



Heavy metal pollution of water and bottom sediments of the Wilanowskie Lake

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ABSTRACT

The study aimed to assess the content of metals in water, suspended solids and bottom sediments sampled from the Wilanowskie Lake. The analyses of zinc, lead, cadmium, and copper showed that the metal concentration in water, suspended solids, and sediments differed at individual measurement points. It can be attributed to the influx of pollutants from the areas adjacent to the lake. During the sampling period, the concentration of dissolved forms of Cu varied from 33.1 to 186.5 $\mu\text{g}/\text{dm}^3$; in the suspended form it ranged from 0.21 to 0.81 mg/dm^3 , and in bottom sediments, it was in the range 17–245 $\text{mg}/\text{kg dw}$. For cadmium, the concentration of dissolved forms ranged from 1.15 to 19.53 $\mu\text{g}/\text{dm}^3$, in suspended form – from 0.02 to 0.1 mg/dm^3 , and in the sediments from 6.2 to 21.6 $\text{mg}/\text{kg dw}$. The concentration of dissolved forms of lead was from 3.19 to 106.7 $\mu\text{g}/\text{dm}^3$, in the suspension from about 0.67 to 1.07 mg/dm^3 and in sediments – from 200 to 450 $\text{mg}/\text{kg dw}$. For zinc, the results were respectively: from 65 to 632 $\mu\text{g}/\text{dm}^3$ for the metal forms dissolved in water, from 1.1 to 2.2 mg/dm^3 for suspended forms and from 70 to 2,900 $\text{mg}/\text{kg dw}$ in sediments.

Keywords: Lake; Sediments; Water; Heavy metals; Contamination

1. Introduction

A major fraction of trace metals that are transported by rivers are associated with sediments, especially during flooding, when erosion and resuspension increase sediment loads [1]. Heavy metals are released into surface waters becoming one of the most troublesome types of contaminants. At the same time heavy metals are considered to be one of the main types of hazardous waste according to the Act on Waste of 14 December 2012, Journal of Laws 01.62.628, as amended, as well as the Hazardous Waste Directive of 12 December 1991 (91/689/EEC), altered by the Council Directive 94/31/EC. Due to a large diversity of processes occurring in the surface waters reservoirs, precipitation and sedimentation lead to the accumulation of metals in the bottom sediments. The chemical composition of surface water sediments, including the content

of substances that are hazardous for living organisms, is dependent on numerous natural and anthropogenic factors [2]. The pollutants originating from the surface runoffs and treated sewage introduced into rivers and lakes are transported along with water flow affecting the water quality [3–5]. The processes depend on the geological structure of the catchment, geomorphology and climate conditions influencing the rock weathering processes, as well as the activation, migration, and accumulation of the elements in the environment [6,7]. Depending on environmental factors, metals can be released from bottom sediments and return to the surface water, posing a threat to water biota [8,9]. The knowledge of the behavior of metals in changing environmental conditions may allow forecasting the absorption of elements by aquatic organisms [10]. The analysis of metal forms provides information about the mobility and bioavailability of the metal, related to the nature of

their binding in sediments [11]. The dissolved metal forms introduced into lake waters, coming into contact with solid particles (sediments and suspensions), are quickly adsorbed on their surface due to the surface charges or as a result of possible chemical reactions [12,13]. An adsorption of dissolved metals in sediment and suspension can significantly influence their chemical and physical forms, diminishing the potential negative environmental impact [14].

This study aimed to evaluate the quality of water in the Wilanowskie Lake, with reference to its general parameters, aquatic biogenic substance content and the heavy metals level in three phases: dissolved, suspended solids and bound in bottom sediments.

2. Experimental

The analyses covered the general water parameters: temperature, pH, water general basicity, dissolved oxygen concentration, permanganate index. As far as aquatic biological productivity parameters are concerned, NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} concentrations and water mineralization indices, such as general water hardness, and the Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} concentration were tested. The most significant part of the study was the determination of heavy metals content (Zn, Cu, Pb, Cd).

