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Factors influencing the accumulation of Pb in sediments of deep and shallow dam reservoirs

by

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Abstract

The study determines the differences in Pb accumulation in sediments of dam reservoirs with respect to locations of the old river beds and their depth (deep Czorsztyn Reservoir and shallow Goczałkowice Reservoir in southern Poland). Parameters (grain size, organic matter content and reservoir depth) that may influence the spatial distribution of Pb concentrations in the sediments were analyzed. Based on the hierarchical cluster analysis, sediment samples from the reservoirs were ranked with respect to particle size distribution. We found differences in the spatial distribution of grain size and organic matter in the studied reservoirs, caused mostly by the topography of these reservoirs. The spatial distribution of Pb concentrations in the sediments of the Czorsztyn Reservoir (range 4.8-35.8 μg g^{-1}) and the Goczałkowice Reservoir (range 11.3-59.4 μg g^{-1}), regardless of their average depth and their type (dimictic, polymictic), depends on the distribution of silty clay and clay fractions, organic matter and reservoir depth. Therefore, Pb spatial distribution was more regular in the Czorsztyn Reservoir than in the Goczałkowice Reservoir. Locations of the old river beds had a significant impact on the Pb distribution in the sediments of both reservoirs.

Key words: deep and shallow dam reservoirs, Pb, sediments, grain size distribution

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Introduction

Heavy metals are toxic and non-biodegradable substances. Lead is one of the most toxic heavy metals and ranked 6th on the list of 10 environmental poisons according to the Commission of Environmental Toxicology of the Polish Academy of Sciences. It also ranks second on the list of priority hazardous substances presented by the Agency for Toxic Substances and Disease Registry and has been classified by the EPA as a toxic element accumulated by organisms (Agency for Toxic Substances & Disease Registry, 2013). The literature does not provide any information that lead is in any way required for living organisms. Förstner (2009) emphasizes the need to improve the knowledge and data available on the sources of priority substances and the ways in which pollution occurs in order to identify targeted and effective control options. They are included in the amendments to the original European Water Framework Directive (WFD) 2000/60/EC (Anonymous 2000; Quevauviller 2007). This applies in particular to a reliable long-term trend analysis of those priority substances that tend to accumulate in sediments and/or biota.

Issues related to Pb accumulation in the sediments of dam reservoirs and factors that affect the accumulation (Brekhovskikh et al.2002; Eggleton, Thomas 2004; Gierszewski 2008; Szarek-Gwiazda 2013; Zhao et al. 2013), Pb potential mobility and bioavailability (Korfali, Jurdi 2011; Szarek-Gwiazda, Mazurkiewicz-Boroń 2006; Zhang et al. 2002) or reconstruction of Pb inputs to the sediment through the analysis of a sediment core (Shotbolt et al. 2006; Wildi et a. 2004) have been frequently discussed in recent years. So far, however, there is not much information available on the influence of the average reservoir depth on the spatial distribution of Pb in the sediments. This is particularly important when assessing the ecological risk in dam reservoirs used as drinking water reservoirs. The location of the old river bed can also affect the spatial distribution of metals in sediments. However, the results of previous studies in this field are divergent (Kruopienie 2007; Ligęza et al. 2004; Pita, Hyne 1975; Szarek-Gwiazda 2013).

The aim of the study was to identify factors influencing the accumulation of Pb in sediments of deep (dimictic) and shallow (polymictic) dam reservoirs. The examined factors affecting the Pb accumulation were: the variable average depth and topography of the bottom, the content of organic matter and the location of the old river bed. Special emphasis was put on the grain size. The objects of the study were the intramontane and deep Czorsztyn Reservoir (CR) and the shallow Goczałkowice Reservoir (GR), located in southern Poland.

Study area

The studies were carried out in CR located on the Dunajec River and in GR located on the Vistula River (southern Poland).

There are many factors that make the reservoirs different from each other, for example: morphometric features, age, water residence time, trophic state, size of the catchment basin and anthropogenic land use (Table 1). CR is a deep intramontane, mesotrophic and dimictic reservoir, located at a high altitude (NWL–529 m). Water circulation occurs in its deeper part in spring and autumn, while stratification develops in the summer. The water mass exchange occurs on average 3.3 times a year (Mazurkiewicz-Boroń 2002). It is a limnetic reservoir.

GR is a shallow reservoir, thus vulnerable to waves. It is a polymictic reservoir where thermal stratification occurs only in winter when the water surface is frozen and waters are completely mixed in the other seasons. It is an eutrophic reservoir. The exchange of water masses takes place on average 1.5 times a year (Czaplicka-Kotas 2004).

The main functions of CR are: flood control, electricity generation and augmentation of the minimum flows of the Dunajec River, while the main functions of GR include: supply of drinking water for the Silesian agglomeration and flood control. GR serves also as a fishery location.

Table 1

Characteristics of Czorsztyn and Goczałkowice dam reservoirs (Mazurkiewicz-Boroń 2002; Czaplicka-Kotas 2004)

Parameter	Czorsztyn Reservoir (CR)	Goczałkowice Reservoir (GR)
In operation since	1997	1956
Normal Water Level (NWL)	529.0	257.0
Capacity (million m^3)	231.9	166.7
Surface area (km^2)	10.5	32
Mean depth (m)	19.0	5.3
Max depth (m)	46	14
Length (km)	11	12
Width (km)	ca. 1	2-6
Water exchange (times per year)	3.3	1.5
Water exchange (days)	111	238

Materials and methods

Sediment samples (0-5 cm surface layer) were collected from 26 sampling sites situated in CR in May 2006 and from 26 sampling sites situated in GR in August 2010. The sampling sites were located in longitudinal transects: the left bank (transect A – CR and transect D – GR), the central part (transects B and E, respectively) and the right bank (transects C and F, respectively) of the reservoirs (Fig. 1). Such location of sampling sites enabled the investigation of the hypotheses about a potentially different range of Pb concentrations in the proposed groups. Seven sampling sites in CR and nine sites in GR were located in the old river beds, while the remaining sites were located outside the old river beds (Fig. 1). In each sample, the total Pb concentrations, texture, and the content of organic matter were analyzed.

