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PHYSICO-CHEMICAL PARAMETERS DETERMINING
THE VARIABILITY OF ACTUALLY AND POTENTIALLY
AVAILABLE FRACTIONS OF HEAVY METALS IN FLUVIAL
SEDIMENTS OF THE MIDDLE ODRÁ RIVER

ALEKSANDRA IBRAGIMOW^{1*}, BARBARA WALNA², MARCIN SIEPAK³

¹Adam Mickiewicz University, Polish-German Research Institute in Collegium Polonicum,
Kościuszki 1, 69-100 Ślubice, Poland

²Adam Mickiewicz University, Jezioro Ecological Station,
P.O. Box 40, 62-050 Mosina, Poland

³Adam Mickiewicz University, Institute of Geology, Department of Hydrogeology and Water Protection,
Maków Polnych 16, 61-606 Poznań, Poland

*Corresponding author's e-mail: ibrisej@amu.edu.pl

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Abstract: The occurrence of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) has been determined in the fluvial sediment samples collected along three transects in the Middle Odra River (western Poland) with a width of 360 m. The total concentrations of the metals were obtained after HNO₃ microwave digestion and the available fractions of heavy metals were determined by single extraction procedures using two extractants: 0.01M CaCl₂ and 0.05M EDTA. The measurement of physico-chemical parameters was also performed. The determination of total and available fractions of heavy metals, except potential available fractions of Cr, revealed high concentrations of studied elements detected in the sediment samples characterized by high content of coarse and very coarse-grained sand fraction and high content of organic matter. It was found that the concentrations of total and available fractions of metals could increase along with the content of organic matter, Eh values and concentrations of H⁺. Apart from the above, those concentrations become the lowest, the higher the content of medium grain size fractions is. Furthermore, the amounts of CaCl₂ and EDTA extractable metals increase in the sediments samples characterized by the lowest total and available concentrations of heavy metals.

INTRODUCTION

For the last three decades river sediments have been recognized as the long term memory of rivers and their catchments [5, 59]. They are stable during normal river flows and may be eroded in the conditions of rising water and floods. Such conditions can lead to the increase of pollution of river bed sediments, river water and floodplain areas, as well as to the remobilization of contaminants such as heavy metals [14]. Heavy metals are subject to sorption, complexation and coprecipitation with solid particles, and the amount of potentially available fractions increases under favorable physico-chemical conditions [13, 14, 48]. The mobility of heavy metal compounds depends on their solubility,

which is affected by redox potential (Eh), pH, grain size composition (especially high content of silt and clay fractions), the content of organic matter and also the content of CaCO_3 [59]. Besides, environmental studies dealing with the determination of the total content of metals do not provide information concerning their mobility and availability because the toxic effects of heavy metals depend on their chemical form [2, 26, 30]. The concentration of the fractions of heavy metals fractions which are potentially absorbed by living organisms, thus determines the degree of threat [52]. The method of single extraction involves subjecting a soil or sediment sample to one extractant in order to determine the fractions of metals that are actually or potentially available for plants or organisms [4], and/or susceptible to eluviation [33, 37]. It involves the use of so-called 'soft extractants', which include non-buffered salt solutions (e.g. KCl , CaCl_2 , NaNO_3) and solutions of complexant agents (e.g. EDTA, DTPA) [42].

Non-buffered salt solutions release the cation – exchangeable fraction [34, 56]. At present, the CaCl_2 extractable pool proved to give a better indication of the actual element availability for plant uptake than concentrations obtained with other extraction reagents [37, 22, 44], whereas EDTA showed good extractive efficiency, with classic complexation reaction of different heavy metal cations and released heavy metals from soil exchangeable and organically complexed 'pools' [41, 47]. It also had an influence on heavy metals bound in iron carbonates and hydroxides [6]. Moreover, 0.05 M EDTA is a widely used extractant for plant-available heavy metal determination [11, 54, 60].

The paper presents the results of determination of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in the fluvial sediment from surface layer (0–30 cm) in the Middle Odra River (western Poland). The aim of this study was to compare concentrations of heavy metals in fluvial sediments collected along transects characterized by the same width and to find the correlations of the fractions of heavy metals with physico-chemical properties of the collected sediments.

