Reservoir recultivation versus forms of heavy metals in sediments: the case of the Kielce City Lake

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Abstract: The Kielce Lake is a water reservoir located in the Kielce city zone. Areas around the reservoir are used for recreational, residential and industrial purposes. Additionally, the nearby state road to the city of Łódź, is a source of transportation pollution, including heavy metals. The reservoir is fed by a watercourse which receives municipal wastewater from the town of Masłów near Kielce. The amount and diversity of organic and inorganic compounds which flow into the reservoir causes heavy pollution of the Lake waters. To reduce the degree of reservoir pollution, a pulverizing aerator was installed in the middle of the Kielce Lake in May 2008. Sediment samples were collected at a depth of 0-20 cm between July 2008 and May 2010 at five sites in the littoral zone of the recultivation area. These environmental samples underwent a five-stage sequential extraction procedure, assisted by microwave radiation. The concentrations of trace metals Zn, Cu, Ni, Cr, Pb, Mn, Fe and Cd in various extracts were determined by means of F-AAS and GF-AAS. The results have shown a high concentration of analytes in reservoir sediments.

Keywords: City lake • Pulverizing aerator • Heavy metals • Bottom sediments

1. Introduction

Recultivation of water reservoirs is a long-lasting process which may take several years and which consists, among other things, in the elimination of possible chemical contamination of water and sediments, the improvement of oxygen and nutrient balances, and the maintenance of flora and fauna at a level appropriate to a given ecosystem. To achieve these goals, physical, chemical and biological methods are used. Yet the choice of a recultivation method is conditioned by several factors, including the size of a reservoir and its use, the types of fauna and flora resident therein, the connection to watercourses and proximity to clean water reservoirs which might be employed in the reservoir renewal process.

One of the objectives of recultivation is to reduce excessive growth of algae and seaweed, which may be accomplished for instance through sparging the reservoir water, i.e., aeration. Wind-driven pulverising aeration, one of the methods for artificial introduction of oxygen into water, consists in water suction from the benthic zone and its subsequent pulverisation, or dispersion into small droplets, thus improving gas diffusion and removing oxygenated water into the intake zone [1].

2. Experimental Procedure

2.1. Research area

The research area covers the Kielce City Lake, located in the northern part of the city in the Szydlówka residential district. The lake was created by the closure of the Silnica river valley with a weir in its eighth kilometre. The Lake’s mean volume amounts to 195,000 m³; maximum depth at the weir is 3.65 m. The area surrounding the reservoir is built-up with residential, services, sports and recreation facilities, as well as containing allotment gardens and a cemetery. Part of the area around the reservoir is wooded [2].
Due to its relatively small depth, the Lake is not stratified, hence water mixing occurs over the entire water column. Consequently, in the warm season of the year, temperatures at the lake bottom tend to be relatively high, fostering organic matter decomposition by microorganisms, which in turn constitutes the basis for the so-called internal supply [1]. Due to its structure as well as the pollution which reaches the reservoir water, the Kielce Lake is a eutroficated lake, highly susceptible to degradation. That is why, since May 2008, the Lake waters have been subject to recultivation with the use of a pulverising aerator complete with a phosphorus inactivation system.

The appliance employed is characterised by a flow efficiency dependent on wind speed, ranging from 200 to 800 m$^3$ d$^{-1}$, and the operating radius of 15 m. Its operation is little affected by water pollution which is significant when aerating the benthic zones. It is driven by a wind rotor engine, the so-called Savonius wind turbine. This makes it a relatively uncomplicated structure, unaffected by changing wind direction [1].

The aerator is equipped with a freely mobile binding system, adjusted to lake depth, as well as a phosphorus inactivation system which enables monthly release of 22 kg of the coagulant FeSO$_4$. In order to determine the extent to which aerator operation affects speciation of selected heavy metals (Fe, Mn, Cd, Pb, Zn, Cr, Cu, Ni) in bottom sediments, five bottom sediment sampling sites have been selected for analysis of selected heavy metal forms (Fig. 1).