2.1. Object of study

The Wilanowskie Lake is a natural water reservoir situated in the valley of the central Vistula, with the area approx. 15 ha, located in the territory of the Wilanów district in the southern part of Warsaw. The lake is approx. 1.5 km long, and its width oscillates between 50 and 100 m. The reservoir is located along the north-south axis, and its depth ranges from 1 to 5 m. The lake bank from its eastern side is arboreous and from its western bank, it is strengthened with a fascine. The bottom of the lake is slimy.

For the study seven sampling points were selected (Fig. 1), where water and bottom sediments were sampled three times: in July, August and October 2017.

2.2. Methods

The water samples for physical and chemical analyses were taken at selected sites from the surface layer (0–0.5 m). A Ruttner sampler (KC Denmark Research Equipment, Denmark) was used for water sampling. The sampler was equipped with a graduated rope allowing water to be taken from a certain depth. The 1.5 l water samples were taken for testing. The collected water samples were transferred to specially prepared plastic bottles.

The samples of the upper sediment layer, about 20 cm thick, were taken with a Kajak sampler (KC Denmark Research Equipment, Denmark). Each sample consisted of approximately 300 g of sediment. The collected bottom sediment was transferred to plastic containers.

The full scope of water examination was performed according to the standard ISO/IEC 17025:2005: pH, conductivity, identification of chlorides and sulfates by the turbidimetric method in the HACH DR 2000 device (Germany), calcium and magnesium, ammonium nitrogen, nitrite



Fig. 1. Sampling points in the Wilanowskie Lake (Source: ©uzytkownicy OpenStreetMap <http://www.openstreetmap.org/>, CC BY-SA, <http://creativecommons.org/licenses/by-sa/2.0/>).

nitrogen, nitrate nitrogen, phosphate phosphorus. The identification of the sediments included the analysis of hydration, granulation, pH, conductivity, the content of chlorides, total nitrogen, and total phosphorus.

The water sample preparation for metal testing included filtration with the membrane filter with 0.45 μm pore diameter and subsequent sample fixation through acidification with pure nitric acid to pH approx. 2.0. In water samples, prepared in this way, Zn, Cd, Pb and Cu concentrations were determined using an atomic absorption spectrophotometer with atomization in a graphite furnace (GF-AAS).

The suspension and sediment samples, after drying, were wet mineralized using a mixture of nitric acid about 65% analytical purity (HNO_3) and chloric acid (VI), about 70% analytical purity (HClO_4) in a ratio of 3:1. After the digestion, the solutions were filtered to a 50 ml volumetric flask. The

heavy metals concentrations were determined in the solutions prepared according to this protocol.

The content of heavy metals (Zn, Cd, Pb, and Cu) was measured by atomic absorption spectrometry with flame atomization (FAAS). The assays were performed based on calibration curves, established for a series of previously prepared MERCK standard solutions (Poland). Hollow cathode Philips lamps (Germany) were used as a source of radiation. Limits of detection of respective metals were determined for double standard deviation in five series: in water (mg/dm^3) – Cu (0.01), Zn (0.01), Pb (0.01), Cd (0.005) and in sediments (calculated for $\text{mg}/\text{kg dw}$): Cd (0.005), Cu (0.03), Pb (0.05), Zn (0.01). To verify the analysis and measurement fidelity, Certified Reference Material Till-3, with the known metal content, was mineralized. The recovery rate of particular metals in reference sediments oscillated within $93\% \pm 110\%$. The error ensuing the comparison of analysis results did not exceed 10%.

2.3. Principal component analysis and cluster analysis

The data were standardized to perform a transformation that would facilitate the comparison of the values of numerous variables, irrespective of their distribution and the units they were measured in. Based on the scree plot and the information about the variance accounted for by particular components, 2 principal components, which explained 51% of the variance, were identified. The cluster analysis (CA) was performed according to Ward's method, using variance as analysis to calculate the distance between the clusters. For cluster formation, the Euclidean distance was chosen [15].

3. Results and discussion

The quality of water from the Wilanowskie Lake varied throughout the test period and at particular sampling sites (Table 1).

