

# Heavy Metals (Cd, Pb, Cu, Zn, Cr) in Bottom Sediments and the Recultivation of Kielce Lake

Anna Rabajczyk\*, Małgorzata A. Józwiak, Marek Józwiak, Rafał Kozłowski

Independent Department of Environmental Protection and Modelling,  
Jan Kochanowski University of Humanities and Sciences in Kielce,  
Świętokrzyska 15 G, 25-406 Kielce, Poland

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## Abstract

Kielce Lake area is a water basin located in Kielce city zone. It determines usage of areas around the basin for recreational, housing, and industrial purposes. Additionally, a state road toward Łódź city located nearby is a source of transportation pollution and heavy metals. The basin is supplied by a watercourse that receives municipal wastewater from Masłów town near Kielce. The amount and diversity of organic and inorganic compounds getting into the basin influences heavy pollution of bay waters. To reduce the degree of reservoir pollution, a pulverizing aerator was installed in the middle of Kielce Lake in May 2008. The main goal of this work is to present the results of analyzing the bottom deposits of Kielce Lake for heavy metals (Cd, Pb, Cu, Zn, Cr) during the recultivation process. Sediment samples collected at a depth of 0-20 cm twice in July 2008 and 2009 from three points located in the littoral zone of the recultivation area and two points outside it. A high concentration of analytes in reservoir sediments was indicated on the basis of the results.

**Keywords:** urban lake, recultivation, sediments, heavy metals, degree of contamination

## Introduction

Water protection as well as appropriate management of water resources are among the most fundamental obligations of each country. Consequently, monitoring plans for water quality and water intakes are developed, alongside the register of protected areas created with the aim of surface and underground water protection. Water economy ought to follow the principle of sustainable development, in particular water resource modelling and protection, water exploitation, and water resources management. One of the objectives is also to perform actions aimed at the restoration of usability status to a particular aquatic ecosystem, i.e. recultivation [1]. This process consists in the elimination of the possible chemical contamination of waters and sediments, improvement of the oxygen and nutrient balances,

maintenance of flora and fauna at a level appropriate for a particular aquatic ecosystem, and engineering elements for flow regulation such as desired depths, anti-erosion protection, and speed. The type of recultivation method used depends on the reservoir size, the fauna and flora that live therein, the connection with watercourses, and closeness to clean water reservoirs in the vicinity of the reservoir being recultivated.

Water quality management of lakes and reservoirs was first oriented to control eutrophication and the factors causing increase of nutrient load [2, 3]. Many solutions are now available to control eutrophication by minimizing the nutrient inflows. But often organic loads, acidity, salinity, or contamination with hazardous substances need to be controlled. The amendmen of the conditions may be very different, in some cases contrary to the technologies developed to control eutrophication [2]. That is why in the sediment or water of the lake was determined:

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\*e-mail: chromium@tlen.pl

- potentially mobile phosphorus (Pmobile) by a sequential extraction technique as the sum of porewater P, iron-bound P, and nonreactive P (i.e. polyphosphates and organic P) – Sønderby, Denmark, [4]
- organic matter in sediments characterized by the N/P ratio, Lake Długie in Olsztyn [5],
- nitrogen compounds between the bottom sediments and overlying water, Lake Długie in Olsztyn [6]
- water chemistry (temperature, dissolved oxygen, pH, specific conductance, and nutrients) and dominant macro-invertebrate taxa, Sand Lake, Alaska [7]

Each catchment and its environment are specific, but it is possible to enumerate – from a practical viewpoint – particular elements and procedures such as water replacement, biomanipulation, hipolimnion water removal, bottom sediment removal (dredging), phosphorus precipitation into bottom sediments, and aeration. In the recultivation process, it is extremely important to limit the quantity of biogenes (phosphates and nitrates) alongside increasing the amounts of oxygen, thanks to which the self-cleaning process of the reservoir is assisted and eutrophization checked.