Three sampling sites (Points 1, 2 and 5) are located in the aerator impact zone; two (Points 3 and 4) – are outside it, on the route of the Silnica river water flow into the lake centre. It must be added that Point 2 is located in the lake bend where no water flow is observed.

2.2. Materials and methods

The test material consisted of bottom sediment samples from depths down to 20 cm collected at five sites between July 2008 (starting time of aeration) and May 2010 in accordance with the PN-ISO 5667-15:2004 standard. Sampling could thus be standardized, which eliminated accidental errors at this stage.

Water and sediment samples were dredged from the lake channels in the littoral zone, where suspended particulate matter is deposited. All samples were collected and stored in glass bottles that had been rinsed with pentane and nitric acid to remove all organic and heavy metal residues. Aqueous samples were collected in 1-litre bottles, rinsed three times with water from the sampling site before filling with sample. Bottles were filled completely, ensuring no air bubbles were present. The water samples were collected for chemical analysis, including pH determination. The pH value was estimated using a CX-701 Elmetron.

The sediments were sampled with an Ekman-Birge grab. Because of frequent multicomponent determinations of trace elements from the same samples, stainless steel sampling tools and sieves, together with polyethylene bags and bottles were used. In addition, one in ten samples was duplicated, so that analyses for the study could be carried out. Blank samples, making up ≥ 3% of the total number of normal samples, were collected to determine the practical limit of detection.

Excess water was removed from sediment samples to prevent dissolution of some of the sediment components. The sediment samples were sieved, then dried at a suitable temperature to prevent the growth of mould and micro-organisms, which would redistribute chemical components, thus altering the composition of the material. After coning and quartering, the dried samples were ground in an automatic agate mortar to a grain size of <100 μm. The pH and heavy metal contents of these samples were then determined. The sediment material was subjected to further preparatory processing – dissolution and extraction – in accordance with the scheme shown in Fig. 2.
The samples were digested with different solutions in a microwave oven (Anton-Paar PE Multiwave 3000) and stored until analysis. Each of the solutions obtained after the various sequential extraction steps, as well as those obtained after mineralisation with conc. HNO₃ was analysed for heavy metal content (Fe, Mn, Cd, Pb, Zn, Cr, Cu, Ni) using a flame (air-acetylene) AAS Savanta spectrometer (GBC) and a graphite cuvette (GBC), with appropriately adjusted parameters.

Quality assurance of analytical results was carried out by checking the reliability of the measuring instruments and the range of applicability of the analytical procedure, as well as by calibrating the procedure periodically with the aid of standard mixtures. For each extraction experiment a blank sample (i.e., a container with no sediment) was prepared through the entire procedure. The reliability of the entire analytical procedure was monitored by adding a standard to the assayed sample. An accuracy check was performed by the analysis of certified reference material CRM 320. The CRM 320 was prepared alongside the environmental samples. Good agreement of results between determined and certified values was obtained.

3. Results and Discussion

The monitoring and analysis of Kielce Lake contamination are of great significance for the implementation of tasks specified in the Framework Water Directive (2000) [4] and for flood hazard. There are no natural sources of heavy metal contamination from the bedrock in the river catchment areas. The presence of heavy metals in the aquatic ecosystems is therefore solely the consequence of human activities.

The main objective of aerator operation in the case of shallow reservoirs, such as the Kielce Lake, is to remove the deoxified bottom layer, called the oxicline.