The analyzed parameters reflected different water purity classes according to the Polish legislation. The average temperature throughout the testing period was 15.5°C . The little differences in temperature at particular sites can be attributed to the fact that the area was partially shaded by vegetation over the bank of the Wilanowskie Lake. The measurement of pH of water from the Wilanowskie Lake yielded values close to neutral, oscillating from slightly acidic (pH 6.57), to alkaline (pH 7.23). A high conductivity in the whole studied area was probably associated with the high content of mineral compounds in water. The concentration of dissolved oxygen was characterized by profound alterations, with a minimum value of $2.98 \text{ mg O}_2/\text{dm}^3$, and the maximum value of approximately $13 \text{ mg O}_2/\text{dm}^3$. The content of dissolved oxygen diminished with time. The mean O_2 concentration in July, August, and October were 9.67, 7.17 and $6.31 \text{ mg O}_2/\text{dm}^3$, respectively. The lowest value was observed three times at the sampling point No. 2. As regards biogenic indices, the highest oscillations of concentration values were noticed in the case of phosphates. Their concentration in the test samples varied in the range of $0.66\text{--}6.87 \text{ mg}/\text{dm}^3$. The concentrations differed depending on the sampling period. The lowest values were obtained in July (average $1.86 \text{ mg}/\text{dm}^3$). The highest concentration of phosphates was observed

in October ($3.92 \text{ mg}/\text{dm}^3$), and slightly lower in August ($3.3 \text{ mg}/\text{dm}^3$). The assessment of water parameters served as a basis for the analysis of interdependencies between heavy metals - zinc, cadmium, copper and lead, and changing environmental conditions.

The waters of the Wilanowskie Lake were characterized by a low concentration of dissolved forms of the studied metals (Fig. 2). The values obtained for copper and lead exceeded the limit values in the waters of the Wilanowskie Lake, which can be classified as representing the 2nd class of water purity, according to the *Directive of the Minister of the Environment of August 5, 2016, on the defining classification for the presentation of surface water and groundwater status, on the method of monitoring and the method of data interpretation and presentation of the state of these waters*. The limit values are as follows: Zn – $1 \mu\text{g}/\text{L}$, Cu – $0.05 \mu\text{g}/\text{L}$. For cadmium and lead, metals included in priority substances, the maximum permitted values of environmental quality standards are 0.25 and $1.2 \mu\text{g}/\text{L}$, respectively.

The suspension present in the water column was characterized by a significant content of tested metals (Fig. 3). In the tested suspension samples, the zinc concentration ranged from 1.1 to $2.2 \text{ mg}/\text{dm}^3$. During the test period, the concentration level of lead in the suspension changed in the range from about $0.67\text{--}1.07 \text{ mg}/\text{dm}^3$, and for copper - in the range from 0.2 to $0.8 \text{ mg}/\text{dm}^3$. The respective data for cadmium content were $0.02\text{--}0.1 \text{ mg}/\text{dm}^3$. For the tested metals, the variable content in three measuring periods was observed. For copper and zinc, the highest values were noticed in August and the lowest in July. The strongest lead and cadmium binding in the suspension was observed in autumn. October was the month in which increased salinity parameters and reduced dissolved oxygen values were found, which could affect the adsorption of metals on solid particles.

Taking into account the geochemical background values for elements determined in water sediments in Poland, constituting the detection limit of the bottom sediments of the Wilanowskie Lake, the sediments can be divided into three purity classes:

- *Class I*: slightly contaminated sediments; metal concentrations are from 2 to 5 times higher in comparison with the geochemical background (it is depended on the element mobility in the environment and its toxicity for the biosphere);
- *Class II*: moderately contaminated sediments; metal concentrations are from 10 to 20 times higher in comparison with the geochemical background;
- *Class III*: contaminated sediments; metal concentrations are from 20 to 100 times higher in comparison with the geochemical background.

The heavy metal content in bottom sediments sampled at defined test sites in the area of the Wilanowskie Lake was rather diversified (Fig. 4). Bottom sediments of the Wilanowskie Lake are noticeably polluted with heavy metals. The content of zinc, cadmium, copper, and lead was, $32\text{--}2037 \text{ mg Zn}/\text{kg dw}$, $2.1\text{--}14.1 \text{ mg Cd}/\text{kg dw}$, $19.2\text{--}272.5 \text{ mg Cu}/\text{kg dw}$, and $16.3\text{--}105.4 \text{ mg Pb}/\text{kg dw}$ (Fig. 4). The major sediment pollutants are copper and cadmium.