Lakes, as aquatic ecosystems, are situated in terrain depressions, hence they provide a natural receptacle of pollution coming from catchment areas. One of the important indicators of changes occurring in the lake ecosystem is bottom sediments [8, 9]. Lake sediment can be regarded as a mirror that provides long-term records of past changes in climate - catchment processes as well as changes in biological communities in lakes. In order to improve understanding and interpretation of information hidden in sediments, there is need for better knowledge about spatio-temporal dynamics of sediment processes. Every particle that has reached into the lake and accumulated into the sediment can be regarded as a carrier of information about its origin and pathways. However, this information is available only for a certain level of generalization [10].

The natural chemical composition of lake sediments depends on several factors, including the geological structure of the catchment, morphometric features of the lake basin, flow rate, the ensuing water replacement rate, and the climate and its changes. Lake pollution with heavy metals depends largely on the extent of the terrain's urbanization, intensity of lake exploitation, and agricultural production, as well as gas

and dust emissions. Regardless of the source, the elements migrating to the water are deposited in bottom sediments or – when dissolved or suspended – transported over distances, and depending on the quantity and form in which they occur, they can lower water quality, as well as threatening plant and animal organisms that inhabit a given terrain.

## Research Area

The research area covers Kielce City Lake, located in the northern part of the city, in Szydłówek residential district (Fig. 1). The reservoir has been created through the closure of the Silnica River valley with a weir in its eighth kilometre. The Lake's mean volume amounts to 195,000 m<sup>3</sup>; maximum depth at the weir is 3.65 m. From the weir, the Lake borders Jesionowa Street. The left shore of the Lake neighbours privately owned land, the right – the City Cemetery and allotment gardens. The area surrounding the reservoir is built-up with several sports and recreational facilities, as well as residential and company buildings, the highest density found on the western part of the Lake with tennis courts, a swimming pool and allotment gardens. To the north, the area adjacent to the reservoir is wooded, and the eastern part with its many benches, a cycling path and a beach is used for recreational purposes [11]. The geological substratum in the north-west of the lake basin is built of middle-Devonian rock, lower-Devonian rock in the north and the south, Silurian and Ordovician rock in the central part, and lower-Cambrian in the north [11].

Due to its relatively small depth, the lake is not stratified, hence water mixing occurs over the entire water depth. 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. Kielce Lake is a eutrophicated lake, highly susceptible to degradation [12]. The reason is the pollution delivered from the catchment, uncontrolled municipal wastewater discharge, waste disposal from a swimming pool and rainwater, migration of contaminants from nearby roads, and the so-called internal supply. That is why, since 2008, the Lake waters have been subject to recultivation with the use of a pulverizing aerator with a phosphorus inactivation system. Hence the lake has been divided into sections (Fig. 2) due to varying aerator impact.

Points 1, 2, and 5 are located in the aerator impact zone; Points 3 and 4 are outside it, on the route of the Silnica river water flow into the lake centre. Point 2 is characterized by limited water flow.

## Experimental Procedures

The test material consisted of bottom sediment samples collected from depths down to 20 cm collected at five sampling sites in June 2008 and June 2009 (Fig. 2). The pH and electrical conductivity (EC) of the collected samples were determined, and the samples were analyzed for heavy metal (Cd, Pb, Cu, Zn, and Cr) content.



Fig. 1. Aerator in Kielce Lake (fot. A. Rabajczyk, 2008).

