

Metal forms in bottom sediments as a bioavailability indicator

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Abstract. *This study assessed the risk of water biocenosis caused by the potentially bioavailable metal forms. In a simple extraction process, the efficiency of metals eluting from the sediments was highest for EDTA solution. Sequential extraction has confirmed the diverse bioavailability of metals in the aquatic environment.*

Keywords: metals, sediments, single and sequential speciation, bioavailability

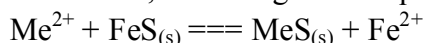
Introduction

Upon reaching water, metals react with substances contained in it, then settle on the bottom and react with the sediment components. The most important processes of metal immobilization in sediments are: chemisorption, precipitation, co-precipitation and complexation [1, 2]. In mineral structures, ion of K^+ or Ca^{2+} can be exchanged for other ion metals (Me^{2+}), e.g in clay or shells. Carbonates and phosphates are other important components in these processes. Chemisorption and co-precipitation of metals heavily depends on the presence of hydrated Fe/Mn oxides. These metals are chemically reactive in their reduced form of Fe(II) and Mn(II), and insoluble forms are present in the oxidized compounds Mn(III, IV), Fe(III). On the surface of these compounds sorption of hydrogen ions or of metal cations occurs as following [3]:



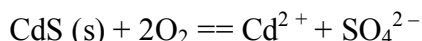
Karczewska [4] showed, that manganese oxides bind 1-30 % of total Cu content, 1-26 % of Pb, 4-27% of Zn and <1% of As, amorphous iron oxides bind 3-24% Cu, 1-54% Pb, 3-25% Zn and 42-90% As, and crystalline oxides: 3- 29% Cu, 1-53% Pb, 9-34% Zn and 5-46% As.

An equally important solid phase of metal binding in sediments are sulfides (eg. FeS), in which iron can be replaced with another metal, according to the equation:



Metals bound in sulfides can be released under appropriate conditions into an aqueous solution.

The high contribution of Cd in mobile sediment forms may be due to the process in which cadmium sulfide is partially or completely oxidized to a soluble form of $CdSO_4$ under aerobic conditions:



This reaction is very likely to happen in the shallow river sediments, where near-bottom layers of the river are well oxygenated and where variable hydrological conditions along with redox potential changes at the water- sediment boundary can be observed.

The chemical composition of bottom sediments is in many cases a better environmental pollution indicator than the water composition. The content of chemical elements changes between the sediment layers, showing the historical contamination changes of the reservoir [5].

In environmental studies of bottom sediment samples, the total metal content is the most popular indicator, because it shows the extent of sediment contamination. Bioavailability and mobility may be assessed by using a single (simple) extraction, where the natural conditions of components passing from the testing sample directly to the solution are simulated [6]. The single extraction method consists of applying the extrahent to the sediment sample to determine the metal forms, which then pass to the extraction solution. It reflects the biological metal

bioavailability by plants or organisms and the susceptibility of the metal leaching [7]. In a single extraction, the following solutions are used: neutral solutions (H_2O , $\text{CH}_3\text{COONH}_4$), complex metal solutions (EDTA, NTA, DTPA) or high ionic strength solutions (CaCl_2 , MgCl_2) which cause the release of adsorbed ingredients [8, 9]. Extraction with MgCl_2 solution can be a measure of the metals availability, which are deposited in sediments in natural environmental conditions [7]. Forms of metals released during the EDTA extraction are forms that are potentially available during the variable environmental conditions (pH, redox potential) [8]. In addition to the single extraction, a sequential extraction is used. This method is applied to separate forms of heavy metals, which can be released into the solution under various environmental conditions.