The organic matter in sediment samples was analyzed using the weight method (loss on ignition, LOI). The grain size of sediment samples (fractions: sand 1-0.063 mm, silty clay 0.063-0.002 mm, and clay <0.002 mm) was determined using the aerometric method.

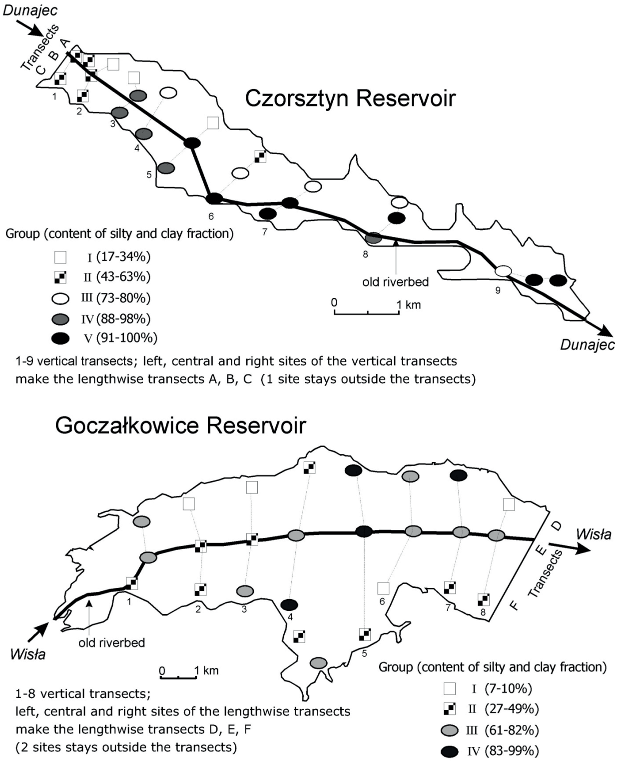


Figure 1

Location of the sampling sites. Identification of groups (clusters) with similar sediment granulations

Prior to Pb analysis, sediment samples were dried at 105°C for 24 h and then sieved through a 0.200 mm sieve. Next, the samples (two subsamples) were digested using 65% HNO_3 in a SpeedWave microwave digester produced by Berghof. Pb concentrations were determined using the AAS method (Varian Spektra AA-20). The Sediment Reference Material (NCS DC 73308, river sediments) was used to check the accuracy of the analytical method. The measured content of Pb in the analytical standard was 28.3 μg g^{-1}, while in the certified Pb sample – 27 μg g^{-1}.

The index of geoaccumulation (I_{geo}) was calculated with the Müller (1981) equation:

$$I_{geo} = log_2\left(\frac{C_n}{1.5B_n}\right)$$

where: C_n is the mean concentration of an element in the bottom sediments, and B_n is the geochemical background of that element in the shale (Turiekian, Wedepohl 1961). Seven categories of sediment contamination, from unpolluted (category 0; I_{geo} <0) to extremely contaminated bottom sediments (category 6; I_{geo} >5), were described according to values of the I_{geo}, Müller (1981).

The ecotoxicological criterion was used to assess the potential hazards related to the presence of Pb in the sediments of the reservoirs. It was based on two thresholds: LEL (lowest effect level, 31 mg Pb kg^{-1}) and SEL (severe effect level, 250 mg Pb kg^{-1}) (Persaud et al. 1992).

Statistics

The data analysis began with normal distribution tests performed on the studied parameters. There were no grounds to reject the hypothesis on the normal distribution for any of the sets of parameters used in this study (n = 26, the Kolmogorov-Smirnov test). Therefore, Pearson linear correlation coefficients were used as measures of parameters' covariance. Pearson linear correlations were used to estimate the relationship between Pb and environmental factors (organic matter, sand, silty clay and clay fractions, depth). Pb concentrations in sediments were analyzed in the fraction <0.2 mm, therefore correlations between Pb and the sand fraction must be treated with caution. While comparing the mean values of parameters for the measurement groups that represent subsets of the whole sample, non-parametric tests were used because in some cases the assumption of normal parameter distribution was not met. Non-parametric tests were also used to compare the mean values of parameters in both reservoirs, because significant differences in the parameter variance were observed.

To estimate the spatial distribution of grain size in the bottom samples collected from the reservoirs, they were classified according to hierarchical cluster analysis. The Euclidean distance and within-groups linkage were used as a grouping method. It was assumed that the groups (clusters) were significantly different from each other when the hypothesis of equality of averages for each possible pair of groups was rejected for two out of three fractions (Mann-Whitney test). Furthermore, it was assumed that the number of groups analyzed was the highest possible with regard to group sizes, which enabled the demonstration of the significance of differences in particle size distribution between groups. The above-mentioned cluster approach was used to investigate the hypotheses whether the resulting classification of the measurement points (sampling sites) relates to their depths, organic content and Pb concentrations. As a result of the hierarchical cluster analysis, dendrograms of similarities were obtained, based on which groups (clusters) of sampling sites can be identified, which show a similar percentage distribution of the three analyzed fractions and are significantly different from each other. Differences in Pb concentrations and environmental parameters in the sediments of the reservoirs were compared: between transects in the reservoirs, between sampling sites located within the old river bed and other sampling sites, as well as between separate clusters (as defined by hierarchical cluster analysis). The analysis was done using the Mann-Whitney test.