**Figure 2.** Scheme of the procedure for bottom sediment samples.
which appears in shallow lakes in the summer half-year as a result of intensification of chemical reactions which occur in the top layer of bottom sediments. Limiting the scope of the oxicline is known to condition the initiation and sustenance of the reservoir self-recultivation process [5]. The recultivation process of the Kielce Lake comprises oxygenation, and phosphorus inactivation using an iron(II) coagulant in accordance with the following equation:

\[ 3\text{FeSO}_4 + 2\text{PO}_4^{3-} \rightarrow \text{Fe}_3(\text{PO}_4)_2 + 3\text{SO}_4^{2-}. \]

Phosphorus falls from the upper water layers not only in the form of dead organic matter, but also bonds with calcium, iron, aluminium ions and mineral suspensions. Of considerable significance to the bonding of phosphorus and heavy metals, as well as deposition in bottom sediments, is not only the presence of organic matter but also the quantity of gases such as oxygen and CO₂, as well as the pH of water.

The pH of the water samples varied from 7.11 (Point 3) to 8.13 (Point 5) in 2008, from 7.50 to 8.88 (Point 5) in 2009, and from 7.21 (Point 4) to 8.83 (Point 5) in 2010. The highest pH value during the research period was found in water samples collected at Point 5, and the lowest – at Point 3. It can be noted that mean pH values in the year 2009 were higher than in 2008, yet in 2010 they were somewhat lower. Water samples collected at Point 3, which was outside the aerator impact zone, were characterised by the lowest pH values, while those collected at Point 4, also outside the aerator impact zone, are comparable to those collected at Point 1.

An analysis of sediment samples for selected analytes was carried out at several selected measurement sites (Tables 1 and 2).

Another relation has been observed in the pH values of bottom sediment samples. The pH of the material collected at Points 2 and 5, within the aerator impact zone, during the sampling period, increased yearly, while the pH of the material collected at other sites decreased or continued at similar levels. The lowest and highest values were recorded in the year 2010 at Point 5: 5.96 and 8.95 respectively.

It is the pH value which determines, to a large extent, the speciation of metals found in bottom sediments. In the Kielce Lake bottom deposits, the total amounts of metals determined were in the following range [mg kg⁻¹]: iron from 2,500 (Point 4) to 18,320 (Point 3); zinc from 11 to 98; copper from 1.4 to 35; nickel from 2.3 to 37; chromium from 3.7 to 168; lead from 56 to 324; manganese from 122 to 940; cadmium from 3.2 to 27. Quantities of all the metals analysed in bottom sediments increased during the research period at all sampling sites.

To assess sediment pollution with heavy metals, according to the adopted geochemical method [6], the geoaccumulation index (Igeo) was used as an indicator. The geoaccumulation index (Igeo) enables assessment of contamination through comparison of heavy metal quantities in sediments with the so-called pre-industrial quantities, mostly in bottom sediments [7]:

\[ I_{\text{geo}} = \log_{10} \left( \frac{C_n}{1.5B_n} \right) \]

where \( C_n \) is the concentration of a given metal in bottom sediment; \( B_n \) is the geochemical background; 1.5 is taken as the natural fluctuation of a given metal content in an environment with little anthropogenic influence.

The geoaccumulation indices for particular elements (Table 3) indicate variation depending on a given metal and a sediment sampling site.

The Kielce Lake can be considered to be unpolluted with zinc and nickel, as shown by negative values of the geoaccumulation indices ranging from – 1.00 to – 0.23. For nickel and zinc - mean values for sampling sites at all points are negative, described as “practically unpolluted sediment”, or Class Zero.

The geoaccumulation indexes for copper and chromium vary significantly by site. At Point 1, the index is less than zero, so the sediments have Class Zero, while at other sampling sites, it is contained in the range 0 < Igeo < 1, which means that the sediment is unpolluted to moderately polluted. Unlike nickel, zinc, and copper and chromium, geoaccumulation indexes for lead (Pb-Igeo) and cadmium (Cd-Igeo) are contained in the range (0 < Igeo < 1 and 1 < Igeo < 2), which points to the presence of sediments which are moderately polluted with these metals. In the case of cadmium, it may be observed that sediment enrichment with this metal is most intense at sampling Points 1, 2, 4 and 5; in the case of lead, these are Points 3 and 5 (Fig. 3).

