

Speciation of heavy metals in bottom sediments of a drinking water reservoir for Gdańsk, Poland – changes over the 14 years

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ABSTRACT

There was conducted a comparative study of the concentrations of heavy metals (Zn, Cu, Pb, and Cd) in the surface layer of sediments collected in two investigation periods: 1999–2000 and 2013. The results demonstrated that the degree of metals pollution decreased over time. The contamination factors (C_i) calculated for Zn, Cu, Pb, and Cd were respectively 3.63, 3.86, 3.23, and 3.25 in the first period of research and 1.35, 3.42, 1.98, and 1.43 in the second one. The metal speciation analysis indicated that Zn was mainly associated with the Fe–Mn oxides fraction and the residual fraction, and Cu – with the residual fraction and the organic fraction in both periods of investigation, while the percentage of geochemical fractions in binding of Pb and Cd changed in time. The share of fractions Fe–Mn oxides/carbonate increased in the case of Pb, and carbonate/exchangeable fractions in the case of Cd. The risk assessment code (RAC) decreased in the following order: Cd > Zn > Pb > Cu and was higher in 2013 - achieved the very high-risk category in the case of Cd. Thus, despite the decrease of sediment pollution, RAC for Cd increased due to changed geochemical speciation.

Keywords: Heavy metals; Speciation analysis; Pollution chronology; Sediments; Risk assessment code

1. Introduction

The occurrence of heavy metals in the aquatic environment due to human activities is a subject of many studies around the world. Excessive pollution of surface and underground water is a result of industrial and household wastewater discharges, inorganic fertilizers and pesticides and atmospheric deposition [1–5]. It is known nowadays, that the chemical composition of bottom sediments may be a better index of environmental pollution than the water composition [6]. Knowledge of the levels of metals in bottom sediments can be used in assessing the geochemical situation in a watershed and the spread of contaminants [7]. To establish the impact of the heavy metal on aquatic communities it is necessary to evaluate their total content as well as to identify the forms in which a metal is present in sediments. Knowledge about chemical forms of heavy metals allows for

the assessment of their bioavailability and mobility [8–10]. Five categories exist due to the major mechanisms of accumulation of heavy metals in sediment: exchangeable, bound to carbonate, bound to Fe–Mn oxides (reducible phases), bound to organic matter and residual. Remobilization of metals under changing environmental conditions proceeds in different ways for each of these fractions [11,12]. Metals bound to exchangeable fractions may be directly adsorbed by aquatic organisms, while metals bound to carbonate, reducible and organic fractions may be released to the water body due to various chemical and biochemical processes occurring in bottom sediments [13–16]. Residual fraction is considered to be relatively inactive because of the lesser possibility of mobility into pore water [10,17]. Based on the percentage of metal in the most labile fractions, that is, exchangeable and carbonate Perin et al. [18] have introduced the risk assessment code (RAC). This indicator was applied

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in many studies [10,19–21] to assess the risk of mobility of the metals. Furthermore, anthropogenic metals mainly appear as liable extractable fractions, whereas those from lithogenic sources are present in the residual fraction. Thus fractionation is also useful to recognize the origin of metals [22–26].

Investigation of changes in metal content between sediment layers may provide information about changes in the pollution of the waterbody in chronological order [7,27–31]. Sediments deposited after the activation of the source of pollution are characterized by higher metal content and, likewise, a limitation of metals delivery to the lake will cause a reduction of metals concentration in the surface layer of sediments. Most studies regarding changes of aquatic environment contamination with heavy metals over time focus only on examination of total concentrations of metals in bottom sediments [26,27,32–35]. There is a general correlation between the degree of pollution and the degree of industrialization in recent decades [36], but the scale of contamination depends not only on the human input but also on a variety of hydrological factors such as flooding or climate change [37–40]. However, there are many phenomena which can cause modification of heavy metals speciation hence serious implication for environment may arise as well.

In this paper, we provided the total content of heavy metals and their speciation in the sediments collected from Lake Straszyn in 1999–2000 and again in 2013. The Straszyn Lake is a freshwater man-made reservoir that was built in 1910 on the Radunia river near Gdańsk city (north Poland). In 1986 the intake and water treatment plant was constructed here because the groundwater resources became insufficient for the growing city. It has become necessary to conduct a detailed assessment of the water quality of the Straszynski Reservoir, as well as to monitor the potential risk of water contamination from bottom sediments. Time of our research - the beginning of the 21st century - was a period of intense changes in the Polish economy that also affected the environment. Many of them, such as changes in agricultural use of the catchment, sewage management, atmospheric pollution or the vicinity of new urban areas, can also affect the fate of heavy metals in the aquatic environment [38,41,42].

The main objectives of this study were: (1) to determine the concentrations of heavy metals including Cd, Cu, Pb, and Zn in the surface sediments of Straszyn Lake in two periods: 1999–2000 and 2013; (2) to investigate the changes of contamination degree of sediments over time; (3) to assess changes of metals mobility in sediments over time using chemical fractionation.

The obtained results may provide useful information about the direction of environmental quality changes in Straszyn Lake.