The first examples of sequential extraction of bottom sediments and soil are from the 1970s. Sequential extraction methods are based on the gradual release of metals in various forms. These methods involve a use of series of solutions with increasing leaching power. The most widespread and commonly used procedure for sequential extraction of five fractional metal fractions from bottom sediments is the Tessier procedure, currently used with minor modifications [10]. In order to obtain comparable results, which would allow for precise interpretation and application in environmental monitoring, it was essential to standardize the procedure for testing metal forms in bottom sediments. Recent years have brought attempts to standardize the research methods, eg. by the Community Bureau of Reference (BRC) [9]. In order to compare results, the European Commission, under the Standard Measurement and Testing Program (SM&T), has adopted common procedures for the heavy metals extraction, both for single and sequential methods. For the heavy metals single extraction it is recommended to use EDTA/ $\text{CH}_3\text{COONH}_4$ solutions. This method allows to determine the metals bioavailability in sediments. Ure et al. [9] have developed a triple-step sequential extraction procedure called BRC in order to standardize the sequential speciation conditions. In the procedure approved by SM&T, Tessier's two fractions were considered to be mobile equivalent. The proposed BRC method is expanded by introducing a fourth extraction step, that allows to determine the residual fraction.

Detailed environmental studies allow to control the natural processes that govern the heavy metals recycling cycle in surface water, including toxicity reduction and tracking the dynamics in the changes of the heavy metals forms in the water- sediment system. Forms of heavy metals (Zn, Cu, Pb and Cd) were investigated in bottom sediments, by using speciation analysis (single and sequential). This allowed us to assess the risk of bioavailable metals in surface water. In order to achieve the goal of the research, the sediments contaminated with metals were obtained from Utrata river (Poland) [11]. The obtained results allowed us to characterize the relationship between heavy metal forms present in bottom sediments and their environmental bioavailability.

Materials and methods. Bottom sediments

The samples of bottom sediments obtained from the Utrata river (Poland) were highly contaminated with metals. Zn, Cu, Pb and Cd contents were analysed in the surface layer of bottom sediments of 5cm thickness. Metal content was defined for dry sediments fractions with the particle diameter <0.090 mm. 1 g of sediment sample was taken from the separated fraction.

Determination of the heavy metals content in sediments

The content of the selected heavy metals (Zn, Cd, Pb and Cu) in the sediment samples was measured by flame atomic absorption spectroscopy (FAAS) based on the standard curves determined for a series of pre-prepared standard solutions by MERC company. Prior to the

measurement, the dry mineralization and extraction of the sediment sample was performed. The detection limits for individual metals were calculated for the double standard deviation of five replicates in sediments (expressed as mg/ kg dry matter): Cd (0,005), Cu (0,03), Pb (0,05), Zn (0,01). In order to verify the correctness of the analysis and the measurement accuracy, a certified reference material Till-3 CRM with a known metal content was mineralized (Tab. 1). Metals recovery percentage from reference sediments varied between 93- 110%. The error resulting from the comparison of the analysis results, did not exceed 10%.

Table. 1.

Content of metals in the certified material Till-3

| Metal | Mineralization in HNO ₃ + HClO ₄ (mg/kg) | Content in CRM (mg/kg) | Recovery % |
|-------|--|------------------------|------------|
| Cu | 21,5 | 23,0 | 93,5 |
| Zn | 45,5 | 43 | 105,6 |
| Pb | 21,8 | 20,3 | 107,4 |
| Cd | 5,9 | 5,3 | 111,3 |

Total metal content

The total metal content was determined in solutions obtained after mineralization of 1 g of air dried sediment with a mixture of acids (9ml HNO₃, 3ml HClO₄). The process of mineralization was carried out in a mineralization block, where the sample of bottom sediment and acids mixture were placed in a teflon pot. The solution obtained after mineralization was filtrated into a flask with volume of 100 ml.

Simple extraction

The effects of metal extraction from air dried bottom sediments using distilled water and solutions of: 1M MgCl₂ and 0.05M EDTA were determined in laboratory conditions. The extraction solution was obtained after mixing the sediment with an extractant in a weight ratio of 10g sediment/100 ml. The extraction was carried out for 1 hour. All metal assays were performed three times, giving as a result the average value.