Natural processes, such as sorption or precipitation create appropriate conditions for removal of Pb and...
Cd from the water, at the same time affecting chemical transitions in sediments. From the above, it follows that the mobility of these elements may also be linked to the accumulation rate in sediments.

The speciation of metals in various bottom sediments at other sampling sites varies (Figs. 4 and 5).

In the case of iron, both the highest and lowest amounts have been found at the sites outside the aerator impact zone, Points 3 and 4 respectively. This is probably connected with land development and water flow together with possibilities for deposition of suspended pollution. At the sites within the aerator impact zone, general iron content is at similar levels. At all sampling sites, a marginally growing amount of iron in Fraction I may be observed, yet in comparison to other fractions, these differences are the smallest. The largest quantity of this element is found in Fraction IV, but it is comparable with those in Fractions III and V at Points 1, 3 and 5. Iron, present in the waters of the Kielce Lake and introduced in the phosphorus inactivation process, falls – together with the suspension – to the bottom in the form of dead organic matter: hence probably its high content in Fraction IV. In the presence of a considerable amount of an organic substance which may be the source of carbon dioxide, increasing pH and simultaneously lowering oxidising potential, deposition of FeCO₃ should occur [8, 9]. This is confirmed by increasing iron content in Fraction II during the research period.

In the case of manganese, the highest value has been recorded at a site within the aerator impact zone (Point 5), and the lowest outside the zone (Point 3). Comparatively high manganese contents have been recorded in Fraction I, in contrast to other metals studied. A relatively high Mn content is to be found in Fraction II; in the cases of Points 2 and 3, these quantities are also comparable to Fractions III, IV and V at the majority of the studied sites.

The highest cadmium values have been found at Point 4, with the lowest at Point 3, both of which were outside the aerator impact zone. In the process of cadmium bonding in sediments, a significant role is played by bacteria which frequently deposit it in the form of sulphides [10]. When water is pH-neutral or alkaline, the cadmium found in sediments is not dissolved and does not pass into the aqueous phase. Mobilization from sediment is also dependent on the form in which the element is found and the solubility of the relevant compound. Only at points 4 and 5, was any Cd detected in Fraction I, and the amounts were extremely small. The quantities of this element which may pass into water as a result of ionic composition of water and shift of balance in the sorption-desorption system, may be considered negligible. Comparatively large amounts of this element have been recorded at Points 1 and 5, in Fractions II and V, and at Point 2 in Fraction IV. In the remaining cases, the cadmium content in its particular forms is similar.

In the case of lead, the process of sorption on the surface of bottom sediment particles is determined by organic matter content and sediment graining. At pH > 6, and when no complex compounds are found, lead is completely adsorbed in the sediments. Since its salts (carbonates, sulphates and phosphates) are poorly soluble in water, its quantity in sediments is relatively high. The highest value has been recorded at Point 5, with the lowest at Point 2, both within the aeration zone. Intermediate Pb values have been noted at Points 4, 1 and 3 respectively. The smallest traces of lead are found in Fraction I, yet at Points 1 and 2 none or negligible quantities of this element have been found, while at Points 3 and 4 (outside the aerator impact zone) the quantity of Pb in Fraction I is considerable. At the sites within the aerator impact zone and at Point 3, the highest lead content is found in Fraction IV (adsorbed on the surface of organic matter or bonded with that

Table 1. pH values (average and min.–max.) in Kielce Lake water and sediment samples between July 2008 and May 2010 at particular sites.