2. Materials and methods

2.1. Study area

The study was conducted on Straszyn Lake, which is located on the Radunia River in northern Poland and lies at the eastern edge of the Kashubian Lakes District. Radunia Valley has been protected as a protected landscape area. The ground-breaking section of Radunia is located within the borders of the Kashubian Landscape Park. In the

central part of the catchment area, “Radunia River Ravine” is protected under the Natura 2000 network. The Straszyn Reservoir was constructed in 1910, primarily to produce energy. A small hydroelectric power plant with a capacity of 2,450 kW is situated here. The catchment area of the Radunia River equals to 837 km², and almost 70% of the area is agricultural land. From the sources to the dam in Straszyn, the length of the river is 70.4 km. The total volume of the Straszyn Reservoir is 3 mln m³ and its surface area is 0.75 km². The reservoir is 3 km long. Since 1986, the main function of this reservoir is the provision of drinking water to several districts of Gdańsk. This is the only intake of surface water in the city.

2.2. Sample collection

The collection of the sediment samples was performed:

- in the first period on 6 occasions between March and October 1999 and on 6 occasions between April and November 2000 at intervals of approximately 40 d;
- in the second period on 8 occasions between May and October 2013 at intervals of approximately 20 d;

The samples of superficial sediment with thickness of 10–15 cm were collected from four locations (Fig. 1) using a KC Kajak sediment core sampler (KC Denmark Research Equipment, Denmark) and stored in acid-washed plastic containers. After collection, the samples were air-dried and sieved using a 2 mm plastic sieve to remove large pieces of detritus.

2.3. Chemical analyses

The sediment samples were analyzed in terms of parameters such as grain size, pH, organic matter content, total nitrogen, and phosphorus content and heavy metals total concentration (Zn, Cu, Pb, and Cd). The grain-size distributions of the sediment samples were measured using the wet sieving method (sand: 1–0.05 mm, clay silty: 0.05–0.002 mm, clay < 0.002 mm) and the Analysette 28 Image Sizer. The content of organic matter was determined using the loss-on-ignition (LOI) technique at 605°C. The total nitrogen content and total phosphorus content in the sediments were determined according to the procedure given by Obarska-Pempkowiak and Klimkowska [43]. To measure the concentrations of the heavy metals, the sediment samples were dried at 105°C to constant weight and sieved through a 0.2 mm sieve. To determine the contents of metals the sediment samples were extracted with aqua regia (HCl:HNO₃ = 3:1) using the Büchi K-438 digestion system [44]. The metal concentrations in the sediments were measured using the Vario 6 flame atomic absorption spectrometer with an air/acetylene flame that was equipped with a single-element hollow cathode lamp and a deuterium lamp to enable background corrections. Standard solutions for Zn, Cu, Pb, and Cd were prepared from the 1,000 mg L⁻¹ Merck Certipur® standard solutions. The accuracy of the method was tested using sedimentary reference material (river clay sediment LGC6139). All of the concentrated acids used for the experiments were supra pure (Merck) quality. The speciation analysis of metals was performed using the five-step Tessier's sequential procedure [12] according to the scheme presented in Table 1.

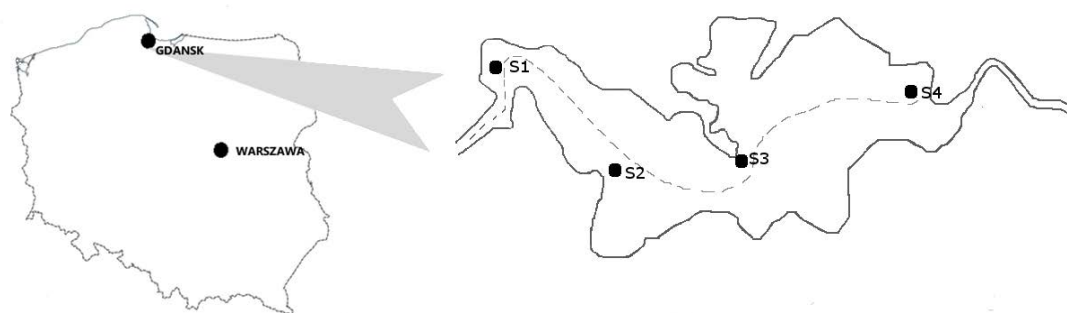


Fig. 1. Location of Straszyn Lake in Poland and the positions of sampling sites.

Table 1
Scheme of metals speciation analysis

Fraction	Method of extraction
F1 - exchangeable	8 ml of $MgCl_2$ (1 mol L^{-1} , pH 7), for 1 h, at room temperature, with continuous agitation.
F2 - bound to carbonates	8 ml of NaOAc, (1 mol L^{-1} , adjusted to pH 5.0 with HOAc), for 8 h, at room temperature, with continuous agitation.
F3 - bound to Fe–Mn oxides	20 ml of $NH_2OH-HCl$ (0.04 mol L^{-1}) in 25% (v/v) HOAc, for 8 h, at $96^\circ\text{C} \pm 3^\circ\text{C}$, with occasional agitation.
F4 - bound to organic matter	3 ml of HNO_3 (0.02 mol L^{-1}) and 5 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3 , the mixture was heated to $85^\circ\text{C} \pm 2^\circ\text{C}$ for 2 h with occasional agitation. A second 3 ml of 30% H_2O_2 (pH 2) was then added and the sample was heated again to $85^\circ\text{C} \pm 2^\circ\text{C}$ for 3 h with intermittent agitation. After cooling, 5 ml of NH_4OAc (3.2 mol L^{-1}) in 20% (v/v) HNO_3 was added and the sample was diluted to 20 ml and agitated continuously for 30 min.
F5 - residual	Mixture of concentrated acids in a ratio of 3:1 of $HCl:HNO_3$ (aqua regia) for 3 h.