Table 1
Quality of water from the Wilanowskie Lake

Position	1	2	3	4	5	6	7
pH	6.5–6.9	6.7–6.9	6.5–6.7	6.4–6.8	6.6–6.7	6.70	6.5–6.7
Temperature, °C	15.50	15.43	15.43	15.53	15.70	15.93	16.63
Color, mgPt/dm ³	41.67	41.67	31.67	30.00	30.00	36.67	38.33
Turbidity, mg/dm ³	5.67	5.67	3.33	3.33	3.33	4.00	4.67
Suspension, mg/dm ³	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BZT5, mg/dm ³	8.51	6.11	4.38	3.76	6.14	7.59	8.13
O ₂ , mg/dm ³	8.51	6.11	4.38	3.76	6.14	7.59	8.13
Basicity, mval/dm ³	4.53	4.47	4.50	4.40	4.40	4.17	4.33
Conductivity, μS/cm	870	828	808	584	598	622	785
Cl ⁻ , mg/dm ³	106.7	99.3	94.7	93.3	95.0	102.0	118.0
SO ₄ ²⁻ , mg/dm ³	96.67	91.33	84.00	89.83	84.83	85.50	99.67
Ca ²⁺ , mg/dm ³	89.0	90.0	88.2	85.8	87.6	87.6	90.0
Mg ²⁺ , mg/dm ³	29.7	26.7	23.2	21.7	21.9	25.1	26.9
Hardness, mgCaCO ₃ /dm ³	344.3	334.9	315.6	303.6	308.9	322.2	335.6
N-NH ₄ ⁺ , mg/dm ³	0.63	0.61	0.62	0.54	0.53	0.47	0.53
N-NO ₂ ⁻ , mg/dm ³	0.05	0.06	0.05	0.04	0.04	0.04	0.05
N-NO ₃ ⁻ , mg/dm ³	1.43	1.50	1.73	1.73	1.73	1.73	1.90
P-PO ₄ ³⁻ , mg/dm ³	3.39	3.44	3.55	3.40	3.74	2.10	1.85

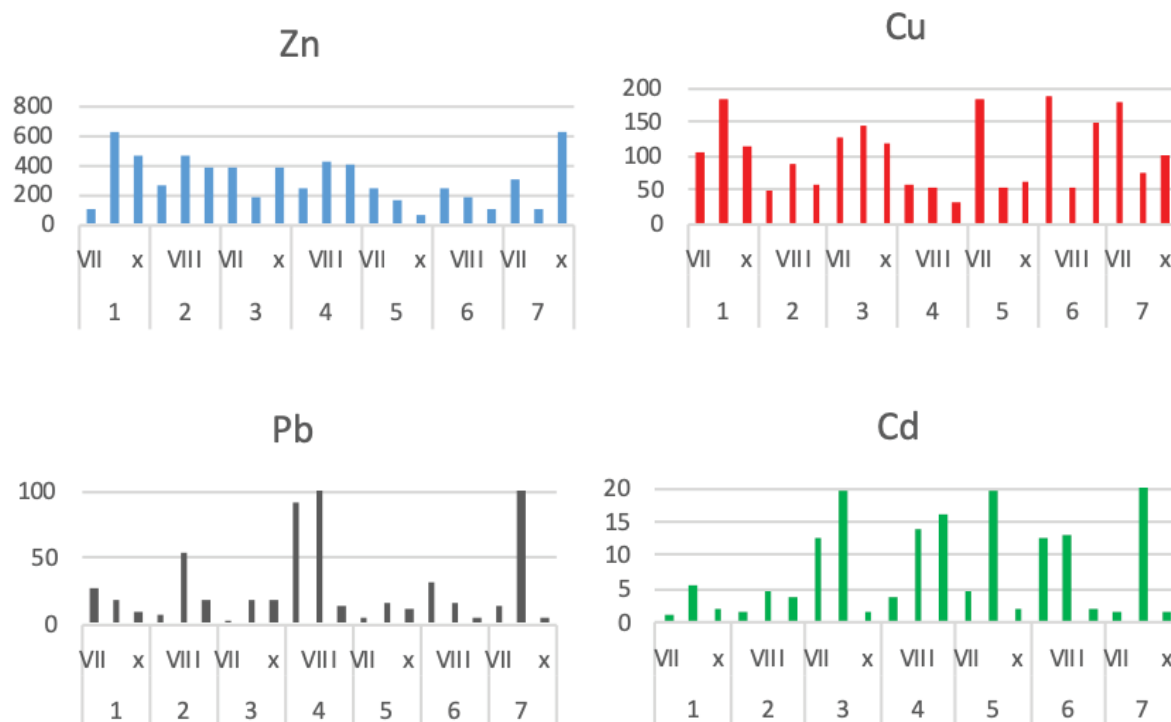


Fig. 2. Heavy metal content in water (mg/L).