| Year | Sample points | Water samples | Sediment samples |
|------|---------------|---------------|------------------|
|      | 1  | 2  | 3  | 4  | 5  |               |                          |                   |
| 2008 | 7.82 | 7.76 | 7.55 | 7.86 | 7.98 | (7.15 – 8.03) | (7.27 – 8.08) | (7.11 – 7.95) | (7.22 – 8.01) | (7.14 - 8.13) |
| 2009 | 7.90 | 8.20 | 8.06 | 7.93 | 8.17 | (7.85 – 8.44) | (7.84 – 8.72) | (7.62 – 8.57) | (7.68 – 8.16) | (7.50 – 8.88) |
| 2010 | 7.92 | 8.02 | 8.01 | 7.92 | 8.22 | (7.22 – 8.47) | (7.65 – 8.69) | (7.21 – 8.34) | (7.33 – 8.07) | (7.52 – 8.83) |
Table 2. Average content of heavy metals (Fe, Mn, Cd, Pb, Zn, Cr, Cu, Ni) in Kielce Lake sediment samples, and distribution in particular fractions between July 2008 and May 2010 at particular sites [mg kg⁻¹ dry matter]. (SD - standard deviation)

| No of the site | Fractions Sum ± SD | Fe          | Mn          | Cd          | Pb          | Zn          | Cr          | Cu          | Ni          |
|----------------|-------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
|                | exchangeable      | carbonate   | oxide       | organic     | residue     | exchangeable| carbonate   | oxide       | organic     | residue     | exchangeable| carbonate   | oxide       | organic     | residue     | exchangeable| carbonate   | oxide       | organic     | residue     |
| 1              | 18.9 552          | 2659        | 2270        | 2840        | 8340±87.2   | 23.6 88.4   | 59.1        | 76.3        | 77.6        | 325±32.8    | n.d. 7.2    | 4.1         | 5.8         | 7.9         | 25±5.5      |
| 2              | 35.9 738          | 1940        | 3950        | 3546        | 10210±97.3  | 14.0 51.0   | 52.0        | 59.0        | 58.0        | 234±36.5    | n.d. 5.9    | 4.7         | 6.2         | 4.2         | 21±4.7      |
| 3              | 190 2370          | 5460        | 5200        | 5100        | 18320±122.1 | 18.0 30.0   | 25.0        | 23.0        | 26.0        | 122±30.1    | n.d. 0.9    | 0.8         | 0.8         | 1.0         | 3.3±1.1     |
| 4              | 54.9 460          | 589         | 1124        | 272         | 2500±82.2   | 45.0 256    | 128         | 125         | 101         | 655±66.3    | n.d. 9.4    | 6.6         | 5.7         | 1.2         | 24±6.1      |
| 5              | 73.9 704          | 2262        | 2300        | 2310        | 7650±93.5   | 58.9 348    | 261         | 151         | 121         | 940±69.7    | n.d. 3.8    | 2.1         | 3.2         | 3.9         | 14±4.2      |
|                |                   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| 1              | 23.6 88.4         | 59.1        | 76.3        | 77.6        | 325±32.8    | n.d. 7.2   | 4.1         | 5.8         | 7.9         | 25±5.5      | n.d. 5.9    | 4.7         | 6.2         | 4.2         | 21±4.7      |
| 2              | 14.0 51.0         | 52.0        | 59.0        | 58.0        | 234±36.5    | n.d. 0.9   | 0.8         | 0.8         | 1.0         | 3.3±1.1     | n.d. 9.4    | 6.6         | 5.7         | 1.2         | 24±6.1      |
| 3              | 18.0 30.0         | 25.0        | 23.0        | 26.0        | 122±30.1    | n.d. 0.9   | 0.8         | 0.8         | 1.0         | 3.3±1.1     | n.d. 9.4    | 6.6         | 5.7         | 1.2         | 24±6.1      |
| 4              | 45.0 256          | 128         | 125         | 101         | 655±66.3    | n.d. 0.9   | 0.8         | 0.8         | 1.0         | 3.3±1.1     | n.d. 9.4    | 6.6         | 5.7         | 1.2         | 24±6.1      |
| 5              | 58.9 348          | 261         | 151         | 121         | 940±69.7    | n.d. 0.9   | 0.8         | 0.8         | 1.0         | 3.3±1.1     | n.d. 9.4    | 6.6         | 5.7         | 1.2         | 24±6.1      |

n.d. – not detected
Figure 4. Examples of metal distribution in particular fractions (Kielce Lake, between July 2008 and May 2009), where a) Mn, b) Zn, c) Cu, d) Ni, e) Cr, f) Pb, g) Fe and h) Cd.