3. Result and discussion

3.1. Physicochemical properties of bottom sediments

The basic physicochemical properties of bottom sediments are presented in Table 2. Based on grain composition, the bottom sediments of Straszyn Lake were classified as silty clay, except the station situated in the inlet zone (S1). At this station, a higher amount of sand was found (up to 49%). The texture of the sediments was similar in both periods of research and typical for horizontal sediment distribution in dam reservoirs. The coarse fractions of sediments are deposited at the head of the reservoirs, forming a delta, and the fine fractions of sediments are observed in the central part of reservoirs and near the dam [45]. The sediments were characterized by pH ranging from neutral to slightly alkaline (6.9–7.6). The organic matter content (OM expressed as LOI) between 2.7% and 18.4% was observed and no significant differences were found in the results of the two periods: mean OM content was 12.7% and 13.5% respectively. According to Stangenberg's classification [46], the deposits can be qualified as a mineral. Total N and total P occurred in the sediments are situated within a narrow concentration range (Table 2). The concentrations of total N changed from 5.32 to 6.35 mg/g d.m. in the period 1999–2000 and between 5.10 and 6.41 mg/g d.m. in 2013. The content of total P ranged from 0.63 to 1.97 mg/g d.m. in the first period of research and was slightly higher in the second (0.88–2.31 mg/g d.m.).

For comparison sediments from the Utrata river (central Poland) contained on average 5.7 mg N/g d.m. and 0.59 mg P/g d.m. and have been described as highly contaminated by biogenic elements [47].

The heavy metals concentrations in sediments sampled from Straszyn Lake in two investigation periods (1999–2000 and 2013) are presented in Table 3. The results showed that the mean concentrations of Zn, Cu, Pb, and Cd were respectively 63%, 11%, 39%, and 56% lower in the second investigation period. The content of heavy metals in the sediments collected in 2013 ranged from 14.69 to 92.47 mg Zn/kg d.m., from 2.34 to 25.65 mg Cu/kg d.m., from 1.26 to 49.20 mg Pb/kg d.m. and from 0.25 to 1.70 mg Cd/kg d.m. In the sediments sampled in 1999–2000 these ranges were: 63.75 to 210.70 mg Zn/kg d.m., from 9.91 to 29.20 mg Cu/kg d.m., from 14.84 to 64.89 mg Pb/kg d.m. and from 0.89 to 2.91 mg Cd/kg d.m. In the first investigation period as well as in the second, the lowest concentrations of all examined metals were found in the inlet zone of the reservoir (at the station S1). The computed coefficients of variation (CV) for individual metals were between 24% and 35% in 1999–2000 and between 45% and 56% in 2013, thus the higher variability of heavy metals concentration was noted in the second investigation period.

The assessment of the anthropogenic contribution to heavy metals concentration in the sediments was based on comparison with the local geochemical background

AQ2 Table 2
Basic properties of bottom sediments

Parameters	Grain size (%)			pH	Organic matter (%)	Total N	Total P	
	Sand	Clay silty	Clay					
Sampling sites				1999–2000				
1	Mean	45.12	51.29	3.59	7.2	11.5	5.39	0.63
	SD	4.09	4.12	0.88	0.1	1.3	1.41	0.22
2	Mean	10.55	83.69	5.76	7.1	10.6	5.61	1.16
	SD	1.21	3.45	1.42	0.1	4.3	0.87	0.65
3	Mean	6.91	87.08	6.01	7.2	14.8	6.25	1.97
	SD	3.23	3.14	0.38	0.1	4.3	1.03	0.77
4	Mean	0	90.36	9.64	7.3	13.9	5.32	1.85
	SD	0	2.21	0.54	0.2	1.4	1.42	0.93
Sampling sites				2013				
1	Mean	46.05	49.34	4.61	7.2	12.4	6.14	0.88
	SD	7.32	5.19	1.69	0.3	2.3	2.32	0.46
2	Mean	8.85	83.33	7.82	7.1	11.9	5.23	1.21
	SD	4.02	6.59	3.81	0.2	6.5	1.85	0.79
3	Mean	5.88	85.68	8.44	7.2	14.1	6.41	2.23
	SD	2.53	5.74	2.14	0.2	4.8	1.79	1.10
4	Mean	0	88.91	11.09	7.3	15.4	5.10	2.31
	SD	0	3.98	2.87	0.2	3.6	2.45	1.48

Table 3
Descriptive statistics of heavy metal concentrations in the Straszyn Lake sediments and values of local geochemical background