Sequential extraction

Tessier sequence was used to determine the metal forms in the air dried bottom sediments [10]. In the extraction five fractions of metal bonds were isolated. Exchangeable fraction (F1) – 1g of a material was supplied with 8 ml of 1 mol/l MgCl₂ (pH 7) and mixed for 1h at room temperature. The sample was then centrifuged and the metal concentration in the solution was determined. Fraction bound to carbonates (F2) – the residue from the first fraction analysis was treated with 8 ml of 1 mol/l sodium acetate acidified with acetic acid to pH 5 and extracted for 8h. Fraction bound to iron and manganese oxides (F3) – 20 ml of 0.04 mol/l NH₂OH × HCl in 25% acetic acid was added to the residue from the analysis of the second fraction and extracted for 8h at a temperature of 96°C. Fraction bound to organic matter (F4) – the residue from the analysis of the third fraction was mixed with a mixture containing 3 ml of 0.02 mol/l HNO₃ and 5 ml of 30% H₂O₂ acidified to pH 2 and heated for 2 h at 85°C. Then the solution was cooled and supplied with 3 ml of 30% H₂O₂ acidified to pH 2 and heated at 95°C for 3 h. After cooling 5 ml 3.2 mol/l of CH₃COONH₄ solution in 20% HNO₃ was added and the sample was mixed for 0,5h.

Residual fraction (F5) – the sample after the last extraction was mineralized in a mixture of acids (5 ml HNO_3 , 2 ml HClO_4 and 1 ml HF).

Results and discussion

The research results showed that the sediments contained heavy load of heavy metals. The average total metal content in sediment samples was equal to 246,6 mgZn/kg, 10,1 mgCd/kg, 148,4 mgPb/kg, 132,2 mgCu/kg dry matter.

Results of single extraction, using three extractants (H_2O , MgCl_2 i EDTA) are presented in Figure 1. The water-leaching process showed a considerable degree of their mobility. 4% Cu, 7% Cd, 10,5% Pb and 20% Zn passed into water. Extraction efficiency with MgCl_2 solution allows to put metals in the following order: 2,3% Cu, 3% Zn, 13%Pb and 41% Cd. Metal extraction with 0.05M EDTA solution removed from sediments on average 11% Cd, 27% Pb, 34% Zn and 60% Cu. The most effective extractant for copper and zinc was 0.05M EDTA solution, however, it was not efficient in extraction of lead and cadmium. The most effective solution for releasing Cd from sediments was magnesium chloride, neutral and of high ionic strength. Pb was released from the sediments to a similar extent by magnesium chloride and water as extractants. Like Zn and Cu, Pb was extracted most efficiently by the EDTA solution.