STUDY AREA

The study areas were located in the Odra River valley in western Poland. The sediment samples were collected along three transects (T1, T2, T3) located on the 548th, 575th and 609th km of the Odra River characterized by the width of 360 m (Figs 1, 2). Transect T1 was situated higher above the sea level (between 38.5 and 41.5 m a.s.l.) than transect T2 (between 23.0 and 24.7 m a.s.l.) and T3 (between 13.5 and 16.5 m a.s.l.) and the elevation differences was over 10 m (Fig. 2). In each transect four sampling sites were established and from each sampling site five sub-samples were collected.

METHODOLOGY

The sampling took place in November 2009. Five sub-samples from the surface layer (0–30 cm) were collected with a stainless steel scoop in each sampling site into polyethylene bags.

In the laboratory, the sub-samples were mixed thoroughly to get a representative sample from each sampling site and they were dried in the room temperature. Every sample was split into two halves. For the purpose of grain size analysis one of the halves was passed through sieves with mesh sizes of (μm): 4000, 2800, 2000, 1400, 1000,

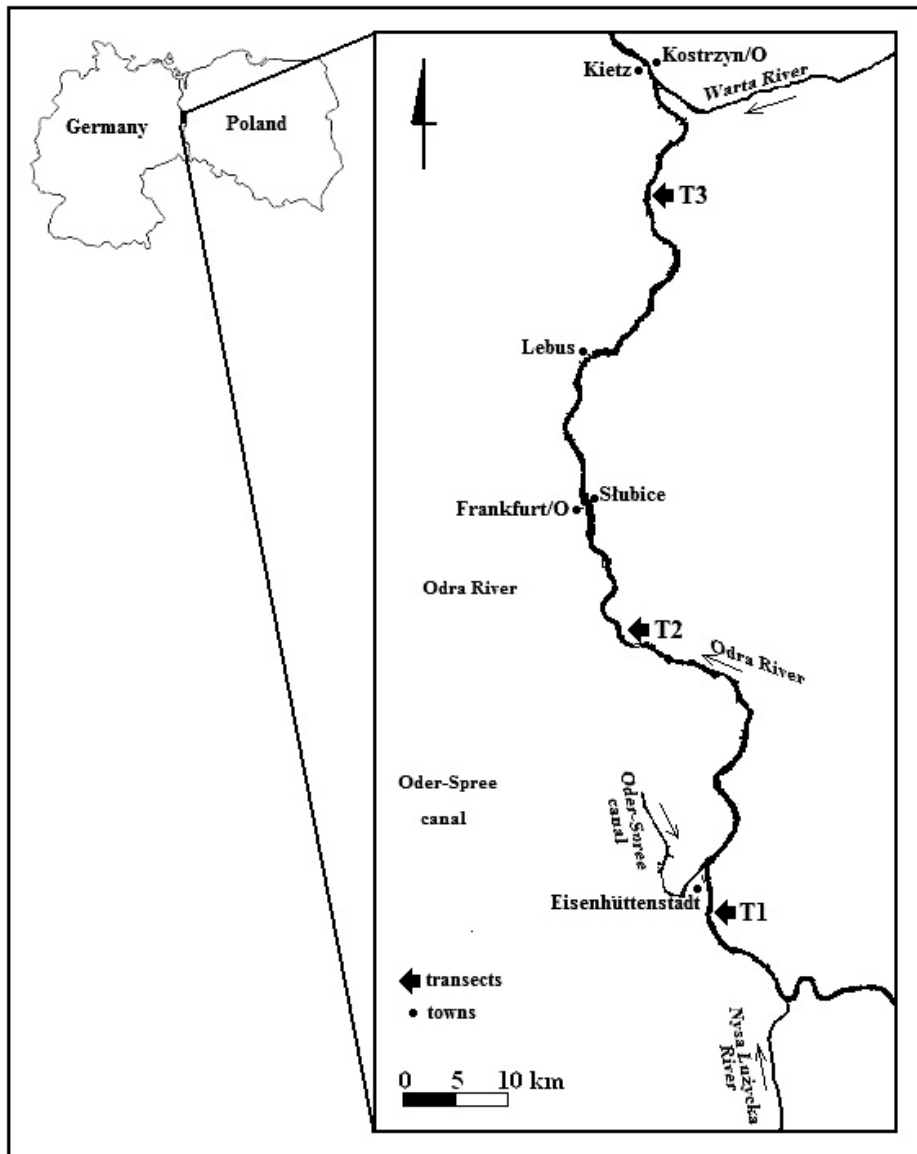


Fig. 1. Study area

800, 630, 500, 400, 315, 250, 200, 160, 125, 100, 90, 50, according to the Polish Norms [38, 40]. The grain size fractions analysis was performed using the grain size analysis program GRADISTAT v. 6.0 [49]. The remaining half was sieved through a non-metallic sieve with 2.0 mm mesh size and subjected to physico-chemical analysis. The pH (H_2O) was measured in a soil-in-water suspension (1:2.5) with the laboratory electrode EH-02 Hydromet. In order to determine the content of organic matter (OM), the air-dried sediment samples were dried at 110°C and then combusted at 550°C. The content of

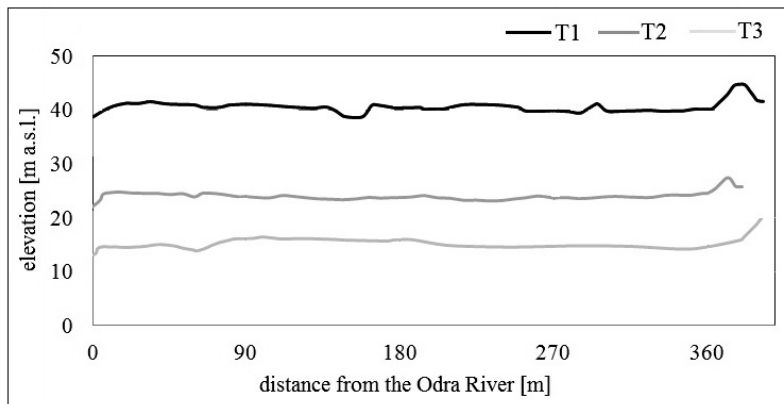


Fig. 2. The location and elevations of the transects