Parameters	Zn	Cu	Pb	Cd
	µg/g d.m.			
1999–2000				
Mean	148.87	19.28	35.58	1.63
Median	154.38	20.22	37.74	1.60
SD	41.61	4.55	12.44	0.45
Range	63.75 ÷ 210.70	9.91 ÷ 29.20	14.84 ÷ 64.89	0.89 ÷ 2.91
CV%	28	24	35	28
Mean C_f	3.63	3.86	3.23	3.25
2013				
Mean	55.19	17.08	21.73	0.72
Median	63.07	20.93	23.73	0.69
SD	24.99	8.25	12.23	0.72
Range	14.69 ÷ 92.47	2.34 ÷ 25.65	1.26 ÷ 49.20	0.25 ÷ 1.70
CV%	45	48	56	51
Mean C_f	1.35	3.42	1.98	1.43
Lis and Pasiczna [48]				
Geochemical background	41	11	5	0.5

values given by Lis and Pasiczna [48] for Gdańsk Region (Table 3) and evaluation contamination factors C_f proposed by Hakanson [49] and used in many studies around the world [50–56]. C_f is the contamination factor for individual metals expressed as Eq. (1):

$$C_f = \frac{C_i}{C_0} \quad (1)$$

where C_i is the concentration of metal i in sediment, C_0 is the background value of the metal in the study area. This

comparison of the average values of heavy metals with the background values showed that all the averages were higher; in particular, in the first investigation period (1999–2000) contamination factors calculated for Zn, Cu, Pb, and Cd were respectively 3.63, 3.86, 3.23, and 3.25. However, when comparing the average values of metals in sediments sampled in 2013 with the background values the results indicated that these differences were lower: contamination factors for Zn, Cu, Pb, and Cd were respectively 1.35, 3.42, 1.98, and 1.43. The mean concentrations of metals exceeding background level were found in the order: Cu > Zn > Cd > Pb for 1999–2000 and Cu > Pb > Cd > Zn in 2013.

According to Hakanson [49] the contamination factor C_f (Eq. (1)) was classified as: $0 < C_f \leq 1$ unpolluted; $1 < C_f \leq 3$ moderately polluted; $3 < C_f \leq 6$ considerably polluted; $C_f \geq 6$ very highly polluted. It means that the sediments of Straszyn Lake sampled in 1999–2000 were classified as considerably polluted and in 2013 as moderately polluted, except Cu (considerably polluted).

The results presented above indicate that the quality of surface sediments in Straszyn Lake has improved over the analyzed period of 14 years. Many probable reasons influence the temporary change in the degree of sediment contamination. Most of them are anthropogenic factors, including sewage discharge, agricultural use of the catchment area, location of regional roads as well as dry and wet deposition. Precipitation is considered to be one of the most important routes through which atmospheric pollutants may reach the surface water [41], and the decrease of heavy metals concentrations in dust on the research area [57] causes the improvement in aquatic environment also. However, rivers flowing through the lakes have proved to be a key factor in the introduction of pollution and most of the available heavy metal fraction into the water body and their accumulation along the flow of river water in the lake [58–60]. Spatial and temporal changes in river runoff can be affected by changes in land use, population density and climate [61]. Some significant differences were also observed between sedimentation in lakes and reservoirs. Rates of water movement through reservoirs such as Straszyn and of sediment inputs into reservoirs are correspondingly higher than for lakes [45]. Although for a large part of the lowland territory of Poland (like a current research area) the denudation index is no greater than 5 t/km² y [62] and linear sedimentation rates for most natural lakes vary from 0.05 to 10 mm/y, an average sedimentation rate for reservoirs reaches around 20 mm/y [45]. Moreover, the extent of climate change impact on runoff is difficult to establish and to differentiate from direct human impacts. European daily rain gauge observations indicate upward trends in mean and heavy precipitation over the past decades and an increase in the percentage of heavy rainfalls to precipitation totals by 3%–4% per decade [63,64]. These trends were confirmed by regional studies: the number of days with intense precipitation is increasing especially in the north-western part of Poland [65]. Additionally, land-cover changes control rainfall–runoff relationships. Straszyn Lake is located on the Radunia River which catchment area is agricultural land. In contrast to urbanized and industrial areas, sediments from reservoirs located at the agriculture, forest or non-industrial catchment usually are only slightly contaminated by metals [66].

However, fertilizers containing heavy metals, including As, Cd, Hg, Ni, Pb, and Zn, as well as inappropriate or excessive fertilization in rural areas can significantly affect the quality of water, bottom sediments and soils [67,68]. Although there is no detailed data on fertilizer consumption in the Radunia catchment, it is known that in Poland the use of nitrogenous and phosphatic fertilizers increased in 1999–2000 by over 60%. In addition, pesticide sales in Poland increased more than 2.5 times in 2000–2012 [57]. These data indicate that the decrease of heavy metals content in Straszyn Lake sediments is not related to changes in agriculture in this area. According to environment monitoring reports of Gdańsk Inspectorate of Environmental Protection [69], the main sources of pollution inflowing to Straszyn Lake are the effluents from municipal sewage treatment plants located on Radunia river and its tributaries, industrial wastewater and runoff from the urbanized area (mainly Żukowo town). Hence, the reason for the improvement of sediment quality was probably the construction and modernization of municipal wastewater treatment plants in Przdokowo (2001–2002) and Somonino (2008–2009) located on Klasztorna Struga (the tributary of the Radunia River) [69]. An important change in sewage management in the Radunia catchment, influencing the runoff, is also the extension of the sewage system (175% in the period 2007–2013) [69].

3.2. Chemical speciation profile

The five chemical fractions of heavy metals in sediments (such as exchangeable, bound to carbonates, bound to Fe–Mn oxides, bound to organic matter and residual) were identified to estimate metals mobility and potential toxicity. The metal distributions in the different fractions varied for each element and both the investigation periods. The mean percentages of fractions for each heavy metal in sediment are illustrated in Figs. 2–5.