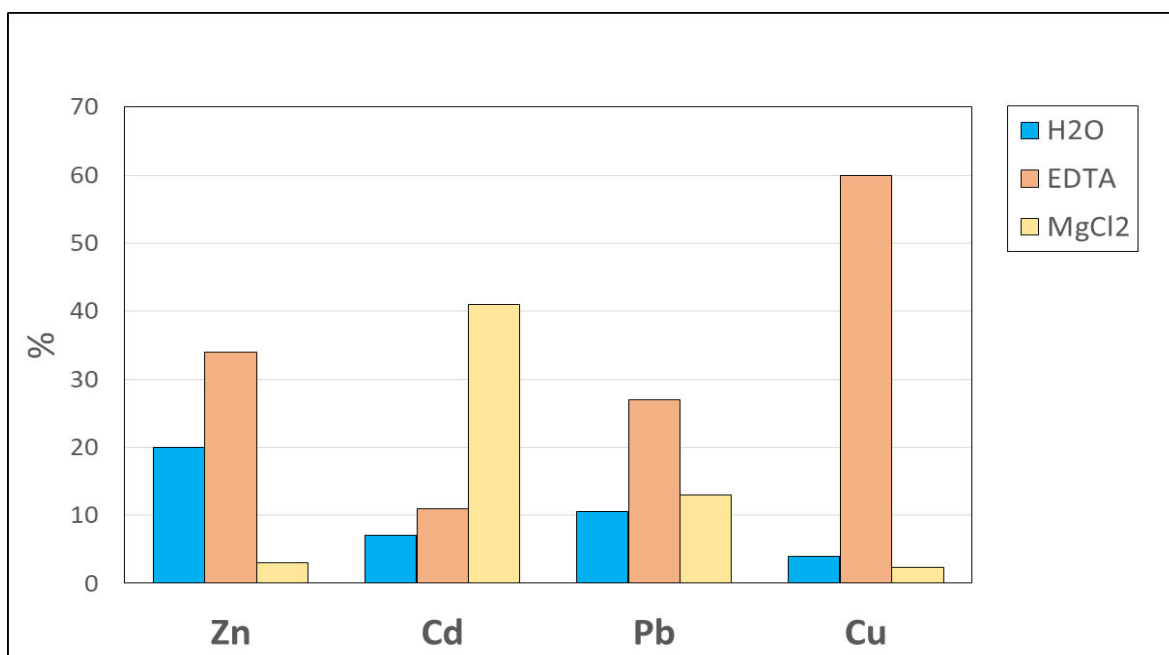


Fig. 1. The percentage of metals extracted from the sediments by water, EDTA and MgCl_2 .

All bottom sediment samples were subjected to Tessier specimen analysis measuring the Zn, Cu, Pb and Cd content. Measurable metals bound in 5 fractions (ion exchange, carbonate, adsorption, organic and residual fraction) showed different bioavailability in aqueous environment [12].

Zinc was mostly bound in the hydrated fractions of Fe/Mn oxides (15,7–49,7%). The comparable amount of this metal was observed also in the residual fraction (8,3–48,8%, average-30%). A significant amount was also in the carbonate fraction (7,7–46,3%). This zinc driving separation between sediment fractions may indicate the mobility of contamination containing this metal (fig. 2). Copper was bound strongly in the organic fraction (average 43%) and the rest fraction (average 42%) (fig. 2). Similar levels of copper binding in sediments were observed by Akcay et al. [2]. They obtained a high copper content in the residual fraction (F5) in sediment

samples from Buyak Menderes and Gediz rivers. In the Utrata river sediments, copper showed low content in mobile fractions (exchange, carbonate and adsorption), where the total amount for these three fractions was maximum 23%. Similar results have been obtained for mobile fractions by other researchers: the copper proportions in the first three fractions (F1+F2+F3), with high mobility, did not exceed 15% of the total content [13].