Results

In order to identify factors influencing the accumulation of Pb in sediments of deep and shallow dam reservoirs, the authors: (1) analyzed the distribution of grain size and the content of organic matter and Pb in longitudinal transects of the reservoirs; (2) selected groups of sites that were significantly different from each other in terms of grain size (using hierarchical cluster analysis); (3) analyzed Pb concentrations in the old river bed and beyond; (4) analyzed correlations between the values of environmental parameters and the Pb concentrations.

The studied reservoirs show different topography (depth) – more regular in the deep CR and less regular in GR (Fig. 2). The amounts of organic matter in the sediments of both studied reservoirs were low, ranging from 1.7 to 11.2% (mean 6.5%) in CR and from 1.1 to 19.5% (mean 5.7%) in GR. In the sediments of CR, the amount of organic matter was significantly higher in the center (transect B) compared to the left bank (transect A), while in GR it was higher in the center (transect E) compared to the right bank (transect F) (Table 2). In both reservoirs, the amount of organic matter in the sediments was positively correlated with silty clay and clay fractions, and in CR also with the reservoir depth (Table 3).

The sediments of the studied reservoirs showed considerable differences in grain size. In the sediments of CR, the silty clay fraction dominated (range 14.1-84.2%, mean 60.0%), while clay (range 3.3-40.6%, mean 14.4%) and sand (range 0.4-82.6%, mean 25.6%) fractions occurred in smaller amounts. Larger amounts of silty clay and clay fractions occurred in the central part (mean 64.6% and 17.3%, respectively) and at the right bank (mean 68.1 and 19.2%, respectively), while smaller amounts – at the left bank (mean 47.8% and 6.4%, respectively) of CR. At the left bank (transect A), the content of sand fractions was mostly high (25.0-82.6%). Their content was higher than in the central part (transect B), while the content of the silty clay fraction was significantly lower compared to the right bank (transect C) (Table 2). The spatial grain size distribution in CR depended on the reservoir depth. The clay fraction correlated positively, while the sand fraction negatively with the reservoir depth (Table 3).

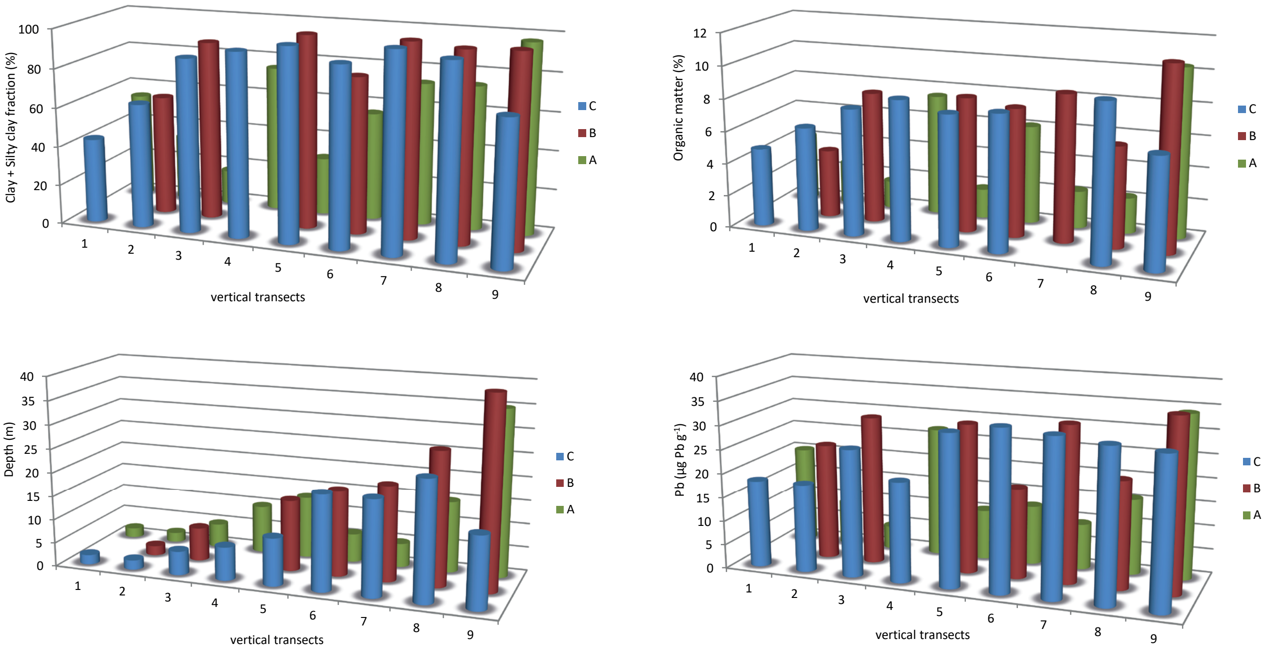
The dendrogram of similarities (Fig. 3), indicating the order of the sampling sites for CR, enabled identification of five groups significantly different in terms of sediment grain size. Sampling sites from group V were located in the deep part of the reservoir (> 15 m, close to the dam), in its central part and on the right bank.