3.2.1. Zinc

Zn was mainly associated with fractions III (Fe–Mn oxides phase, 45.3% in 1999–2000 and 43.5% in 2013) and V (residual phase, 27.8%, and 26.3%, respectively). The Fe–Mn oxides fraction was proved to be sensitive to anthropogenic inputs [70], however, the residual fraction is the most chemically stable and biologically inactive. Zn was also found in the carbonate phase (14.3% and 19.0%) and the organic phase (12.1% and 10.4%, respectively). In both the investigation periods < 1% of Zn was bound to fraction I. The significant role of fraction III and V in binding of Zn was consistent with the result of [6,15,71]. In summary, the distribution of Zn (mean values) has not changed over 14 years and was as follows: Fe–Mn oxides > Residual > Carbonate > Organic > Exchangeable (Fig. 2).

3.2.2. Copper

The distribution of Cu, as in the case of Zn, was also similar in both the investigation periods (Fig. 3). Cu was dominated by the residual fraction with the mean proportions 49.5% in 1999–2000 and 58.1% in 2013, and by the organic fraction with the mean proportion 44.5% and 38.2%,

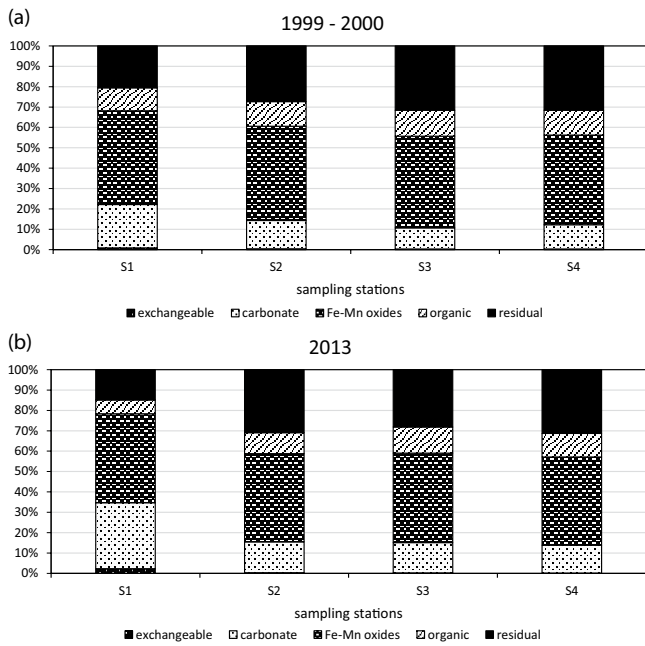


Fig. 2. Percentage of each fraction of Zn in the bottom sediments for sampling points of Straszyn Lake.

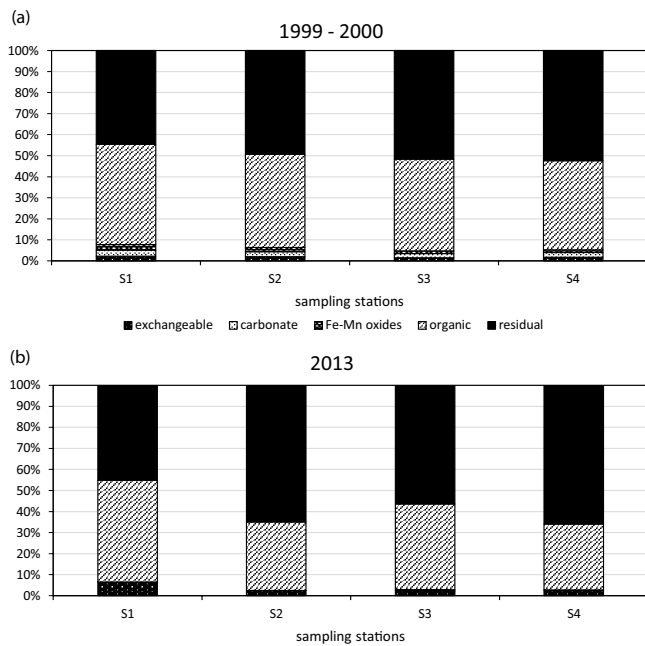


Fig. 3. Percentage of each fraction of Cu in the bottom sediments for sampling points of Straszyn Lake.

respectively. A high amount of Cu in the residual fraction was also observed by [15,25,72]. The high percentage of the organic fraction in Cu binding was similar to other works [6,15,21] due to the high affinity of Cu to organic matter [73]. Scanty amounts of Cu were connected with fractions I – III: up to 6% (together) in the first investigation period and up to 3.7% in the second. The distribution of Cu (mean values) was as follows: Residual > Organic >> (Fe–Mn oxides + Carbonate + Exchangeable).

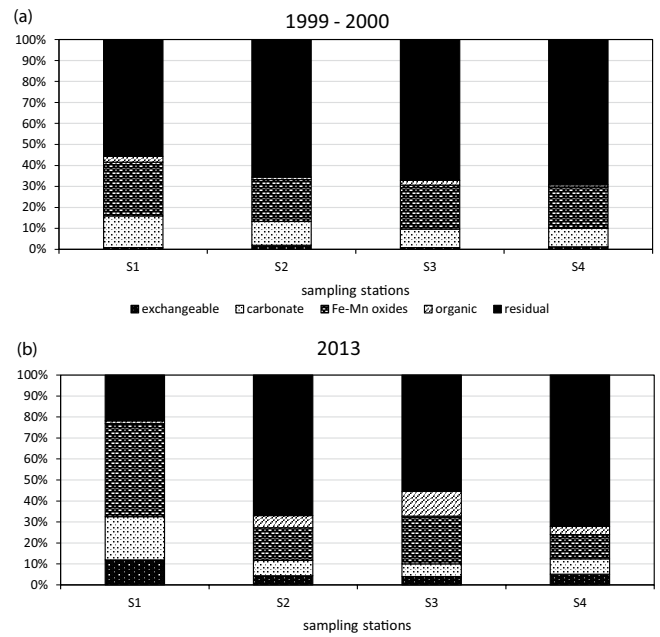


Fig. 4. Percentage of each fraction of Pb in the bottom sediments for sampling points of Straszyn Lake.