Table 3. Mean values of the geoaccumulation index of bottom sediment contamination in Kielce Lake.

| Sampling site | Cd- $I_{geo}$ | Pb- $I_{geo}$ | Zn- $I_{geo}$ | Cr- $I_{geo}$ | Cu- $I_{geo}$ | Ni- $I_{geo}$ |
|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 1             | 1.52          | 0.73          | -0.29         | -0.39         | -0.81         | -0.38         |
| 2             | 1.45          | 0.4           | -1            | 0.55          | -0.23         | -0.44         |
| 3             | 0.64          | 1.11          | -0.05         | 0.93          | 0.37          | -0.41         |
| 4             | 1.51          | 0.67          | -0.58         | 0.66          | 0.48          | -0.31         |
| 5             | 1.27          | 1.16          | -0.17         | 1.27          | 0.59          | -0.38         |
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In the case of zinc, the highest amounts have been recorded at Point 3, outside the aerator zone, and the lowest at Point 2 within the zone. The forms of zinc depend largely upon the pH value. At pH = 7 – 7.5, hydrolysis of zinc salts occurs, and at pH > 8 a hydroxide sediment of Zn(OH)$_2$ appears, which is an amphoteric compound. As zinc is easily adsorbed on the surface of suspension and bottom sediment particles, some amounts of this element have been noted in Fraction I at Points 1, 3 and 5, out of which only Point 3 is outside the aerator impact zone; yet the proportion of the exchanger form, considered bioavailable, is the lowest. According to the literature, the predominant forms of zinc in bottom sediment are sulphides and carbonates, as observed at Points 1 and 4. Zinc is also found in bottom sediments in a form bonded with Mn oxides and amphoteric Fe oxides. Yet the content of this metal in the form of organic bonds is higher, and in the case of Points 2, 3 and 5, this form predominates.

The highest chromium content has been recorded at Point 5, and the lowest – at 1, both within the aerator zone. Similarly to zinc, small amounts of this metal have been recorded in Fraction I at Points 1, 3 and 5. No or Figure 5. Example of metal distribution in particular fractions (Kielce Lake, between July 2009 and May 2010), where a) Mn, b) Zn, c) Cu, d) Ni, e) Cr, f) Pb, g) Fe and h) Cd.

matters. At Point 4, outside the zone this content was highest in Fraction II, i.e., in the form of carbonates or co-precipitated with carbonates.

In the case of chromium, the highest amounts have been recorded at Point 5, and the lowest – at 1, both within the aerator zone. Similarly to zinc, small amounts of this metal have been recorded in Fraction I at Points 1, 3 and 5. No or
negligible amounts of this element have been found, while considerable amounts have been found at Point 5. Most of the chromium found at all sampling sites was in a form bonded with organic matter, i.e., Fraction IV, while in the form permanently bonded with minerals (Fraction V) the amounts were negligible.

Similarly to chromium, the highest amount of copper has been recorded at Point 5, and the lowest at Point 1. Also at Points 1 and 2, none or negligible traces of this element have been found. In accordance with the literature, undissolved forms of copper are found in water as sulphides, hydroxides and carbonates [8,11]. Small amounts of copper are found also in Fraction I, but the highest content is in Fraction IV for all sampling sites.

In the case of nickel, comparable amounts have been recorded at the various sampling sites, but in the case of Fraction I these were small or trace quantities. The highest Ni quantities have been found in Fraction V (remnant), built into a crystal network of minerals, both secondary and natural, except at Point 4, where the largest amounts have been found in Fraction IV.