calcium carbonate was determined by the Scheibler method [39]. The total metal concentrations were obtained after HNO_3 microwave digestion [16]. The concentrations of the available fractions of the metals were obtained after a single-stage extraction with 0.01M CaCl_2 with the ratio 1:10 sediment/solution and they were mixed by shaking on an end-over-end shaker for 3 h [29]. The concentrations of the potential available fractions of the metals were obtained after a single-stage extraction with 0.05M EDTA with the ratio 1:10 sediment/solution and they were mixed by shaking on an end-over-end shaker for 1 h [28, 29]. Every sediment sample was analyzed three times and the result was calculated as the average value.

Heavy metals were determined using atomic absorption spectrometer with acetylene-air flame atomization (F-AAS). A fast sequential atomic absorption spectrometer SpectrAA 280 FS (Varian, Australia) was used. The samples were batched using an SPS3 autosampler (Varian, Australia). The reagents used in the analyses were analytically pure, and the water was deionised to the resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ in a Direct-Q[®] 3 Ultrapure Water System apparatus (Millipore, France). Standard solutions were prepared using Merck commercial standards for AAS (Merck, Darmstadt, Germany). The accuracy of the total heavy metal measurements was determined on the basis of certified reference material (CRM055-050), with a recovery rate of (%): 98.0 for Cd, 98.3 for Cr, 98.6% for Cu, 97.5% for Ni, 99.4 for Pb and 98.1% for Zn.

The statistical analysis of the results was performed in the *Statistica v. 8.0* program. Along with the basic statistical parameters, the analysis of the correlation between the variables at the relevance levels $\alpha < 0.05$ was conducted. The measurement of the correlation forces was determined based on the values of correlation coefficient, and strong correlation was determined based on the $r > 0.50$ value.