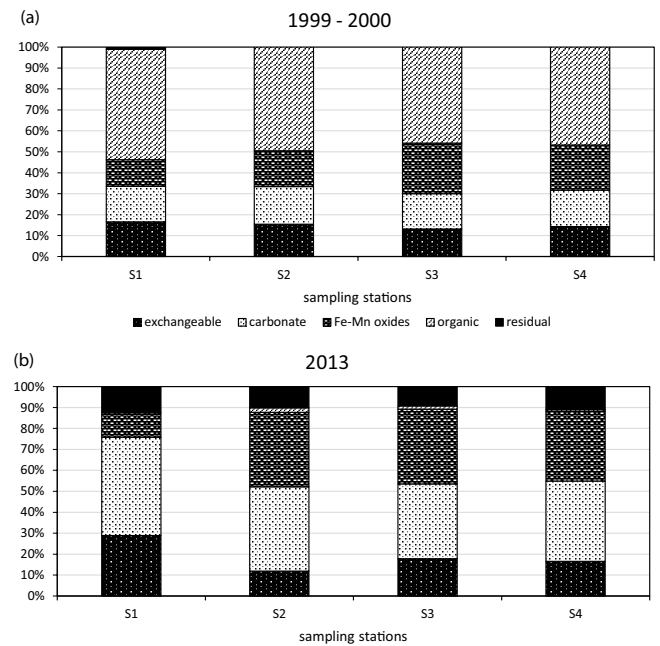


Fig. 5. Percentage of each fraction of Cd in the bottom sediments for sampling points of Straszyn Lake.

3.2.3. Lead

In the case of lead, some differences were observed between the mean percentages of fractions in the analyzed investigation periods (Fig. 4). In particular, at the station S1 in 1999–2000 Pb was mainly associated with the residual fraction (55.7%) and with the Fe–Mn oxides fraction (25.6%), while in 2013 Pb was present, above all, in the Fe–Mn oxides fraction (44.4%) and in the residual fraction (21.9%) as well

as in the carbonate fraction (20.6%). These results indicated that the potential mobility of lead in the inlet zone of Straszyn Lake has increased over the considered 14 years. This phenomenon was also observed, although to a lesser extent, at the other sampling stations of Straszyn Lake. The mean percentage of the residual fraction in Pb binding has decreased from 64.4% in 1999–2000 to 54.1% in 2013. Additionally, Pb associated with the exchangeable fraction constituted 1.2% in 1999–2000 and 6.4% in 2013. A similar share of the residual fraction in binding of lead was observed by [16,72,74]. The distributions of Pb (mean values) were as follows: Residual > Fe–Mn oxides > Carbonate > Organic > Exchangeable (in 1999–2000) and Residual > Fe–Mn oxides > Carbonate > Exchangeable > Organic (in 2013).

3.2.4. Cadmium

Compared with the other metals, Cd revealed more significant differences in chemical speciation over the analyzed 14 years (Fig. 5). In the first investigation period Cd preferentially bound to the organic fraction (48.8%), however, it was also present in the fractions: exchangeable, carbonate and Fe–Mn oxides, with mean proportions of 14.8%, 17.3%, and 18.8%, respectively. Scanty amounts of Cd – up to 1% – were connected with the residual fraction. Thus, Cd exhibited higher potential mobility and bioavailability and these results were consistent with previous studies [6,75]. In 2013 Cd remained mainly associated with the carbonate fraction (40.3%). Similar observations were also made by Singh et al. [19], Baran and Tarnawski [21] and Farkas et al. [76]. Cd was also bound to fractions: Fe–Mn oxides (29.1%), exchangeable (18.8%) and residual (10.7%). These results indicate, that almost 60% of Cd was connected with the labile fraction (exchangeable and carbonate), while in 1999–2000 total share of these fractions constituted for over 30%. The distributions of Cd (mean values) were as follows: Organic > Fe–Mn oxides > Carbonate > Exchangeable >> Residual (in 1999–2000) and Carbonate > Fe–Mn oxides > Exchangeable > Residual >> Organic (in 2013).

3.3. Assessment of heavy metals mobility

The analytical results obtained from sequential extractions can be utilized to calculate the RAC [18–20] (Eq. (2)):

$$\text{RAC} = \frac{(F1 + F2)}{\text{Totalcontent}} \times 100 \quad (2)$$

This indicator was used to assess the mobility of the heavy metals according to the five-level classification consisting of the following grades/categories: no risk (<1%), low risk (1%–10%), medium risk (11%–30%), high risk (31%–50%), and very high risk (>50%) [18]. The RACs calculated for the examined metals were summarized in Table 4.