Table 2

Differences in the values of environmental parameters and Pb concentrations in the sediments of Czorsztyn Reservoir and Goczałkowice Reservoir between the studied transects (Mann-Whitney test); only significant differences are noted

Reservoir	Parameter	Transects	Z	p
Czorsztyn	Pb	A-B	-2.15	0.031
		A-C	-2.17	0.030
	Sand fraction	A-B	2.05	0.041
	Silty clay fraction	A-C	-2.26	0.024
	Organic matter	A-B	-2.05	0.042
		A-C	-2.17	0.030
Goczałkowice	Pb	E-F	2.57	0.010
	Sand fraction	E-F	-2.05	0.041
	Clay fraction	E-F	3.26	0.001
	Organic matter	E-F	2.05	0.041
	Depth	E-F	2.21	0.027

Czorsztyn Reservoir



Goczałkowice Reservoir

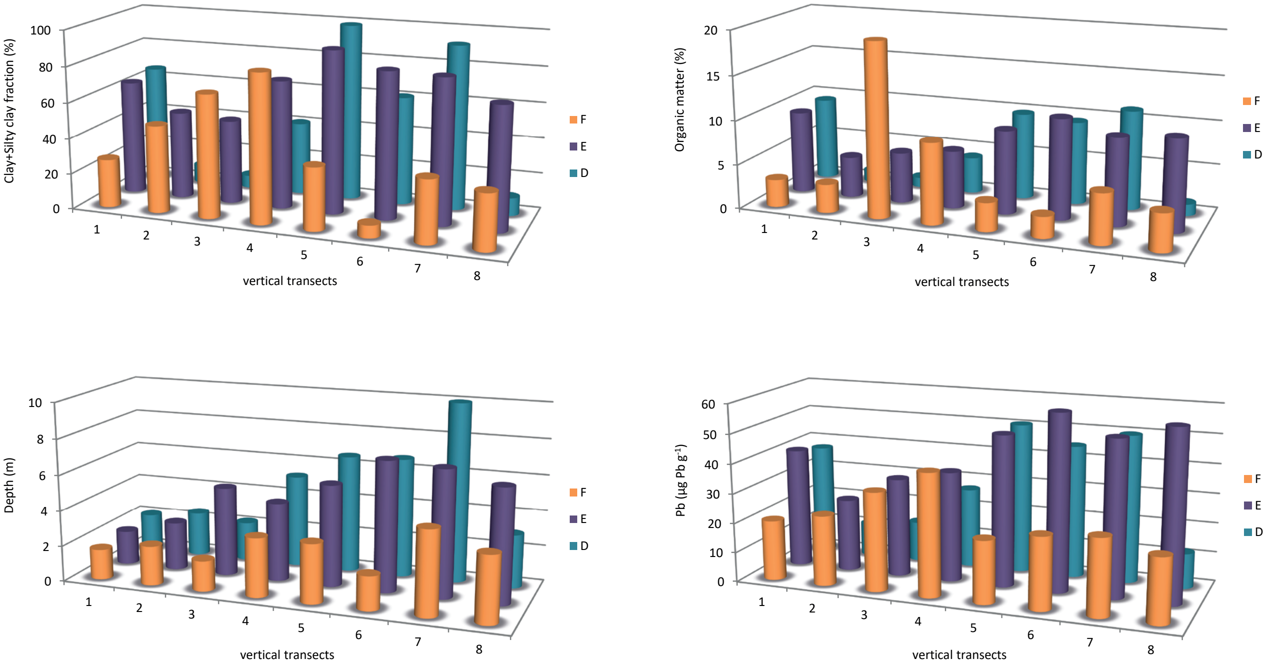


Figure 2

Distribution of selected parameters in Czorsztyn and Goczałkowice Reservoirs (A,B,C,D,E,F – lengthwise transects)

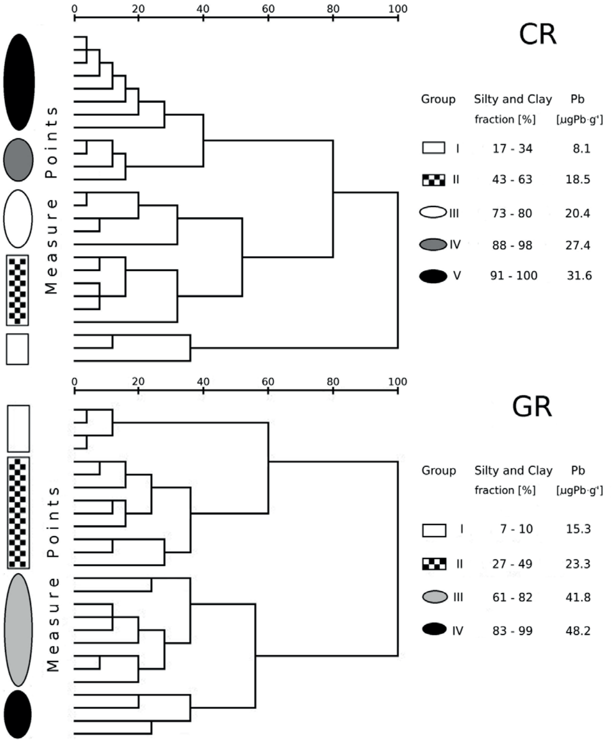


Figure 3

Hierarchical cluster analysis based on sediment granulation in Czorsztyn (CR) and Goczałkowice (GR) Reservoirs. The content of clay and silty clay fractions (range) as well as Pb (mean) in different clusters is given.