RESULTS AND DISCUSSION

Physico-chemical properties of fluvial sediments

Considering the grain size distribution of the studied flood sediments, it can be generally concluded that the samples are dominated by sedimentary material of medium sand size

(500–250 μm), coarse sand (1000–500 μm), and very coarse sand (2000–1000 μm) (Tab. 1). They are also negatively and symmetrically skewed (83.3% samples) and their distribution is mesokurtic (75% samples). A precise granulometric analysis of the collected sediments was difficult because their density had a bimodal distribution. There consist mineral grains with densities corresponding to mineralogical densities of the minerals involved, and fragments of organic matter with densities close to $1 \text{ g}\cdot\text{cm}^{-3}$. In the size fractions where the grain size distribution could not be obtained by sieving ($< 50 \mu\text{m}$), the separation of the individual size categories of particles by the usual sedimentation method (based on Stoke's Law) is thus strongly inhibited [35]. With respect to these difficulties, the finest fractions (silt and clay) were not separated. However, the content of silt and clay in the analyzed sediment samples was low and did not exceed 2.3% (Tab. 1). It is well known that the grain size of the sediment had a crucial effect on the concentrations and spatial distribution of heavy metals [18, 19 27]. It was found that the highest concentrations of Cd, Cr, Cu, Ni and Zn were observed in the fine fraction ($< 63 \mu\text{m}$) and in the gravel fractions ($> 2000 \mu\text{m}$) [31, 32, 33]. Also a negative correlation was showed for the medium sand fraction (500–250 μm) and heavy metals concentrations [18, 19]. Therefore it can be concluded that in the sediment samples collected from the transects T1 and T2, which are characterized by high contents or very coarse and coarse fractions of grain size (Tab. 1), the highest concentrations of heavy metals can be demonstrated.

The collected sediment samples are characterized by high values of Eh above 363 mV and average Eh values above 376 mV (Tab. 1). At such high values of Eh the reduction of NO_3^- to NO_2^- , MnO_2 to Mn^{2+} , $\text{Fe}(\text{OH})_3$ to Fe^{2+} , SO_4^{2-} to S^{2-} and the decomposition of organic matter and methane production do not take place [25, 43]. Moreover, it was found that in such conditions heavy metals occur in hardly soluble fractions [20, 24]. However, flooding can cause the decrease in Eh values [25]. With the decrease in Eh flooded soils the solubility of Fe and Mn increases by a reductive dissolution process [23]. Hydrous Mn and Fe oxides are thought to immobilize the heavy metals by providing sites for their sorption in most soils [23, 25, 32, 57]. The dissolution of Fe and Mn from oxides should, therefore, be accompanied by the release of heavy metals [25]. Moreover, under the indirect effects of flooding conditions (low Eh) sulphate ions are reduced to the sulphide form that may form a complex with Cd, Ni and Zn and immobilize them as a sulphide salts (e.g. CdS) [55]. The study area is characterized by frequent flooding that changes aerobic and anaerobic conditions of sediments. Previous research showed that the fluvial sediments of the Middle Odra River are characterized by high concentrations of Cd, Cu, Pb and Zn [7, 8, 21]. For this reason, changes in the Eh values can be a serious threat.

The pH values of the collected sediments were neutral, slightly acidic and acidic (Tab. 1), and the lowest average $\text{pH}(\text{H}_2\text{O})$ values and $\text{pH}(\text{KCl})$ values were 5.61 and 4.91 (Tab. 1). The pH is the most important factor which governs the solid-solution equilibrium of metals in soils [1]. The more acidic is the soil, the less likely it is to bind heavy metals steadily and the higher proportion remains in available fractions in the solution or the more it infiltrates into deeper levels of the soil profiles [50]. The indicated pH values can contribute to the release of heavy metals – especially the cadmium and the zinc – whose migration occurs even at pH values between 6.5 and 6.0 [50].

The average sediments moisture was up to 4.3% and the content of organic matter in the analyzed sediment samples was high, and the highest maximum values were up to 30% (Tab. 1). High organic matter content can be the most important parameter that influences

the accumulation of heavy metals in sandy sediments characterized by low sorption capacity [10]. It was also shown that the adsorption of most heavy metals in the sediments increased with the increase of organic matter content [3, 31, 45, 46]. However, by the decomposition of organic matter the associated heavy metals can be released, migrate to the groundwater and accumulate in the layer with a higher sorption capacity [10, 31].