According to the classification presented above, Cd exhibited the highest mobility and potential bioavailable risk: in 1999–2000 RAC = 32.1% (high risk) and in 2013 RAC = 59.1% (very high risk). Zn and Pb presented a medium risk in both the periods, while Cu showed a low risk. Sundaray et al. [74] and Ke et al. [10,77] based on RAC observed also the

crucial role of Cd for ecological risk in an aquatic environment. Despite the increase in time of the percentage of metals (except Cu) associated with the labile fractions (exchangeable and carbonate), the amounts of these metals (expressed in $\mu\text{g/g d.m.}$) were lower in 2013, due to the lower total content of metals in sediments. The largest differences were noted for Zn and Pb, but we observed it even in the case of Cd, which in 2013 was almost 60% associated with labile fractions. The sum of the content of metals associated with fractions I and II in the bottom sediments of Straszyn Lake in the research periods 1999–2000 and 2013 are presented in Fig. 6.

The mobility and availability of metals in the sediments depend on many factors such as the content of organic matter and clay fraction, pH, salinity, presence of sulfur and carbonates [25,76,78–80]. Additionally, relationships between heavy metals themselves as well as between heavy metals and other properties of sediment provide information on metal sources and pathways in the environment [10,52,81]. The results of Pearson correlations analysis among geochemical fractions of metals and physicochemical properties are summarized in Table 5. The exchangeable fraction (F1) of Cu and Pb was significantly positively correlated with silty clay and clay but inversely correlated with sand. However, Zn and Cd showed the opposite correlations: fraction F1 of Zn and Cd was significantly positively correlated with sand, but inversely correlated with sand silty clay and clay. The positive correlation existed also between the carbonate fraction (F2) of all the

Table 4
Mean RAC calculated for sediments sampled in 1999–2000 and in 2013

RAC %		Zn	Cu	Pb	Cd
1999–2000	Mean	14.8	4.2	12.3	32.1
	SD	3.9	0.9	5.0	6.9
	Risk	Medium	Low	Medium	High
2013	Mean	19.8	3.3	16.6	59.1
	SD	4.7	1.6	3.8	7.3
	Risk	Medium	Low	Medium	Very high

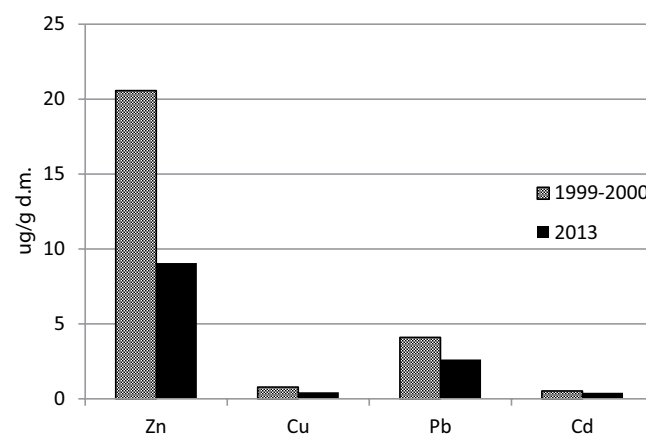


Fig. 6. Sum of content of metals (expressed in $\mu\text{g/g d.m.}$) associated with fractions I and II in the bottom sediments of Straszyn Lake in the research periods 1999–2000 and 2013.

Table 5
Pearson correlation analysis among chemical fractions of heavy metals and sediment physicochemical properties

Parameters		Properties of sediments							
		Total metal content	pH	Organic matter	Total N	Total P	Sand	Silty clay	Clay
Fraction F1 exchangeable	Zn	ns	0.38 ^b	ns	ns	ns	0.97 ^a	-0.98 ^a	-0.79 ^a
	Cu	ns	ns	ns	ns	ns	0.91 ^a	0.91 ^a	0.74 ^a
	Pb	ns	ns	ns	ns	0.33 ^c	0.80 ^a	0.81 ^a	0.66 ^a
	Cd	ns	ns	ns	ns	ns	0.79 ^a	-0.80 ^a	-0.70 ^a
Fraction F2 carbonate	Zn	0.30 ^c	ns	ns	ns	0.29 ^c	ns	ns	0.58 ^a
	Cu	0.36 ^c	ns	ns	ns	ns	-0.82 ^a	0.83 ^a	0.66 ^a
	Pb	ns	ns	ns	ns	ns	-0.89 ^a	0.90 ^a	0.67 ^a
	Cd	ns	-0.36 ^c	ns	ns	ns	-0.86 ^a	0.88 ^a	0.62 ^a
Fraction F3 Fe–Mn oxides	Zn	0.93 ^a	0.32 ^c	0.45 ^b	0.36 ^c	0.63 ^a	-0.89 ^a	0.90 ^a	0.74 ^a
	Cu	ns	ns	-0.34 ^c	ns	-0.44 ^b	0.76 ^a	-0.74 ^a	-0.89 ^a
	Pb	0.70 ^a	ns	ns	ns	ns	-0.78 ^a	0.79 ^a	0.67 ^a
	Cd	0.56 ^a	ns	0.32 ^c	ns	0.34 ^c	-0.84 ^a	0.85 ^a	0.72 ^a
Fraction F4 organic	Zn	0.93 ^a	ns	0.56 ^a	ns	0.67 ^a	-0.88 ^a	0.88 ^a	0.74 ^a
	Cu	0.88 ^a	ns	0.41 ^b	ns	0.46 ^c	-0.78 ^a	0.79 ^a	0.57 ^a
	Pb	0.44 ^b	ns	ns	ns	ns	ns	ns	ns
	Cd	ns	ns	ns	ns	ns	0.91 ^a	-0.89 ^a	-0.94 ^a
Fraction F5 residual	Zn	0.90 ^a	ns	0.51 ^a	ns	0.67 ^a	-0.90 ^a	0.90 ^a	0.80 ^a
	Cu	0.90 ^a	0.43 ^b	0.38 ^b	ns	0.52 ^a	-0.88 ^a	0.89 ^a	0.73 ^a
	Pb	0.89 ^a	0.42 ^b	0.45 ^b	ns	0.55 ^a	-0.93 ^a	0.93 ^a	0.84 ^a
	Cd	-0.32 ^c	ns	ns	ns	-0.29 ^c	0.98 ^a	-0.99 ^a	-0.81 ^a