They were characterized by a high content of silty clay and clay fractions (much higher than in the other groups) and a low content of the sand fraction (lower than in groups I-III) (Tables 4, 5). Sediment samples of group IV were also characterized by a high content of silty clay (higher than in groups I-III) and clay (much higher than in groups II and I) fractions and a low content of the sand fraction (significantly lower than in groups I-III). They were collected in the middle of the right side of the reservoir, at a depth of 5-10 m. Sediment samples of group III were collected mainly on the left side of the reservoir, at a depth of 5-18 m. Their parameter values ranged between the values of groups IV and V and groups I and II. Sediment samples belonging to groups I and II were collected from the upper and shallow (< 3 m) part of the reservoir. They had a significantly higher content of the sand fraction, and a lower content of silty clay and clay fractions compared to groups III-V (Tables 4, 5). In total, the content of silty clay and clay fractions in groups I-V was: 17-34%, 43-63%, 73-80%, 88-98% and 91-100%, respectively. Sediment samples of group V came from deeper sections, while sediment samples of group II were collected at lower depths compared to groups III and IV. Samples of groups I, III and IV were collected at a similar depth. Sediment samples of groups IV and V had a significantly higher organic content compared to groups I-III (Tables 4, 5).

The sediments of GR had a significantly lower

Table 3

Relationship (Pearson's correlation coefficients) between the particle size, the content of organic matter and Pb in sediment, and depth of Czorsztyn Reservoir (N=26) and Goczałkowice Reservoir (N=26)

Reservoir	Parameter	Silty clay fraction	Sand fraction	Organic matter	Depth	Pb
Czorsztyn	Clay fraction	ns	-0.75 p = 0.000	0.74 p = 0.000	0.93 p = 0.000	0.69 p = 0.000
	Silty clay fraction		-0.93 p = 0.000	0.69 p = 0.000	ns	0.73 p = 0.000
	Sand fraction*			-0.83 p = 0.000	-0.61 p = 0.001	-0.83 p = 0.000
	Organic Matter				0.62 p = 0.001	0.86 p = 0.000
	Depth					0.60 p = 0.001
Goczałkowice	Clay fraction	0.53 p = 0.005	-0.70 p = 0.000	0.58 p = 0.002	0.75 p = 0.000	0.84 p = 0.000
	Silty clay fraction		-0.98 p = 0.000	0.73 p = 0.000	ns	0.73 p = 0.000
	Sand fraction*			-0.76 p = 0.000	-0.58 p = 0.002	-0.83 p = 0.000
	Organic matter				ns	0.77 p = 0.000
	Depth					0.74 p = 0.000

* – concentration of Pb in the 0.2-0.063 mm sand fraction; ns – statistically insignificant (level of significance p>0.05)

Table 4

Mean Pb concentrations and values of the environmental parameters in the sediments of Czorsztyn Reservoir and Goczałkowice Reservoir in the studied clusters

Reservoir	Cluster	Pb (µg g^{-1})	Organic matter (%)	Depth (m)	Fraction (%)		
					Sand	Silty clay	Clay
Czorsztyn	I	8.1	2.0	6.7	73.2	22.1	4.7
	II	18.5	5.0	2.7	44.1	50.7	5.2
	III	20.4	5.3	12.6	25.2	61.1	13.6
	IV	27.4	8.1	7.3	7.4	80.3	12.3
	V	31.6	9.0	25.4	3.1	70.3	26.6
Goczałkowice	I	15.3	1.5	2.4	91.5	6.2	2.2
	II	23.3	3.9	3.4	61.9	30.7	7.5
	III	41.8	9.9	4.4	29.4	55.6	15.0
	IV	48.2	9.9	6.4	8.7	77.8	13.5

Table 5

Significant differences in the values of the environmental parameters and Pb concentrations in the sediments of Czorsztyn Reservoir and Goczałkowice Reservoir between the clusters (Mann-Whitney test)

Clusters	Pb	Organic matter	Depth	Sand	Silty clay	Clay
	significance level (p)					
Czorsztyn Reservoir (CR)						
I, II	0.0201	0.0196	-	0.0201	0.0201	-
I, III	-	-	-	0.0253	0.0253	0.0253
I, IV	0.0339	0.0339	-	0.0339	0.0339	0.0339
I, V	0.0141	0.0164	0.0134	0.0140	0.0140	0.0143
II, III	-	-	0.0072	0.0062	0.0176	0.0062
II, IV	0.0109	0.0103	0.0121	0.0105	0.0105	0.0105
II, V	0.0030	0.0042	0.0015	0.0019	0.0030	0.0019
III, IV	-	0.0275	-	0.0143	0.0143	-
III, V	0.0083	0.0183	0.0077	0.0034	0.0281	0.0281
IV, V	0.0500	-	0.0061	-	0.0066	0.0066
Goczałkowice Reservoir (GR)						
I, II	-	0.0085	-	0.0052	0.0054	0.0344
I, III	0.0087	0.0054	-	0.0053	0.0053	0.0054
I, IV	0.0209	0.0209	0.0219	0.0194	0.0202	0.0384
II, III	0.0041	0.0023	-	0.0003	0.0003	0.0132
II, IV	0.0055	0.0054	0.0370	0.0054	0.0054	-
III, IV	-	-	-	0.0054	0.0054	-

content of the silty clay fraction ($p = 0.006$) and a higher content of the sand fraction ($p = 0.005$) as compared to CR. In general, the sediments of GR were characterized by larger amounts of sand (range 1-93%, mean 47%) and silty clay fractions (range 4-82%, mean 42.8%) and smaller amounts of the clay fraction (range 1-26%, mean 10.2%). Sand fractions in the bank areas showed a considerable variability (ranges: left bank 1-93%; right bank 17-93%). The amount of the silty clay fraction in the studied transects was similar. The right bank (transect F) of the reservoir was characterized by a significantly larger amount of the sand fraction and a smaller amount of the clay fraction as compared to the central part (transect E) (Table 2). The clay fraction showed a positive correlation, while the sand fraction a negative correlation with the reservoir depth (Table 3).