In the collected sediment samples the content of CaCO_3 ranged between 2.3% and 5.4%, and the highest average value was 4.3% (Tab. 1). There are no direct relationships between the CaCO_3 content and heavy metals content of the sediments. However, CaCO_3 influences the binding of heavy metals in the sediments through the formation of carbonates and indirectly, though the modification of the pH [50]. With the decrease of pH increases the solubility of CaCO_3 increases and ion exchange becomes the most important process which controls the uptake and accumulation of heavy metals [15]. However, taking into account the fact that the pH of the analyzed sediments is in most cases low, the influence of this parameter on the immobilization of cadmium, chromium, copper, nickel, lead and zinc may be very little.

Concentrations of heavy metals

In the fluvial sediment samples collected from transects T1 and T2 on the 548th and 575th km of the river course total and available concentrations of most studied metals were the highest (Fig. 3, 4, 5).

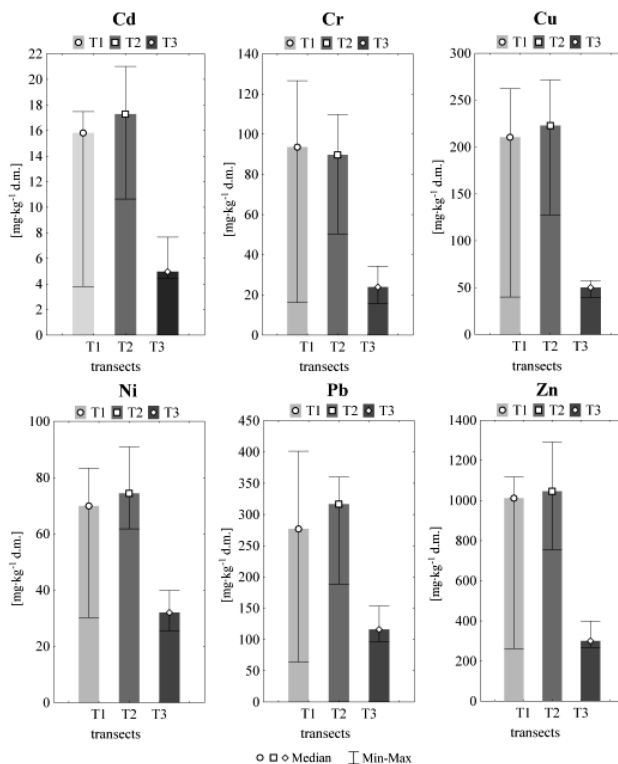


Fig. 3. The total concentrations of heavy metals found in the sediment samples

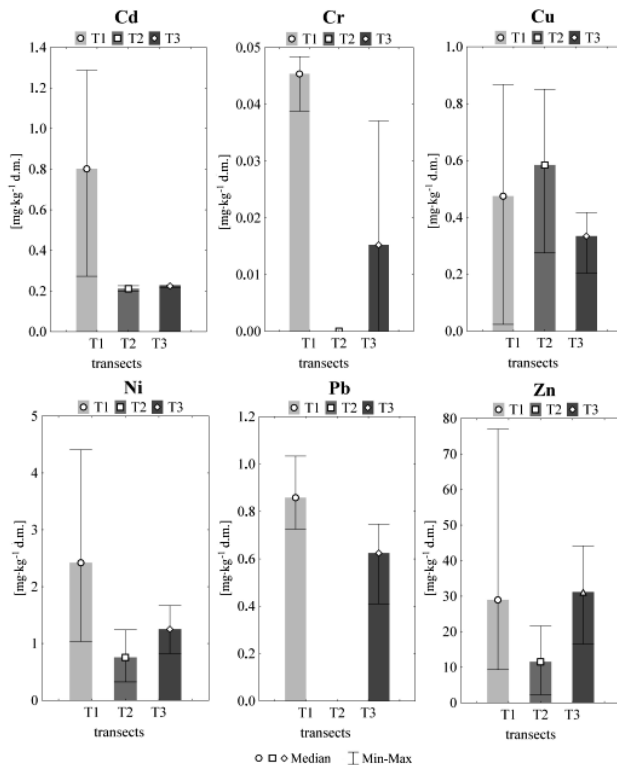


Fig. 4. The concentrations of the actually available forms (CaCl₂ extractable) of the heavy metals found in the sediment samples