^a $p < 0.001$

^b $p < 0.01$

^c $p < 0.05$

ns: not significant.

metals and silty clay (except Zn) and clay, while fraction F2 of Cu, Pb and Cd were negatively correlated with sand. The Fe–Mn oxides fraction (F3) of Zn, Pb, Cd was positively correlated with silty clay and clay, while negatively with sand. Cu showed the opposite correlation. Zn bound in fraction F3 was positively correlated with pH, organic matter, total N and total P content. Organic matter was also positively correlated with fraction F3 of Cd, fraction F4 (organic) of Zn and Cu and fraction F5 (residual) of Zn, Cu, and Pb. These relationships proved that the distribution of Zn and Cu depend on organic matter content [19,21,82]. Fraction F4 of Zn and Cu was positively correlated with silty clay and clay, but negatively with sand. Instead, Cd bound in fraction F4 was positively correlated with sand and negatively with silty clay and clay. Of all analyzed geochemical fractions, fraction F5 showed the strongest correlation with the physicochemical properties of sediments. Zn, Cu, and Pb bound in this fraction were positively correlated with organic matter, total P, silty clay and silty, but negatively correlated with sand. The residual fraction of Cd showed a positive correlation with sand and negative with total P, silty clay and clay. The strong correlation (positive or negative) between sand, silty clay, clay and all the fractions of the metals (except the carbonate fraction of Zn and the organic fraction of Pb) indicated, that grain size distribution of sediments significantly affected the mobility and potential mobility of the metals. The crucial role of fine particulate fractions of sediments in metals binding was also

observed in many previous studies [83–86]. The lack of correlation between pH and all the fractions of the metals except for few cases (the exchangeable fraction of Zn, the carbonate fraction of Cd, the Fe–Mn oxide fraction of Zn and the residual fraction of Cu and Pb) indicated, that pH did not significantly affect the distribution of metals among different geochemical fractions.

In the present study, a strong positive correlation was found between the total content of metals and the Fe–Mn oxides fraction (in the case of Zn, Pb, and Cd), the organic and residual fraction (in the case of Zn, Cu, Pb). These results were compatible with the important role of fraction F3 in binding Zn and Pb, fraction F4 in binding Cu and fraction F5 in binding Zn, Cu, and Pb. Additionally, the positive correlation between the residual fraction and the total content of given metal could indicate a lithological source for Zn, Cu and Pb [25]. The very strong correlation between the total content of metals was also observed in the previous study of Straszyn Lakes sediments [87] and these results indicated their common origin [10,15,25,38]. The inverse relationships than in the case of Zn, Cu and Pb were noted between Cd and physicochemical properties of sediments. Cd bound with the exchangeable, organic and residual fractions was strongly negatively correlated with silty clay and clay. The total content of Cd showed a positive correlation with the Fe–Mn oxides fraction and the weak negative correlation with the residual fraction. These results and the important role of the

mobile fraction in binding of Cd could indicate the anthropogenic source of this metal [88].

4. Conclusions

The results of the present study showed that the concentrations of heavy metals in the surface layer of the bottom sediments of Straszyn Lake have changed over time. The total content of Zn, Cu, Pb, and Cd was lower in the second investigation period. According to the classification of the contamination factor, C_f , the sediments of Straszyn Lake sampled in 1999–2000 were classified as considerably polluted and in 2013 as moderately polluted, except Cu (considerably polluted). The analysis of metals speciation indicated that metal distributions in the geochemical fractions of sediments were similar in both research periods for Zn and Cu. Zn was bound mainly to the Fe–Mn oxides fraction and the residual fraction, and Cu – to the residual fraction and the organic fraction. However, mobility of Pb and Cd increased, due to growth in the share of fractions: Fe–Mn oxides (Pb), carbonate (Pb, Cd) and exchangeable (Cd) in the binding of these metals. The granulometric composition of sediments was an important factor that controls metal mobility in the studied sediments. RAC values increased with time (with exception to Cu), changing the classification from ‘high’ to ‘very high’ risk in the case of Cd. The significant of the role the labile fractions in binding of Cd indicated high potential mobility and bioavailability of this element, as well as an anthropogenic origin. Thus, the occurrence of Cd in water and sediments of Straszyn Lake should be carefully monitored for preventing environmental risk. Moreover, to protect this reservoir from human contamination, the quality of the Radunia river and its tributaries should be permanently improved and controlled.

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