With reference to the three purity classes, zinc and lead had the lowest content values. At one site, the same element is present in the concentration at the level of tens of mg per kg, whereas at another site the value is over one thousand times higher. In the case of the Wilanowskie Lake, there is one regularity: the highest accumulation of all five elements

occurred at 4 sampling sites: number 5, 6, 7 and 8 (Fig. 4). The samples from these sites were characterized by extreme values. In the mentioned area, a characteristic feature is the natural, vegetation-covered lakeshore, slimy at places, which is due to a profound accumulation of decomposing biomass. With the exception of lead, for other metals, the values

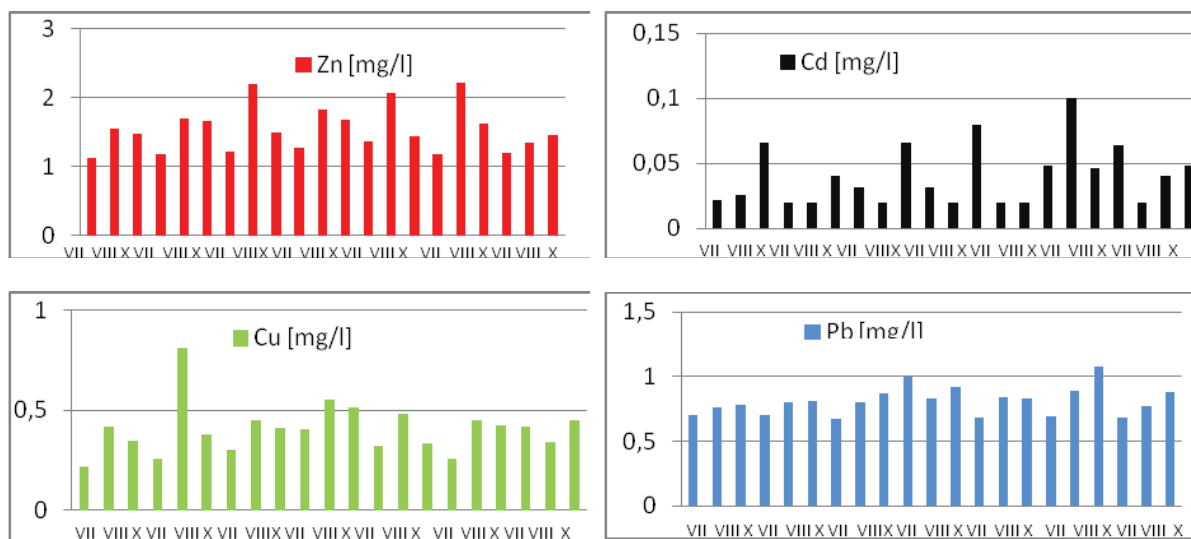


Fig. 3. Heavy metal content in the suspended phase.