Such varied occurrence of analytes, both in terms of quantity and speciation, at the various sites is likely to be linked to land development, water movement, fauna and flora which occur in a given area, availability of oxygen and organic matter. A noticeable change in the pH values of water samples collected between the years 2008 and 2009 may have been the reason for increasing intensity of deposition processes of metals in the form of poorly soluble compounds. However, direct impact of the aerator upon the forms of metal occurrence in bottom sediments has not been observed.

Still, it must be remembered that between the pelagic zone and the benthic sediment there exists a certain state of equilibrium, typical of a particular ecosystem. Yet if oxygen-rich conditions occur in the contact zone between the bottom sediment and water, the iron ions Fe$^{+3}$ bond phosphate ions by trapping them and are deposited in this form in bottom sediments. This process decelerates the appearance on the sediment surface of Fe$^{+2}$ and sulphide complexes, originating from sulphates present in aquatic ecosystems under extremely reductive conditions [8,12]. If oxygen begins to be lacking in the hypolimnion, trivalent iron passes into bivalent, followed by breakdown of iron and phosphorus complexes, which in turn causes phosphorus to be released from the bottom sediments into water (the intra-reservoir enrichment process). Moreover, it must also be remembered that substances which are removed from water in the course of recultivation change their form and pass into bottom sediments. Processes occurring in the water, both natural ones, related to the working of the aquatic ecosystem, and those brought about by human activity, may cause its imbalance. A consequence of that may be recurrent release of substances gathered in the bottom sediment into the liquid phase, which is usually detrimental to the reservoir as typically toxic substances, such as heavy metals, may be released.

This process is considerably intensified in the case of sediment resuspension. Under extremely reductive conditions, sulphates which are found in the water turn into hydrogen sulphide, and then a large proportion of metals, e.g. iron Fe$^{+2}$, form complexes with the sulphides on the bottom sediment surface. When iron bonds with sulphides, its inclusion occurs – from phosphorus deposition – even during the circulation period. Copper dissolution is advanced by the presence of dissolved oxygen and nitrates in the water.

A high pH (Points 2 and 5) causes poorly soluble compounds (including heavy metal carbonates and phosphates) to precipitate, which reduces the concentrations of these analytes in the water. The total metal content in the bottom sediment provides evidence for the deposition of anthropogenic loads of analysed metals therein. However, the rate of metal migration into water may rise in the presence of organic compounds and carbonates, or when high temperatures prevail. The invariable functioning of the ecosystem may be additionally threatened by the discharge of sewage, as well as acid rains and surface run-off, which may increase the acidity of the lake water, and consequently the solubility of heavy metal compounds bound up in the sediment. The pulverizing aerator (installed in the centre of the Kielce Lake) influences the pH of water samples, but does not influence the forms of heavy metals found in bottom sediments.

4. Conclusions

The water reservoir recultivation process aims to eliminate biogenes, mainly phosphates, from the water zone. Research is being conducted in order to develop new methods, but changes to the structure or physical and chemical properties of the bottom sediments present have not been considered. The present study has demonstrated that:

- the influence of the aerator’s work has not been observed in pH values and metal contents in the materials analysed;
- the quantities of heavy metals analysed are increasing in bottom sediments;
- the distribution of metals in various bottom sediments at various sampling sites varies;
- at all the sampling sites, only a few of the
metals analysed were detected in Fraction I (comprising exchangeable metal cations), these being primarily Mn, and – in smaller amounts – Fe, Pb, Zn and Cr;
• at Point 4, most Zn, Cd, Mn and Pb occurs in Fractions II and V, while most Cu, Ni, Cr and Fe occurs in Fraction IV;
• at Points 1, 2, 3, and 5, most Zn, Cu, Cr and Pb occurs in Fraction IV, while most Ni, Cd and Fe occurs in Fraction V;
• if the aerator can not supply enough oxygen to the water, anaerobic conditions appear, the pH value decreases or the water’s ion composition changes, which can cause secondary pollution of the reservoir.

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