The dendrogram of similarities for GR (Fig. 3) enabled us to distinguish four groups with a significantly different sediment grain-size distribution. Sediment samples belonging to group III were located mainly in the center of the reservoir, along the longitudinal axis, but occasionally also close to its banks and were rich in silty clay and clay fractions (in total 61-82%) (Fig. 1). Sites from groups I, II and IV were located mainly close to the banks (group I, IV – the left bank, group II – the right bank), along the longitudinal axis of the reservoir and in its shallow central part (group II). Sediment samples from group I and II showed a low content of silty clay and clay fractions (in total 7-10% and 27-49%, respectively) and a high content of the sand fraction, as compared to groups III and IV (83-99%) (Fig. 1, Table 5). Sediment samples from groups III and IV had a significantly higher content of organic matter compared to groups I and II (Table 5). They were collected from the deeper part of the reservoir (mean depths for groups I-IV: 2.4, 3.4, 4.4, 6.4 m, respectively; significant differences between group IV compared to groups I and II). It must be emphasized, however, that the topography of the shallow GR was not as regular as that of CR (Fig. 2).

Concentrations of Pb (fraction < 0.2 mm) in the CR sediments ranged from 4.8 to 35.8 $\mu g\ g^{-1}$ (mean 23.1 $\mu g\ g^{-1}$), while in GR – from 11.3 to 59.4 $\mu g\ g^{-1}$ (mean 32.3 $\mu g\ g^{-1}$). They were significantly higher in the sediments of GR compared to CR ($N_1 = 26$, $N_2 = 26$, $p < 0.025$). The highest Pb concentrations in the CR sediments were found near the dam (30.9-35.8 $\mu g\ g^{-1}$), while the lowest in the upper part of the reservoir, near the mouth of the Dunajec River. When comparing the transects, it was found that the mean Pb concentration was higher at the right bank (transect C, 27.06 $\mu g\ g^{-1}$) and in the central part (transect B, 26.94 $\mu g\ g^{-1}$) as compared to the left bank (transect A, 15.66 $\mu g\ g^{-1}$). The differences in the Pb concentrations between the center/right bank and the left bank were statistically significant (Table 2).

Taking into account the CR sediment grain size (separate groups), a significantly higher Pb content was found in samples from group V. They were collected from the deeper part of the reservoir, rich in clay, silty clay and organic matter as compared to the other groups (Tables 4, 5; Fig 1). Sediment samples from group IV, also abundant in silty clay, clay and organic matter, had significantly higher Pb concentrations than samples from groups I and II. The concentrations of Pb in group III (intermediate) were similar to groups II and IV. Sediment samples from group I (the highest content of the sand fraction and the lowest content of silty clay and clay fractions and organic matter) had the lowest mean Pb concentrations (Table 4). Pb concentrations in the CR sediments showed a significant positive correlation with silty clay and clay fractions, organic matter and the depth of the reservoir, and negative correlation with the sand fraction (Table 3). The best correlations were found between Pb concentrations and the content of the silty clay fraction and organic matter.

The mean Pb concentration at the sampling sites located at the old Dunajec river bed was 1.4 times higher than in the remaining part of the reservoir (Table 6). The differences in the Pb concentrations between the old river bed and the remaining part of CR were statistically significant (Table 6).

High Pb concentrations (≥ 40 $\mu g\ g^{-1}$) in the GR sediments occurred in the central upper and lower parts, and on the left and right side of the reservoir (Fig. 1, 2). The mean Pb concentrations in transects D, E and F were 32.0, 44.4 and 22.9 $\mu g\ g^{-1}$ respectively. Significantly higher concentrations of Pb were observed in the central part of the reservoir (transect E) as compared to its left bank (transect F) (Table 2).

Considering the grain size distribution in the reservoir (separate groups), much higher Pb concentrations were found in the sediments from groups III and IV (rich in silty clay, clay and organic matter), compared to groups I and II (Tables 4, 5). Similarly to CR, the lowest Pb concentration was found in the sediments with the highest content of the sand fraction (mean 91.5%) and the lowest content of silty clay, clay and organic matter (group I) (Tables 4, 5). Pb concentrations in the GR sediments showed a significantly positive correlation with the content of silty clay and clay fractions, organic matter content and the reservoir depth, and a negative correlation with the content of the sand fraction (Table 3).

At the sites located at the old river bed, the mean Pb concentration in the sediments was twice as high as the values determined in the reservoir (Table 6). The differences in the Pb sediment concentrations

Table 6

Mean Pb concentrations, standard deviations and the significance levels of Pb concentrations between the old Dunajec river bed and the Czorsztyn Reservoir and the old Vistula river bed and the Goczałkowice Reservoir (Mann-Whitney test)

Reservoir	Area	N	Pb ($\mu g \cdot g^{-1}$)	Significance level
Czorsztyn	Old river bed	7	29.1 ± 4.9	0.046
	Remaining area	19	20.9 ± 9.4	
Goczałkowice	Old river bed	9	41.7 ± 14.2	0.025
	Remaining area	17	27.3 ± 12.7	

N – the number of sampling sites within the area

observed between the old Vistula river bed and the remaining part of GR were statistically significant (Table 6).