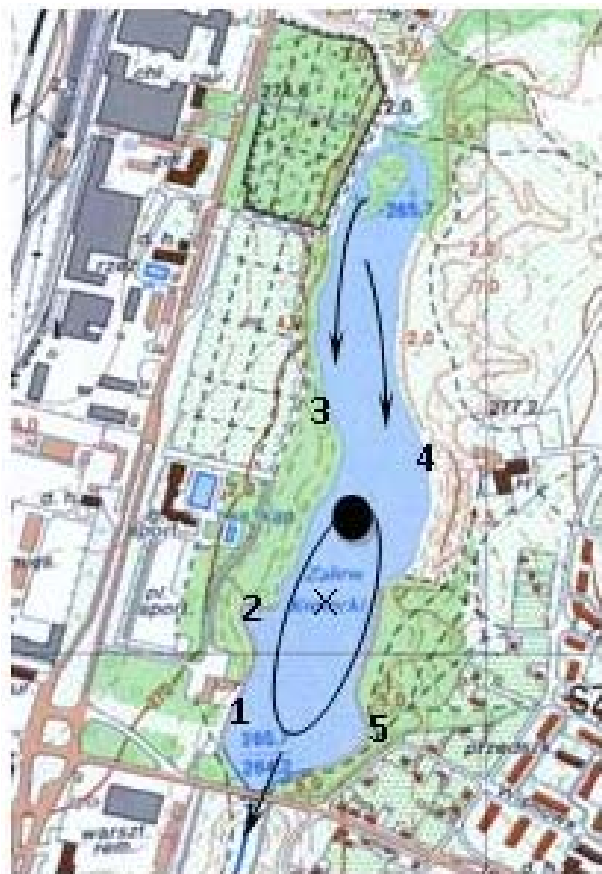


Fig. 2. Bottom sediment sampling sites (x – aerator impact zone, point – direct influence of aerator, arrows represent directions of reservoir water flow).

The crushed samples of bottom sediments, upon plant material removal, were dried to constant weight at 45°C, ground in an agate mortar and sieved to obtain the fraction of grain size ≤100 μm. From representative and homogeneous portions of the material, three samples of weight 2.0000±0.0001 g were taken for mineralization. Water and bottom sediment samples were subjected to the process of mineralization assisted by microwave radiation with the use of a mixture of concentrated HCl and HNO<sub>3</sub> acids. In the solutions thus obtained, the concentrations of heavy metals were determined by means of F-AAS or GF-AAS techniques. The remaining sediment was dried and weighed, which enabled determination of the extent of the material's destruction. In order to verify the conducted works, certified reference materials for bottom sediments (CMR 320) and water (TMDA-52.3) were used.

Microwave-assisted mineralization of environmental samples was performed in a multi-station microwave mineralization system, the Anton Paar *Multiwave 3000*. Analysis of the solutions' heavy metal content with the F-AAS method was conducted with the use of the AAS-SavantAA Sigma or the AAS-SavantAA Zeeman spectrometers (depending on concentration levels in the analyzed solutions).

For the assessment of the sediment pollution with heavy metals, according to the adopted geochemical method [13], the following indicators were applied: geoaccumulation index ( $I_{geo}$ ), contamination coefficient ( $C_f^j$ ), and contamination degree ( $C_{deg}$ ). The geoaccumulation index ( $I_{geo}$ ) enables a contamination assessment to be made through comparison of heavy metal quantities in sediments with the so-called pre-industrial quantities, mostly in bottom sediments [14]:

$$I_{geo} = \log_{10} (C_n/1.5B_n)$$

...where  $C_n$  is the concentration of a given metal in bottom sediment;  $B_n$  is the geochemical background; and 1.5 is the natural fluctuation of a given metal content in the environment with little anthropogenic influence.

On the basis of the geoaccumulation index value, bottom sediment samples are classed accordingly, which testifies to the quality of the investigated material (Table 1).

The pollution status of the sediments was determined with the use of parameters such as the coefficient ( $C_f^j$ ) and degree ( $C_{deg}$ ) of contamination [10], calculated on the basis of the relation:

Table 1. Classes of geoaccumulation index [15].

Class	Index value	Sediment quality
0	$I_{geo} \leq 0$	Practically unpolluted sediment
1	$0 < I_{geo} < 1$	Unpolluted to moderately polluted
2	$1 < I_{geo} < 2$	Moderately polluted
3	$2 < I_{geo} < 3$	Moderately to strongly polluted
4	$3 < I_{geo} < 4$	Strongly polluted
5	$4 < I_{geo} < 5$	From strongly polluted to extremely polluted
6	$5 < I_{geo}$	Extremely polluted

Table 2. Descriptive pollution classes depending on the values of the coefficient of contamination and the degree of contamination [16].

