile fraction and the fraction with particles < 0.06 mm through positive and significant correlations with Fe, Cu and Pb in the sediment equal to 0.5302, 0.3951 and 0.3597, respectively (Table 5). These metals are associated with the volatile fraction and the fraction with particles < 0.06 mm. Therefore, any conclusions based on one low correlation coefficient may be inaccurate or even wrong.

Further studies of Bagry Lake are planned on seasonal variability of metals in waters and sediments, changes in metal concentrations in the depth profile and bioavailability of metals contained in the aquatic environment for the laboratory strain *Chironomus riparius* performed in situ.

In order to improve the quality of the water environment of this lake, metal parts lying on its bottom should be removed, and a strip of vegetation should be planted between the railway tracks and the lake, which would intercept metals flowing from the railway tracks together with rainwater into the lake. After these activities, measurements of metals in the waters and sediments of the lake should be performed again at the same measurement points where they were examined in this work to determine to what extent the quality of the aquatic environment has improved. It would be worth taking measurements in other post-exploitation lakes of this type in order to compare the quality of the water environment in such reservoirs.

8. Conclusions

The work showed that the content of iron and manganese in the sediments of Bagry Lake is at the level of the geochemical background. Determining the geochemical background for these metals in the water of Bagry Lake is difficult due to the contact of the lake water with groundwater at a depth of about 1 m below the surface. On the other hand, the concentrations/content of copper, cadmium, zinc and lead both in the water and in sediments exceed the geochemical background values; therefore, they are of anthropogenic origin. Based on the LEL/SEL ecotoxicological criterion, it was indicated that copper content in sediments, in 2 out of 18 measurement sites, has a harmful effect on benthic organisms, and the contents of iron, manganese, copper, lead, zinc and lead in sediments have a potentially harmful effect on benthic organisms, in 3 to 13 out of 18 measurement sites. Significant positive correlations were also found between the contents of the metals in question in the sediments and the silty-clay and clay fractions of the sediments (particles with a granulometry of <0.06 mm), as well as the content of these metals in the volatile (organic) fraction and negative correlations with sand fraction (particles with a granulometry of ≥ 0.06 mm). These results were confirmed using the equilibrium model: supernatant (water)—mineral fraction of sediment—volatile fraction of sediment. The share of the mineral fraction of sediments shows a significant positive correlation with sand fraction (particles with a granulometry of ≥ 0.06 mm). On the basis of the cluster analysis, connections between the concentration of metals in water and sediments were found. Relatively strong relationships were indicated for all metals present in sediments (except calcium) and for all metals present in water (except zinc). In addition, it was shown that the volatile fraction of sediments has a dominant effect on the migration of lead, zinc and cadmium between sediments and water. It is noteworthy that despite the fact that copper accumulates mainly in the volatile fraction of sediments, the

quantitatively dominant mineral fraction of sediments has a stronger impact on the migration of this metal between sediments and water.

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