The highest average concentrations of actually available fractions of Cd (0.80 mg·kg⁻¹) and Ni (2.42 mg·kg⁻¹) and potentially available fractions of Ni (12.2 mg·kg⁻¹) and Zn (277 mg·kg⁻¹) were found in sediment samples collected from the transect T1 (Fig. 4, 5). These sediments are classified as poorly sorted coarse and medium sand with a high content of very coarse-grained sand fraction of grain size 2000–1000 μm (up to 61%) and low maximum content of the smallest fractions of grain size < 50 μm (up to 1.3%). They were negatively and symmetrically skewed and their distribution was mesokurtic. Besides, in those sediments the Eh values were high (average 410 mV), pH(H₂O) was slightly acidic (average 5.61) and pH(KCl) was acidic (average 5.06), the organic matter content was high (average 21%) and the content of CaCO₃ was low (average 3.1%) (Tab. 1). In the sediment samples collected from transect T2 the highest average total concentrations of the following metals were found: Cd (16.6 mg·kg⁻¹), Cr (84.9 mg·kg⁻¹), Cu (211 mg·kg⁻¹), Ni (75.4 mg·kg⁻¹), Pb (295 mg·kg⁻¹) and Zn (1034 mg·kg⁻¹), actually available fractions of Pb (1.24 mg·kg⁻¹) and potentially available fractions of Cd (3.95 mg·kg⁻¹), Cu (107 mg·kg⁻¹) and Pb (103 mg·kg⁻¹) (Fig. 3, 4, 5). These sediments are classified as poorly sorted medium and coarse sand characterized by negatively skewed and mesokurtic distribution. The content of coarse-grained sand fraction of grain size 1000–500 μm was high (up to 33%), and the content of the smallest fractions of grain size

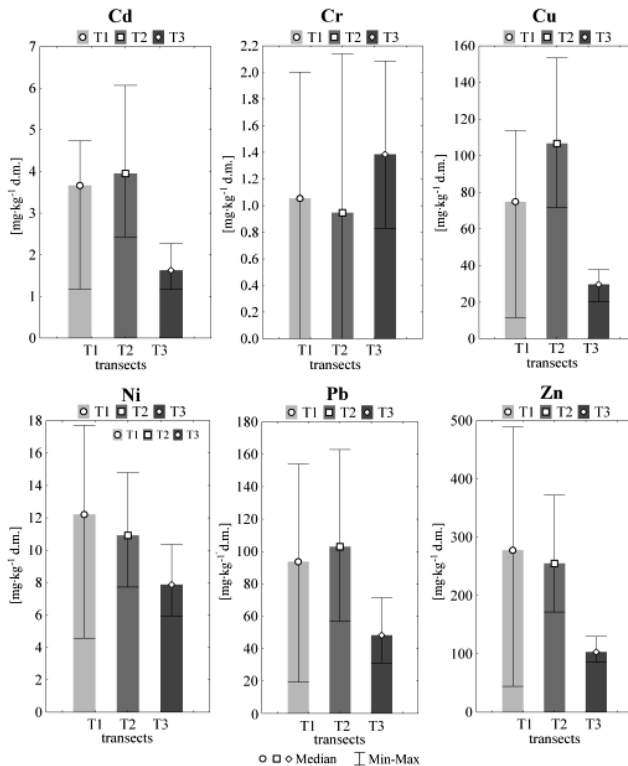


Fig. 5. The concentrations of the potentially available forms (EDTA extractable) of the heavy metals found in the sediment samples

< 50 μm was low (up to 2.2%) (Table. 1). Those sediments were poorly sorted, negatively skewed and their distribution was mesokurtic. Furthermore, they were characterized by moderately reduced Eh values (average 376 mV), slightly acidic pH(H₂O) (average 6.27) and pH(KCl) (average 5.65), high organic matter content (average 17%) and low CaCO₃ content (average 3.5%). It was also shown that the total concentrations obtained in the sediment samples from transects T1 and T2 were up to several times higher than the concentrations obtained in the sediment samples from the transect T3 collected on the 609th km of the river course and located above 20 m a.s.l. than the ones obtained from transects T1 and T2 (Fig. 3).