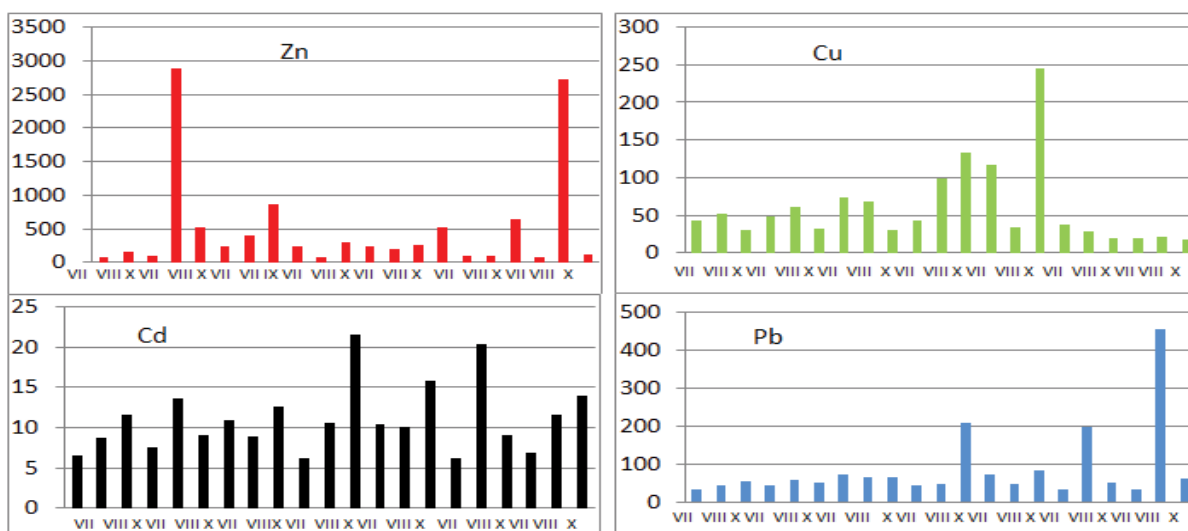


Fig. 4. Changes in sediment metal concentration values at sampling sites (mg/kg dw).

exceeded the threshold of the purity of sediments defined for Class I. It should be stressed that the neighborhood of the Wilanowskie Lake is not highly industrialized.

As far as the sediment zinc concentrations are concerned, two samples stand out: the sampling at site 2 in July and that at site 7 in August. For the testing points 2 and 7, zinc concentrations in sediments were 2,900 and 2,750 mg/kg dw, respectively. Excluding the above-mentioned extreme values for Zn, the remaining results reached the values from approx. 70 to 860 mg/kg dw. The sediments in the majority of sites can be assigned to Class II and III, according to the geochemical criteria. An exception is the sampling site No. 1, where zinc concentration did not exceed the Class I threshold in any of the test months. The lead content in sediments at sites 4 and 6 was approximately 200 mg/kg dw, while at site 7 - about 450 mg/kg dw. Such values are very high for lead and indicate heavy sediment pollution. Additionally,

200 mg/kg dw is a threshold value. The remaining values for lead content in sediments ranged from 33 to 84 mg/kg dw, making the sediments belonging to Class III, according to the classification of sediments, based upon the geochemical criteria [5]. This means that they are contaminated sediments. A cadmium concentration in bottom sediments reached the values from 6.2 to 21.6 mg/kg dw. The lowest values were observed in July. The particularly high cadmium values were observed in October at site 4 and in August at site 6. The results were similar to those obtained in the case of the lead analysis in sediments. In the case of bottom sediments, the highest copper content was observed at site 5 in October. The obtained value of 245 mg/dm³ exceeds the threshold values, defined in the Directive and classifies the sediments as highly contaminated, according to the geochemical criteria. Excluding the highest values of the copper content in bottom sediments, it remained in the range 17–100 mg/

kg dw, and therefore, most often the sampled sediments fell into the Class II category of purity.

The correlation analysis suggests a strong relation between Pb in sediments and Cd in surface water. The following significant correlations occur between surface water and suspension (Cd–Zn) or suspension and sediments (Zn–Cd), which points to a significant role of suspension in contamination transfer. It should be emphasized that there are strong relations between metals in sediments (Zn–Pb, Pb–Cd) and the necessity of further study of their competitiveness in the aquatic environment (Table 2).

The principal component analysis (PCA) shows differences and similarities in data concerning water indices. The biplot of the variables projection onto the factor-plane is presented in Fig. 5. The analysis points to a high interrelation of the tested parameters, mainly between the Ca, Cl, P, Zn content, conductivity, and hardness. The correlations of these parameters may indicate their similar sources.

The similarity analysis involves all tested water parameters (without suspension and sediments). The CA rests in grouping the tested objects in such a way as to assign similar items to separate sets, according to defined criteria. It is based on the principle of internal similarity and external dissimilarity. In CA, three main similarity sets can be distinguished. The first set comprises parameters such as pH, alkalinity, turbidity, nitrite nitrogen, and ammonium nitrogen, Mg, Cd, and Pb. The second set contains oxygen agents and the third one – other parameters (Fig. 6).