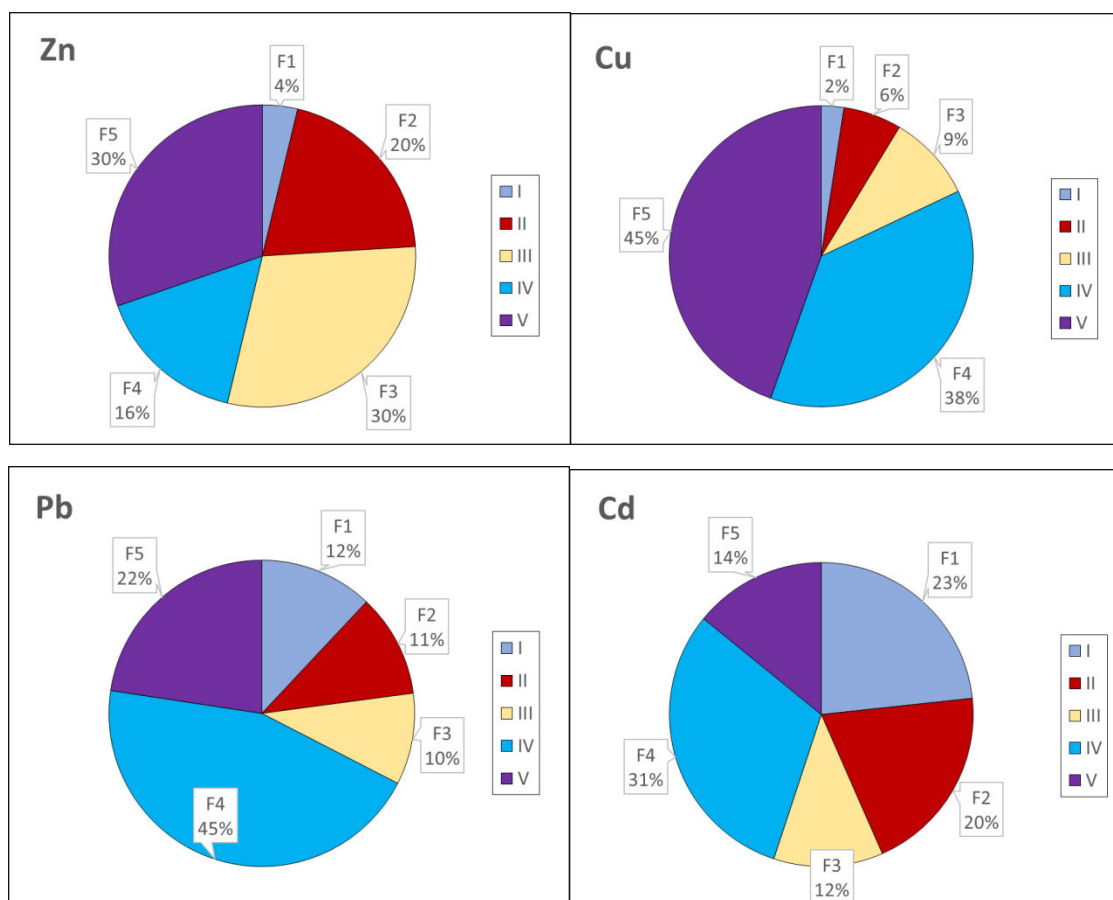


Fig. 2. Percentage of zinc, copper, cadmium, lead forms in the bottom sediments of Utrata river.

The highest amount of cadmium was observed in the organic fraction and in the mobile fractions: exchangeable and carbonate fractions (fig. 2), which proves the strongest bond of cadmium to these fractions. In the other two fractions, the percentage was: in adsorption 3-23% and in the residual fraction 6- 25%. The cadmium percentage in mobile fractions (F1, F2, F3) exceeded 50% and even reached over 60% of the total content. The high content of reactive cadmium fractions was also obtained by other authors [14]. The lowest involvement in the residual fraction (F5) for Cd was 14%. Lead, like copper was poorly bound in the exchangeable fraction, stronger in carbonate and adsorption and the strongest bond was observed in organic fraction (fig. 3). In most conducted studies, the results show a high lead affinity for adsorption fraction [15, 16]. The obtained results for Utrata river bottom sediments indicate a different lead binding ability. Lead present in the sediments remained in high percentages in low reactive fractions. Very low involvement in the residual fraction (fig. 2) was stated for lead (average 23%). However, the three bioavailable fractions (F1, F2, F3) periodically contained more than 50% Pb.

Heavy metals in sediments are separated between geochemical forms and the bonding degree strongly depends on the sediment composition [18]. Metals from anthropogenic sources are considered to be labile associated with the solid phase surface [19], leading to their mobility

and bioavailability. Studies have shown a high cadmium content in mobile bottom sediment fractions from Utrata River comparing to other metals. Cadmium, which is strongly bound in these sediment fractions (more than half of the total amount), can be released into water, resulting in an increase of bio- absorbable forms which are toxic to biomass. As a result, the whole environment and the whole food chain is affected. The amount of exchangeable form of Zn and Cu in sediments was negligible. The conducted speciation analysis showed the absolute dominance of the organic fraction in copper and lead binding. Cadmium as well showed strong affinity for this fraction.

The metal binding in individual fractions can be ordered in the following order:

F1: $Cd > Pb > Zn > Cu$

F2: $Zn > Cd > Pb > Cu$

F3: $Zn > Cd > Pb > Cu$

F4: $Cu > Pb > Cd > Zn$

F5: $Cu > Pb > Zn > Cd$

In the Mexican Lerma- Chapala Watershed study, in which only total concentration was analyzed, they found that the sediments transported by the Lerma river to Chapala lake are the final deposition destination of Cd, Cr, Ni, Cu, Pb, Zn. A proper risk assessment of the metal migration from contaminated sediments to water in Chapala lake was performed only in the following studies, using a five-step sequence of sequential metal extraction [20].