According to the geoaccumulation index (I_{geo}), the CR sediments were unpolluted (22 sites) or only slightly polluted (4 sites) with Pb ($-3.4 \leq I_{geo} \leq 0.6$). In the case of GR, slight contamination with Pb was found at 16 sites, and moderate contamination ($0.2 \leq I_{geo} \leq 1.9$) at 9 sites. Moderately polluted sediments occurred mostly at the bottom of GR (the central part and the left bank).

The ecotoxicological criteria showed that the SEL value was not exceeded in any of the reservoirs in this study; the LEL value was exceeded at 7 sampling sites in CR and at 13 sampling sites in GR.

Discussion

The Pb concentrations in the CR sediments were relatively low and typical for the Carpathian dam reservoirs (Gruca-Rokosz 2004; Szarek-Gwiazda, Mazurkiewicz-Boroń 2006; Szarek-Gwiazda 2013) and other slightly polluted sediments (Kruopiene 2007; Krywult et al. 2008; Pokorny et al. 2013). Although sediments of GR showed a low and moderate level of pollution with Pb (according to the geoaccumulation index), the Pb concentrations were much lower than those observed in the dam reservoirs and other aquatic ecosystems under strong human impact from the industrial activities, e.g. up to 1280 $\mu g\ g^{-1}$ in the Cajarc Reservoir, France (Audry et al. 2004), up to 3600 $\mu g\ g^{-1}$ in the Patroon Reservoir, USA (Arnason, Fletcher 2003) and up to 12 000 $\mu g\ g^{-1}$ in small ponds of Upper Silesia, southern Poland (Ciszewski et al. 2013).

Diverse pollution of the sediments results from the location of the reservoir and the catchment land use. The catchment of the intramontane CR is covered with forests and agricultural lands. There is almost no industry there, and the density of the population is low. Potential sources of Pb include: municipal sewage from two cities (population up to 90 000 and about 30 000 tourists/year) and villages located within the catchment area, surface runoff from agricultural lands and illegal waste dumps. GR is more exposed to industrial emissions. It is located close to the large industrial districts of Ostrava-Karviná and Upper Silesia, with a number of industrial plants, e.g. Zn and Pb smelters. Industrial emissions from these areas can reach the reservoir. Also some metal plants, such as an iron foundry and a forging plant (Skoczów) are located within the reservoir catchment area. Additional sources of Pb include agricultural runoff and road transport – both reservoirs are situated close to high-traffic roads.

The reservoirs differ in terms of grain size (higher content of silty clay and clay fractions than the sand fraction in CR compared to GR) due to a different geological structure and different soils in the catchment area. The GR catchment soils include loams and rendzinas, as well as alluvial soil in the river valleys. There are also silty loam soils, carbonate rendzinas and silty loess soils, as well as valley peats in depressions of small permeability (Pasternak 1962). The CR catchment area is covered by rendzinas, silty soils and acid clay soils. There are also acidic peat soils, while the river valleys are covered with silty soils (Pasternak 1968).

The topography of the deep CR was different from the shallow GR, therefore also high content of silty clay and clay fractions was found in different parts of the reservoirs. Grain size sorting, typical for deep reservoirs, was observed in the central part of the deep intramontane CR (decrease in the sand fraction and increase in the clay fraction from its upper to lower part). The high content of the fine fraction (silty clay and clay) along the right bank could be caused by the old bed of the Dunajec River and carbonate rocks found in this area (Szarek-Gwiazda et al. 2011). A higher content of sand along the left bank of the reservoir could be attributed to at least six small local tributaries that allow their coarser fractions to settle while entering the reservoir.

As evidenced by hierarchical cluster analysis, the shallow polymictic GR is characterized by less regular pattern of spatial distribution of sediment grain size across the reservoir basin, compared to CR. In general, higher content of silty clay and clay fractions and organic matter, so potentially capable of binding heavy metals, was present in the deeper central and left bank parts of the reservoir. The sand fraction dominated mainly in the bank parts of GR (also close to the dam) and may be associated with the grain size of soils occurring in the direct catchment basin as well as with the resuspension of fine particles from the shallow part and their accumulation in the deeper part of the reservoir. A similar phenomenon was observed in other reservoirs (Wetzel 2001). Less regular pattern of grain size and organic matter distributions in the shallow GR may also be attributed to waves, resuspension and saltation and consequently sediment movement to other regions. Such a phenomenon was also observed in another polymictic reservoir – Włocławek Reservoir, central Poland (Gierszewski et al. 2006).

The results indicate that the Pb distribution in the sediments, regardless of the depth and the type of reservoirs (polymictic, dimictic), depends on the distribution of silty clay and clay fractions and organic matter. The dominant fractions in the sediments, i.e. the silty clay fraction in CR, and the clay fraction in GR, had a stronger impact on Pb accumulation. It is well known that both clay minerals and organic matter bind heavy metals; the sorption properties of these complexes are determined by their large surface area. The role of grain size (silty clay and clay fractions) in Pb accumulation was observed in other dam reservoirs (Brekhovskikh et al. 2002; Pita, Hyne 1975; Szarek-Gwiazda 2013; Zhang et al. 2002). A positive correlation between the Pb concentrations and fractions of 0.006-0.002 mm and less than 0.002 mm was found in other Carpathian reservoirs, such as Dobczyce and Rożnów Reservoirs, southern Poland (Szarek-Gwiazda 2013), fractions below 0.01 mm in the Ivankovo Reservoir, Russia (Brekhovskikh et al. 2002), silty clay fractions in the Gibson Reservoir, USA (Pita, Hyne 1975), and fractions below 0.02 mm in the Guanting Reservoir, China (Zhang et al. 2002). No correlation between silty clay and clay fractions and Pb concentrations (or other metals) was found in the polymictic Wloclawek Reservoir, Poland (Gierszewski 2008). The author explained it as a predominance of redeposition conditions, which favor sediment mixing and equalize the concentration of metals. The high dynamics of the environment also play an important role in the exchange of elements between sediments and the water in a reservoir. The important role of organic matter (regardless of its content in sediments) in Pb accumulation was also observed in other dam reservoirs (Gierszewski 2008; Szarek-Gwiazda 2013).