The study confirms the hypothesis that lakes limit the transport of pollutants from the catchment area. On the example of the Wilanowskie Lake, it can be shown that the lake is the most important link in the river–lake system, in which a significant part of the pollution transported from the catchment area is collected. It protects the river from excessive pollution. At the same time, there is the problem of the state of the lake ecosystem, which can be aggravated by the accumulation of toxic substances. The chemical composition of surface water sediments depends primarily on the geological structure of the catchment, geomorphology and climatic

conditions affecting the rock weathering process, as well as the activation, migration, and accumulation of elements in the environment. It results in the deterioration of the lake, being a biogeochemical barrier for heavy metals. The conducted research shows that the degree of metal accumulation is variable in the lake area. It depends on the morphology of the reservoir, the distance from the sampling point and the river inflow, the depth of the lake, the nature of the coastal zones, as well as the location of measuring stations [16]. The spatial distribution of forms (dissolved and suspension) of metals depends on the intensity of water exchange, and hence the flow rate. This modifies the nature of the lake's water and bottom sediments, including their organic and mineral composition [17,18].

This article presents the problem of heavy metal distribution in the water column and bottom sediments. In the study of three forms of heavy metals (dissolved, suspension and in sediments) the hypothesis of strong binding of metals in the solid phase and, consequently, their deposition in bottom sediments was confirmed. Although rivers are thought to be an external source of lake pollution, the study indicates that the bottom sediments can serve as an internal source of water pollution [19,20]. The study also confirmed the correlation of heavy metal content with anthropogenic pollution. The presence of high concentrations of nutrients in water results from the influx of river water heavily loaded with nitrogen and phosphorus forms. These substances may contribute to the circulation of heavy metal forms in the water – bottom sediment system. Particular attention should be paid to the high cadmium load in Wilanowskie Lake, which shows a strong correlation with other metals, especially with Zn. The PCA has revealed that there is a relationship between the occurrence of Cd and water macronutrients. The form of this metal depends on the pH of the water. This can affect the mobility and release into the water of the cadmium compounds deposited in the sediments, which poses a threat to living organisms at the bottom. The cadmium content in bottom sediments was significantly above the geochemical background. The high lead

Table 2

Correlations between heavy metals contained in surface water, suspension and bottom sediment. The mean values and standard deviation of variables, number of samples ($n = 21$)

Variable	Mean	SD	Zn s	Pb s	Cd s	Cu s	Zn su	Pb su	Cd su	Cu su	Zn se	Pb se	Cd se	Cu se
Zn s	307.65	159.70	1.00	-0.10	-0.28	0.10	-0.07	-0.10	0.06	0.34	-0.33	-0.28	0.10	-0.20
Pb s	28.74	33.87		1.00	0.41	-0.33	-0.02	0.13	-0.19	0.24	0.27	0.43	-0.15	-0.08
Cd s	8.05	7.47			1.00	-0.22	0.47	-0.04	-0.00	0.13	0.28	0.62	0.22	0.00
Cu s	108.70	49.93				1.00	-0.23	-0.38	0.12	-0.24	-0.30	-0.29	-0.38	-0.19
Zn su	1.54	0.33					1.00	0.41	-0.09	0.57	-0.16	0.10	0.45	0.01
Pb su	0.81	0.11						1.00	0.27	0.38	-0.17	0.08	0.33	-0.04
Cd su	0.04	0.02							1.00	-0.16	-0.20	0.16	0.34	-0.00
Cu su	0.41	0.13								1.00	-0.19	-0.00	0.39	0.00
Zn se	515.3	792.27									1.00	0.52	-0.10	-0.06
Pb se	87.16	96.22										1.00	0.46	-0.00
Cd se	11.07	4.22											1.00	0.39
Cu se	59.66	53.45												1.00

s - solution; su - suspended, se - sediment.