Coefficient of contamination	Description	Degree of contamination	Description
$C_f^j < 1$	Low contamination coefficient	$C_{deg} < 8$	Low degree of contamination
$1 \leq C_f^j < 3$	Moderate contamination coefficient	$8 \leq C_{deg} < 16$	Moderate degree of contamination
$3 \leq C_f^j < 6$	High contamination coefficient	$16 \leq C_{deg} < 32$	High degree of contamination
$6 \leq C_f^j$	Very high contamination coefficient	$32 \leq C_{deg}$	Very high degree of contamination

Table 3. Heavy metal contents in Kielce Lake bottom sediments [ $\text{mg}\cdot\text{kg}^{-1}$  d.m.] ( $n \geq 5$ ).

Sampling site	Year	pH	EC [ $\mu\text{S}\cdot\text{cm}^{-1}$ ]	Cu	Zn	Pb	Cd	Cr
1	2008	7.15	193.7	1.2	51	115	22.1	3.7
	2009	7.22	153.7	1.7	49	98.1	22.6	5.1
2	2008	7.33	425.3	3.6	9.7	47.3	17.6	38
	2009	7.54	466.2	3.2	12	67.2	16.5	43
3	2008	7.37	201.6	20	62	228	2.32	26
	2009	7.4	233.4	21	67	218	2.67	33
4	2008	7.11	288.3	19	21	95.3	18.2	45
	2009	7.15	273.9	22	23	101	21.5	36
5	2008	7.65	525.2	28	62	274	11.8	62
	2009	7.58	512.7	26	68	291	13.2	64
SD <sup>a</sup>		0.11	210.8	1.05	5.2	34.2	4.35	8.7
TDP <sup>b</sup>				6.0	73.0	15.0	< 0.5	6.0

<sup>a</sup> standard deviation; <sup>b</sup> geochemical background of water sediments for Poland (PIG, 2010); n – number of samples.

Table 4. Mean values of the geoaccumulation index, as well as the coefficient and degree of bottom sediment contamination in Kielce Lake.

Sampling site	Metal	Geoaccumulation index ( $I_{deg}$ )	Coefficient of contamination ( $C_f^i$ )	Degree of contamination ( $C_{deg}$ )	Share of $C_f^i$ in $C_{deg}$ [%]
1	Cu	-0.79	0.24	53.45	0.45
	Zn	-0.34	0.68		1.27
	Pb	0.68	7.10		13.28
	Cd	1.45	44.7		83.63
	Cr	-0.31	0.73		1.37
2	Cu	-0.42	0.57	45.39	1.26
	Zn	-1.00	0.15		0.33
	Pb	0.41	3.82		8.42
	Cd	1.36	34.1		75.13
	Cr	0.65	6.75		14.87
3	Cu	0.36	3.42	29.08	11.76
	Zn	-0.23	0.88		3.03
	Pb	1.00	14.9		51.24
	Cd	0.52	4.99		19.90
	Cr	0.52	4.92		19.62
4	Cu	0.36	3.42	56.71	6.03
	Zn	-0.70	0.30		0.53
	Pb	0.64	6.54		11.53
	Cd	1.42	39.7		70.00
	Cr	0.65	6.75		11.90
5	Cu	0.48	4.50	59.72	7.54
	Zn	-0.23	0.89		1.49
	Pb	1.10	18.8		31.48
	Cd	1.22	25.0		41.86
	Cr	0.85	10.5		17.58

$$C_j^i = C_{0-1}^i / C_n^i$$

...where  $C_{0-1}^i$  is the metal content in bottom sediment and  $C_n^i$  is the geochemical background.

The sum of individual coefficients  $C_j^i$  expresses the contamination degree ( $C_{deg}$ ) of a location/area. After Håkanson [16], four descriptive pollution classes were adopted (Table 2).