Since the Pb concentrations in the sediments were related to the content of silty clay and clay fractions and organic matter, their distribution in the reservoir bottom determined the Pb spatial distribution. Due to sorting of the CR sediment grain size, the distribution of Pb concentrations in the sediments was rather regular – an increase in Pb concentrations in the central part and at the right bank was observed; the Pb concentration increased towards the dam. A similar increase in the Pb concentrations in the sediments along the reservoir depth was also observed in other deep reservoirs, e.g. the Altenwörth Reservoir on the Danube River, Austria (Colley 1988) and the Manwan Reservoir on the Lancang River in China (Zhao et al. 2013). Location of the old river bed and outcrops of carbonate rocks located at the right bank (Szarek-Gwiazda et al. 2011) could be responsible for increased Pb concentrations there. Low Pb concentrations in the left-bank sediments could be attributed to the numerous local tributaries, which induced changes in the sediment grain size.

The less regular topography of the shallow GR favors less regular spatial distribution of Pb in the GR bottom. Pb was mainly accumulated in deeper places, situated in the central and left bank part or at the shallow sites located along the right bank, rich in silty clay and clay fractions and organic matter. Irregular distribution of Pb concentrations was also found in the shallow Kaunas Reservoir, Lithuania (Kruopiene 2007) and Domaniów Reservoir, Poland (Policht-Latawiec, Kanonik 2012).

The obtained results indicate that the determination of Pb concentrations in the sediments in the longitudinal transects of the reservoirs provide only a general overview of Pb distribution in the sediments. The use of hierarchical cluster analysis and identification of sediment samples with a significantly different grain size helped to better understand the Pb concentration distribution in the bottom sediments, especially in the case of the shallow GR (with more varied topography).

The results indicate that the original location of the old river bed had an important role in the Pb distribution in the sediments. This effect was more pronounced in the case of the strongly contaminated and shallow GR since its main tributary – the Vistula River – carries a significant load of this metal. The results show that the Pb accumulation occurs within the area of the old river bed. The small difference in the Pb concentrations in the river bed within CR, despite the difference in the pollution level, could be associated with a stronger sediment sorting, typical of deep reservoirs (e.g. resuspension of sediments down to the deeper parts). Other authors (Kruopiene 2007; Ligęza et al. 2004; Pita, Hyne 1975; Szarek-Gwiazda 2013) reported either no differences or an increase/decrease in metal concentrations close to the old river bed. An increase in Pb concentrations in the sediments near the old river bed was found in the

Gibson Reservoir, USA, located close to Cd, Zn and Pb mines and smelters (Pita, Hyne 1975) and in the Kaunas Reservoir on the Nemunas River, Lithuania (Kruopiene 2007). No differences or lower Pb concentrations close to the old river bed were observed in reservoirs less polluted with the metal (Ligęza et al. 2004; Szarek-Gwiazda 2013).

Since sediments are an integral part of the aquatic environment and provide a habitat for many aquatic organisms, high concentrations of heavy metals pose a threat to biota. It should be noted, however, that the bioavailability of contaminants depends on many factors related to both pollutants and characteristics of the aquatic environment (Zhang et al. 2014). The results of the LEL/SEL method indicate a potential harmful effect of Pb on benthic organisms, as well as on the fish feeding on them.

Conclusions

The accumulation of Pb in the sediments of the deep intramontane CR and the shallow GR was influenced by similar factors: the content of silty clay and clay fractions and organic matter in the sediments, the reservoir depth, and the location of the old river bed. One of the most important factors influencing the spatial distribution of Pb content in the bottom sediments was the reservoir depth. The bottom topography was more regular in the deep CR and less regular in the shallow GR. CR had a grain size sorting typical for deep reservoirs; the sand fraction decreased and the clay fraction increased from the upper to the lower part. The less regular topography of the shallow GR (deeper place in the central and left bank part) favors the accumulation of silty clay and clay fractions and organic matter in these areas. The obtained results indicate that slightly different topography of deep and shallow reservoirs favored different patterns of spatial distribution of silty clay and clay fractions and organic matter with a potential capacity to bind Pb in the bottom. The use of hierarchical cluster analysis enables us to identify sediment samples with similar grain size within the bottom of the reservoirs. It was a good tool to better understand the spatial distribution of Pb concentration in the reservoir bottom. The location of old river beds also had a strong impact on Pb concentrations in the sediments of both reservoirs. Higher Pb concentrations were found within the old river bed, and this phenomenon was more apparent in the shallow and strongly contaminated GR. The higher content of fine fractions in the right bank part of CR was also associated with the old river bed. We must remember, however, that the number of other factors, like small scale water circulation, influence of smaller tributaries, contamination sources in the direct catchment and waves favoring the resuspension, may also affect the Pb accumulation in the bottom sediments.

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