The metal separation results in Utrata river sediments showed that the exchangeable fraction represented between 11% and 26% of the total cadmium content. The second metal with a significant participation in this fraction was lead (6 - 12%). For zinc and copper the content in this fraction was much lower, respectively 1,5- 5% and 1,4-3%. Such participation in the F1 fraction indicates that cadmium and lead pose a high risk for flora and fauna located at the bottom part of the river. Percentages of cadmium (13% -24%) and lead (4-22%), similar to those exchangeable fraction, were found also in the carbonate fraction. Zinc also showed a high participation of carbonate binding (8 - 46%). This proved that carbonates fraction had a strong affinity for the testing metals [21]. For copper, the percentage in F2 was very low (1,9% -5,6%). A high amount of carbonates (average 12%) was found in contaminated sediments of Utrata river, as well as a significant content (up to 22%) of lead in this fraction. Cadmium binding in the reactive carbonate fraction occurred also in the sediments of Volvi and Koronia lakes ([17] and in the river within Iberian Pyrite area on Iberian Peninsula [22]. The carbonate fraction contained a significant amount of total cadmium and lead content in Poraj reservoir sediment [23] and Povang lake [24], lead in Rybnicki reservoir [25] and in reservoir sediments of Kozłowa Góra [26] and cadmium in sediments analyzed by Yang et al. [27]. Our own studies have confirmed the studies of Billon et al. [28], proving that metal ions can be absorbed on the carbonated mineral's surface and then incorporated into crystalline structure, eg $Cd_xCa_{1-x}CO_3$. The Cd contribution in the carbonate fraction may be due to the similarity of cadmium and calcium ions. These metals have similar ionic ion radius Cd (0,97Å) and Ca (0,99Å), so co-precipitation of cadmium and its incorporation into the crystalline calcite network can occur in the environment [29]. Turka's studies [30] proved that carbonate fraction is dominant for Pb speciation only when carbonates are a minor part of the sediment composition. Singh et al. [31] observed a similar carbonates role in binding Pb and Zn in contaminated sediments of Gomti river, a tributary of the Ganges.

Results, obtained in my own studies, showed the strongest binding of zinc (16 – 50%) in the fraction of hydrate oxides of Fe/Mn, which is sensitive to redox potential changes. For the

residual metals, the average participation in the adsorption fraction was 14% Cd, 8,5% Pb and 7,5% Cu. Because of large surface, hydrate oxides Fe/Mn are one of the most important geochemical phases affecting the mobility and metal behavior in sediments [32]. This was confirmed under the waste water environment conditions of Utrata river, where the precipitation of sparingly soluble iron forms (hydroxides, phosphates) was observed. Zinc sorption may occur on the precipitates [33]. Many studies have confirmed the high adsorption efficiency of hydrated Fe/Mn oxides in zinc removal process from water [33, 34].

In studies of bottom sediments from Utrata river, similar to Besser et al. [35] studies, a high content of Cu (43%), Pb (43%) and Cd (37%) in organic and sulfide fractions and low of Zn (14%) was confirmed. Wang et al. [34] confirmed the copper presence mainly in organic sulfide fraction. The organic fraction of metals is often assessed as stable, with low hazard. Basing on that, it can be assumed that the concentration of metals in interstitial and benthic water and the concentration of dissolved forms decreases, and thus the toxicity of these metals decreases. Current opinions differ on the metal toxicity bounded by organic substances. Yao et al. [36] studies have shown that metal complexation by organic matter, which serves as nourishment, can increase its toxicity for annelids (oligochaetes). On the other hand, in sediments of shallow Utrata river, where superfluous water layers are well oxygenated and varying hydrological conditions are observed, a high amount of Cd in organic and sulphide fraction (F4) may indicate toxicity of Cd for benthos invertebrates. It is caused by the process where CdS will be oxidized to the soluble form of CdSO₄ in aerobic conditions [34].