### Discussion of Results

Kielce Lake is an example of negative consequences of strong human impact. City lake sediments were characterized by a slightly alkaline reaction, a rather high salinification degree expressed with the values of electrical conductivity (EC), and high metal content (Table 3).

The pH values and conductivity indicate the presence of sediments in the reservoir that contain washed-out, and hence mobile, alkaline elements (e.g. calcium, magnesium, potassium and – occasionally – sodium). Such a high reaction is controlled by free ions of alkaline metals and their carbonate forms in the sediments. It can be stated, however, that sampling points 2 and 5 are characterized by higher pH and EC values, while points 1 and 4 – by the lowest. This situation can also be caused by the location of points 2 and 5 in small bays where water flows very slowly, thus intensifying sedimentation processes.

Such a high reaction is the result of poorly soluble metal salts, present in the Kielce Lake water, being precipitated out of the water. It must be stressed, however, that heavy metal content in investigated bottom sediment samples varies (Table 3).

In the case of Zn, its value does not exceed the value of the geochemical background at any sampling site, while the quantities of Pb and Cd are in all cases exceeded several times. By analyzing the distribution of Cu and Cr, it can be observed that in the case of Point 1, the quantities of these elements in the studied material do not exceed the geochemical background; for Cu, this occurs also at Point 2. Hence, it may be assumed that Pb and Cd are major polluting elements for the reservoir's bottom sediments, and for the lake itself.

The quantity of metals in individual sampling points is on a similar level in respective years. The diversification of the level of pollution is the problem in every point separately. Probably this is the effect of the bottom shape of Kielce Lake, shoreline development, the directions of lake water, and pollution migration. The Silnica River entering the north side of Kielce Lake carries suspended particles, different substances from the catchment, the uncontrolled municipal wastewater discharge. Sediments can carry substantial quantities of absorbed heavy metals. The waste disposal from the swimming pool and rainwater, migration of contaminants from the nearby roads and the so-called internal supply on the south side of Kielce Lake. So different pollution is entering at different points. Suspended particles begin to settle once they reach the relatively quiescent lake environment. The rate of sedimentation and types of mate-

rials deposited, processes relating to mixing water and possibilities of pollution deposit on various places have the essential meaning and determine the physical characteristics of the bottom substrate.

The geoaccumulation indexes for particular elements (Table 4) indicate variation depending on a given metal and sediment sampling site. The indexes calculated for copper ( $Cu-I_{geo}$ ) ranged from -0.79 to 0.48, which indicates lack of pollution of Kielce Lake by this metal. Mean values for sampling sites at points 1 and 2 are negative, thus confirming the condition of  $I_{geo} \leq 0$ , described as “practically unpolluted sediment,” or Class Zero. Kielce Lake can also be considered to be unpolluted with zinc due to negative values of the geoaccumulation indexes ( $Zn-I_{geo}$ ) ranging from 1.00 to -0.23. At Point 1, the condition of  $I_{geo} \leq 0$  is also fulfilled for chromium, while at other sampling sites it is contained in the range  $0 < I_{geo} < 1$ , which means that the sediment is unpolluted to moderately polluted.

Unlike copper, zinc, and chromium, geoaccumulation indexes for lead ( $Pb-I_{geo}$ ) and cadmium ( $Cd-I_{geo}$ ) are contained in the range  $0 < I_{geo} < 1$  and  $1 < I_{geo} < 2$ , which points to the presence of sediments that are moderately polluted with these metals. 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. In the case of cadmium, it may be observed that the process of sediment enrichment with this metal is intensified at sampling points 1, 2, 4 and 5; in the case of lead, these are points 3 and 5 (Fig. 3).

It should be stressed that the geochemical indexes, calculated with the use of the geochemical background, have revealed the direction of the pollution which differs in dimension only. This is significant for the studies in which the variety of methods for pollution assessment frequently breeds opposite conclusions.