In the sediment samples collected from transect T3 the highest average concentrations of actually available fractions of Zn (31.1 mg·kg⁻¹) were found, as well as the potentially available fractions of Cr (1.38 mg·kg⁻¹) (Figs 4, 5). These sediments are classified as moderately sorted medium sand, characterized by negatively skewed and mesokurtic distribution. The content of the smallest fractions of grain size < 50 μm was very low (maximum 2.3%) (Table. 1). Furthermore, they were characterized by oxidizing Eh values (average 401 mV), acidic pH(H₂O) (average 5.67) and pH(KCl) (average 4.91), high organic matter content (average 8.8%) and low CaCO₃ content (average 4.3).

Tab. 1. Physical and chemical characteristics of the sediments

Transects	Statistical parameters	Eh	pH (H ₂ O)	pH (KCl)	OM [%]	CaCO ₃ [%]	Content [%] of grain size frsctions [μm]					
							2000-1000	1000-500	500-250	250-100	100-50	<50
T1	min	385	5.18	4.56	5.5	2.3	17	25	6.4	3.9	0.8	0.3
	max	448	6.17	5.52	30	3.8	61	35	31	17	5.2	2.2
	average	410	5.61	5.06	21	3.1	29	31	21	14	3.0	1.3
	median	403	5.55	5.08	24	3.2	19	32	23	17	3.0	1.3
T2	min	363	6.00	5.40	16	2.7	20	27	20	16	3.6	1.5
	max	363	6.00	5.40	16	2.7	29	33	28	19	5.2	2.2
	average	376	6.27	5.65	17	3.5	23	29	24	18	4.5	1.9
	median	373	6.29	5.65	17	3.4	21	28	24	18	4.6	2.0
T3	min	390	5.52	4.67	6.5	3.9	1.5	5.0	30	15	1.3	0.6
	max	422	5.98	5.21	10	5.4	26	29	45	41	5.3	2.3
	average	401	5.67	4.91	8.8	4.3	15	21	36	23	2.8	1.2
	median	396	5.58	4.88	9.2	3.9	17	26	35	18	2.3	1.0

It also seems noteworthy that the concentrations of actually available fractions of Cr found in the sediment samples collected from transects T1, T2 and T3 were below the detection limit or were very low between 0.02 and 0.05 mg·kg⁻¹ (Figs 3, 4, 5). Also, the concentrations of actually available fractions of Cu, irrespective of the physical and chemical parameters of the sediments, were found to be on the same level between 0.33 mg·kg⁻¹ and 0.58 mg·kg⁻¹ (Figs 3, 4, 5) in the sediment samples from each transect.

Taking into account the fact that on the 559 km of the River course the town of Eisenhüttenstadt is located with its metallurgical plant and Oder-Spree canal flowing into the Odra River, one should expect to find a content of analyzed metals especially in the sediment samples from transect T2 located on the 575th km of the river course. However, it was found that the highest concentrations were obtained in the sediment samples collected on the 548th km of the river course. In the case of the lower reaches of the Odra River, the contaminant also comes from the upper reaches of the Odra River and from the Nysa Łużycka River [7, 8, 21]. The lowest concentrations of the investigated metals, except the actually available fractions of Zn and potentially available fractions of Cr, were found in the sediment samples collected about 50 km further in transect T3 on the 609th km of the river course. A consistent trend showing a decrease in the concentration of heavy metals with the increasing distance from the sources of pollutants was observed in the past [36, 58]. These results are not completely consistent with the studies which showed that the highest concentrations of the metals are found in the sediment samples collected from transects with the lowest elevations below sea level [51]. Those transects were frequently inundated by flooding and they remained inundated for a longer time than transects with the highest elevation below sea level [10, 51]. Low concentrations of heavy metals found in a sediment sample collected from transect T3 could be also defined by the physico-chemical parameters of the collected sediment samples, i.e. sediment grain size