The content of the analysed metals in the residual fraction, constituting the insoluble fractions, varied in Utrata river sediments. Metals were associated with this fraction with different strengths for zinc, copper, lead and cadmium, respectively about 26%, 42%, 37% i 13% of total content. This part of metal is theoretically inaccessible to microorganisms and should not be activated in predictable time. In sediment studies from Poraj reservoir, which is tributary with Warta river waters [23], Kozłowa Góra reservoir sediments [26], sediments from Dongting lake [36] or Taihu lake [37] have shown a significant role of residual fraction in binding zinc process. Fityanos et al. [17] used a five- step metal extraction procedure to evaluate the assessment of sediment contamination by six metals (Cd, Cr, Pb, Mn, Zn, Cu) in two lakes (Volvi and Koronia), in northern Greece. Their results showed that Cd, Cr, Cu and Pb were mainly associated with the residual fraction and, to a lower extent, with carbonate fraction, posing a low risk of secondary lakes contamination.

A single extraction was performed to confirm the results of sequential extraction of the labile metal binding in sediments. The degree of water-leaching of lead and zinc was more than 10 percent, while cadmium and copper up to 10 percent. This has confirmed the labile nature of the metal binding in sediments and high probability of passing them to the dissolved phase. Using a MgCl₂ solution with stable pH and high ionic strength for extraction, a higher degree of elution with respect to cadmium (>40%) and lead (>10%) was obtained for the extraction and low for copper and zinc (<5%). Extraction with MgCl₂ showed higher results than extraction with water, which was due to the character of magnesium chloride and the competitiveness of heavy metal cations with respect to the large Mg²⁺ ion. High concentrations of metals were obtained in EDTA extracts. The affinity for the chelating solution was predominantly copper, passing to the solution in about 60%. Lower extraction efficiency was found for zinc and lead, the lowest for cadmium.

Significant metal leaching ability with water and used solutions, indicates the presence of metals in mobile forms, which is typical for short time deposited sediments. Mobility of the

metals bound in sediments depends on their individual properties and the composition of the over sedimentary water and the variable character of sediments. Under the conditions simulating minor environmental changes (magnesium chloride effluent), more toxic metals (Cd and Pb) were released, indicating a high bioavailability of their forms. Similar metal behaviour was observed in studies and research conducted in the Amur, Rhine and Dommel river valleys [38, 39, 40] and in the middle part of Vistula valley [41]. Metals reaching the aquatic environment are deposited in bottom sediments and temporarily immobilized, but may pose a threat to aquatic life. Under favourable conditions, metals may be released back into the water and then incorporated into the trophic chain and participate in further biological cycle stages. Changing environmental conditions can transform metal forms into sediments and change their bioavailability. Therefore, knowledge of the metal form contribution in sediments is necessary to describe their mobility and bioavailability in the aquatic environment as well as, in risk assessment. The metal tendencies for migration depend on their sediment forms, which are indicators of long term changes of water pollution and biological and chemical changes in the aquatic environment.

Conclusions

Heavy metals accumulation in the surface sediment layer is an ecological reflection of the rivers conditions and as well as the intensified anthropopression associated with the progressive urbanization of the catchment area. Metal fractionation showed different strength in metal binding processes in five bottom sediment fractions. Significant amounts of metals were bound in mobile fractions, indicating their high bioavailability. Possibility of heavy metal remobilisation from the bottom sediments to deep water, indicates a postponed environmental hazard. An important element of the bottom sediment research testing tool is use of more than one analytical method (simple and sequential extraction). Conducted research proved that sequential analysis of metal specimens should be co-used with single extraction to evaluate the metals transformation in biogeochemical cycles in aqueous environmental, which significantly reduced ambiguous results and misinterpreted them. The results of single and sequential extraction in conducted research, proved correct, indicating the potential possibility of metal migration in water-sediment system as a result of water quality parameters, indicating their mobility and bioavailability.

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