A detailed assessment of the reservoir's pollution was conducted with the use of contamination coefficients ( $C_j^i$ ), whose mean values enabled sediment classification according to the geochemical background data. However,

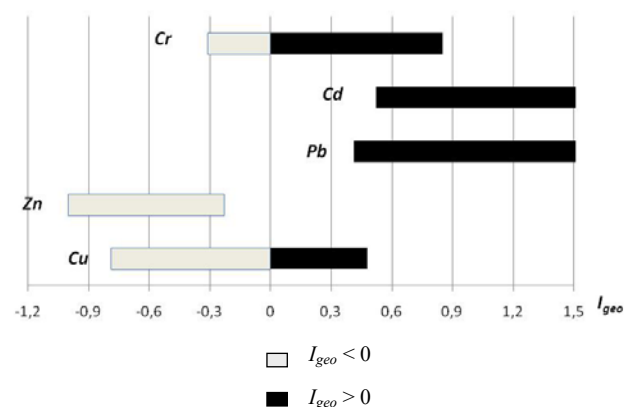


Fig. 3. The range of values of Indices of geoaccumulation ( $I_{geo}$ ) for metals in the bottom sediments of Kielce Lake.

the overall assessment of the studied reservoir's pollution at particular sampling sites was developed on the basis of data describing the degree of contamination ( $C_{deg}$ ) (Table 4).

In accordance with the adopted classification by Håkanson [16], two classes can be distinguished: at Point 3, where the value of the coefficient of contamination is contained in the range  $16 \leq C_{deg} < 32$ , this is a considerable degree of contamination. At other sampling sites, where coefficients of contamination  $C_{deg} \geq 32$ , this is a high degree of contamination. This indicates that Point 3, which is outside the aerator operation zone, is less polluted than points 1, 2, and 5 within its operation zone and Point 4 outside the aerator operation zone. Most probably at Point 4, sediment pollution occurs due to this site's being used for recreational purposes, while increased metal content in the sediment at points 1, 2 and 5 results from the aerator's operation: due to the oxygenation of water and the introduction of the coagulant, alkalization of the environment and precipitation of poorly soluble salts of heavy metals occurs.

All the sediments that are moderately to highly polluted are those samples obtained from locations surrounded by areas with industrial estates and high human activities as a result of population and commerce. The elevated geo-accumulation index recorded for areas with an influx of industrial waste and effluent is in consonance with similar studies [17-19].

Still, it must be remembered that bottom sediments, highly polluted with heavy metals that may be toxic, as is the case with cadmium or lead, pose a threat to the reservoir, its usability and the organisms that live therein. If physicochemical conditions are changed, such as the ion composition of water, lowering the pH value or appearance of anaerobic conditions, the forms in which metals occur in sediments may be changed, and metal release into water may occur. Consequently, their bioavailability will increase, and – as a result – introduction into the food chain will take place. The sediments that appear at the bottom of a reservoir under recultivation through aeration and phosphorus inactivation ought to be removed (through a dredging process) from the ecosystem due to the threat they pose.

### Conclusions

An assessment of bottom sediment pollution with the application of the geoaccumulation index, the coefficient and the degree of contamination, has shown that sediments collected from various sites in the reservoir, within and outside the aerator operation zone, vary in chemical composition. In the cases of Cu, Zn, and Cr, their mean contents do not exceed the value of the geochemical background, thus constituting a small proportion of the reservoir sediment pollution. The proportions of cadmium and lead, in turn, in the general overview of Kielce Lake bottom sediment pollution is the highest. The most polluted sediments are found at points 1, 2, and 5 (within the aerator operation zone) and Point 4 (outside the zone), while the least polluted are found at Point 3 (outside the zone).

Such considerable differentiation in qualitative and quantitative composition of bottom sediments at individual sampling points indicates considerable significance of the aerator's operation, as well as of hydrological parameters at a particular sampling point for the shaping of the chemistry of the reservoir's bottom sediments.

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