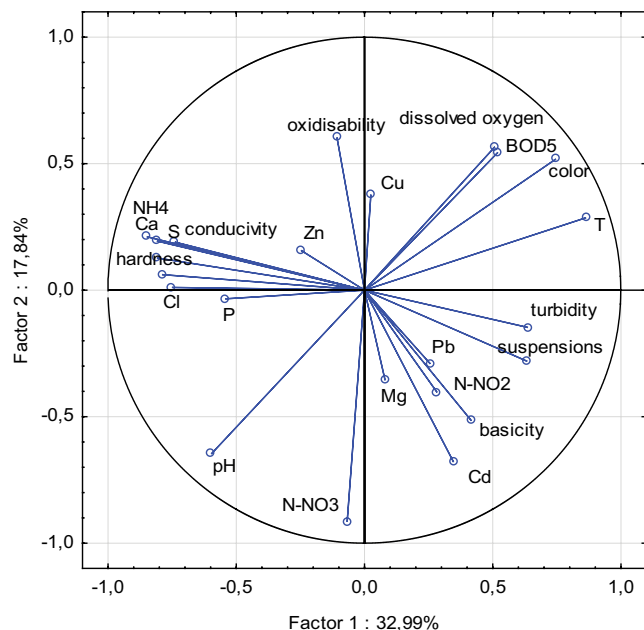


Fig. 5. Principal component analysis (PCA).

concentration in lake in Wilanów may result from the use of areas adjacent to the lake, and, in particular, from the proximity of roads and the intensity of their use. The observed heavy metal contents, especially in bottom sediments and suspended solids, are high and indicate significant contamination of the aquatic environment, which can pose a serious threat to organisms. The retention of heavy metals in water and lake sediments promotes self-purification of river water and limits the transport of harmful substances outside the catchment area. Some amounts of metals, in addition to those in the form of water suspension and accumulate in sediments, can be absorbed by macrophytes or aquatic organisms.

4. Conclusions

The high metal content, particularly that of copper and cadmium, in surface water and bottom sediments, point to a high accumulation of these pollutants, which are probably released to the lake through inlet watercourses and surface runoff, as well as from polluted air, due to a dry and wet deposition. The zinc content in bottom sediments revealed profound discrepancies: from the slightly contaminated sediments to the highly contaminated ones. This can be attributed to a high sensitivity of this element to the changing environmental conditions, particularly when the reservoir's acidic and alkaline conditions change [21]. The obtained values for lead, both in water and in the sediments, indicate a considerable contamination of the Wilanowskie Lake with this element. The above can be attributed to the lake's location in a highly urbanized area, surface runoff from the streets and the inflow of water from the Potok Służewiecki tributary, which is a pollution repository for the vast part of the city. Cadmium, as an element present in the environment at the lowest quantities, poses a threat for biomass in the Wilanowskie Lake, even at the lowest values noticed in July. According to the

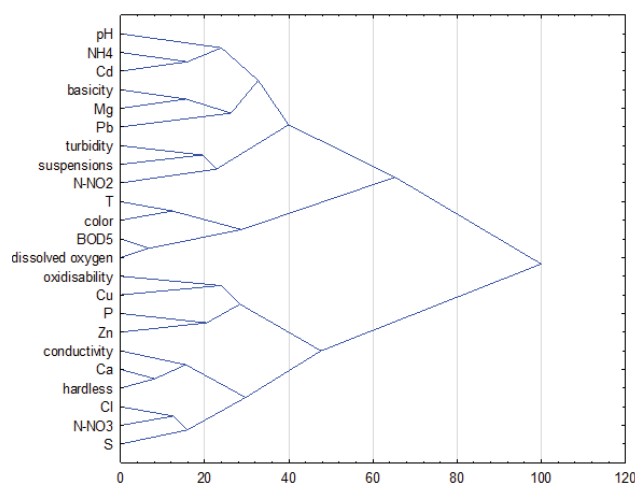


Fig. 6. Cluster analysis.

classification based on geochemical criteria [6], the content of cadmium in sediments exceeding 6 mg/kg dw points to a highly contaminated sediment. Contamination of the lake with trace elements can be attributed to the misuse of the area adjacent to the reservoir.

The Wilanowskie Lake is one of the few natural water reservoirs located in the area of the Warsaw agglomeration, and therefore its waters should be monitored for their quality. The loss of such a valuable flora and fauna habitat would be serious damage to the Warsaw landscape.

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