(high content of medium sand fraction) and the content of organic matter lower than in the sediment samples from transects T1 and T2. For the total concentrations of Cd, Cr, Cu, Ni, Pb and Zn, strong positive correlation with the content of organic matter (r from 0.70 to 0.83) was found, as well as strongly negative correlation with the content of the medium sand fraction (r from -0.71 to -0.80). Also for the potential available concentrations of Cd, Cu, Ni, Pb and Zn, strong positive correlation with the content of organic matter (r from 0.62 to 0.91) and strong negative correlation with the content of the medium sand fraction (r from -0.65 to -0.72) were found. While the actually available fractions of Cd and Ni are strongly positively correlated with Eh values (r from 0.72 to 0.88), Cd, Ni and Zn are strongly correlated with the content of H^+ calculated on the basis of $pH(H_2O)$ and $pH(KCl)$ (r from 0.60 to 0.94), Cd, Cu and Ni are strongly correlated with the content of organic matter (r from 0.63 to 0.74). It has been shown that the available fractions of the studied heavy metals can be determined by physico-chemical parameters of the fluvial sediments that may change rapidly as a result of inundation of fluvial sediments. A consistent trend was observed in previous studies which also showed that the total and actually available concentrations of heavy metals are strongly positively correlated with the content of organic matter [9, 12, 17, 56] and strongly negatively correlated with the content of medium sand fraction [18, 19, 56]. Heavy metal concentrations can also be strongly positively correlated with the content of silt and clay fractions [45, 53, 55]. However, in this study this relationship has not been confirmed. This is undoubtedly due to the fact that the content of silt and clay fractions was low in the investigated sediments (average < 2.0%).

By comparing the actually and potentially available concentrations of heavy metals with the total concentrations of heavy metals, the amount of their extracted available fractions was identified. For the actually available fractions of Cu, Ni, Pb and Zn the extracted amounts were the highest in the sediment samples collected from transect T3. However, in those sediment samples the concentrations of Cu, Ni, Pb and Zn was not the highest. Besides, the average $CaCl_2$ extracted amounts in the analyzed sediment samples from transects T1, T2 and T3 were the highest for Zn (about 9%), Cd (about 6%) and Ni (about 4%). Also for the potentially available fractions of Cd, Cu, Ni, Pb and Zn the same conclusion was drawn. The highest amounts of the potentially available fractions of Cd were obtained in the sediment samples from transect T2 and of Cu, Ni, Pb and Zn in the sediment samples from transect T3, although the concentrations of heavy metals in these sediments were not the highest. Besides, those average amounts were about 60% for Cu, about 40% for Pb, between 20% and 30% for Cd, Ni and Zn and about 6% for Cr.

These results are not completely consistent with the studies which showed that the highest concentrations of available fractions of heavy metals found in the sediment samples increase along with the increasing concentrations found in those sediments [4]. However, it can be concluded that the high amounts of $CaCl_2$ and EDTA extractable heavy metals can be obtained in the sediment samples collected from transects with the lowest elevations below sea level characterized by long duration of inundation.

CONCLUSIONS

1. The highest total and available concentrations of investigated heavy metals – except for potentially available fractions of Cr – were detected in the sediment samples which

- are characterized by high content of coarse and very coarse-grained sand fractions and high content of organic matter.
2. For the concentration of total and potential available fractions of heavy metals high positive correlations with organic matter content (r between 0.62 and 0.91) and high negative correlations with medium grain size fractions (r between -0.65 and -0.80) were showed.
 3. For the available fractions of heavy metals strong positive correlations were found with the Eh values (r between 0.72 and 0.82) and concentrations of H^+ (r between 0.60 and 0.94).
 4. The highest amounts of extracted available fractions of heavy metals are detected in the sediment samples from the transects characterized by long duration of inundation and the lowest total and available concentrations of heavy metals.

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