

FRACTIONATION OF CHOSEN HEAVY METALS IN BOTTOM  
SEDIMENTS OF SMALL WATER RESERVOIRSMAREK MADEYSKI<sup>\*</sup>, MAREK TARNAWSKI<sup>1</sup>, CZESŁAWA JASIEWICZ<sup>2</sup>,  
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al. A. Mickiewicza 24/28, 30-059 Kraków, Poland<sup>\*</sup> Corresponding author e-mail: rmmadeys@cyf-kr.edu.pl**Keywords:** Bottom sediments, heavy metals, sequential extraction, fractionation.

**Abstract:** The aim of the study was fractionation of Zn, Cu, Ni, Pb in the bottom sediments of two small reservoirs: at Krempna on the Wisłoka River and at Zesławice on the Dłubnia River. The partitioning of metals for various fractions was performed with the use of Tessier's sequential chemical extraction method. All together five metal fractions were distinguished: exchangeable metals (fraction I), metals bound to carbonates (fraction II), metals bound to hydrate Fe-Mn oxides (fraction III), metals bound to organic matter (fraction IV), and metals bound to minerals (fraction V). The largest quantities of metals were bound with fraction V, the smallest occurred in the forms most easily available for living organisms, in fraction I. Proportions of Zn, Ni and Pb in the exchangeable fraction were about 1%. The amounts of metals bound with fraction II were also relatively low, except for Zn in bottom sediment at the Zesławice Reservoir. In this bottom sediment the share of Zn bound to carbonates was 33%. Medium metal quantities were associated with hydrate Fe-Mn oxides (fraction III) and with organic matter (fraction IV). Relatively high proportion of metals in fraction V and trace amounts of metals in fraction I as well as alkaline and neutral reaction of the sediments may prove a potentially low hazard of the metal release in the case of chemical changes in the reservoirs.

## INTRODUCTION

In consequence of high antropopression heavy metals may constitute a serious source of water ecosystem pollution [5, 10, 28, 35]. In water environment these elements, adsorbed by suspension in the case of sedimentation processes, are deposited in bottom sediments of rivers [9, 12, 18, 49], of reservoirs [25, 30, 42], of lakes [11, 22, 36] and of fish ponds [24]. Numerous investigations report that under the influence of water decrease reaction, increased salinity or change of redox potential metals accumulated in bottom sediments may become secondary water pollutants [8, 9, 10, 13, 33]. A consequent activation of metals also occurs during the desedimentation works of reservoirs by use of various systems [23, 32], their transportation and deposition on refullation fields [31].

The mobility, transport and partitioning of metals in aquatic system are depended on the chemical form of the elements [10, 26, 36, 39]. Hence, recognition of chemical forms can be the source of valuable information on conditions of secondary reservoir water pollution and metal toxicity. Thus, in appraise of potential threat on the part of

metals deposited in bottom sediments speciation and speciation analysis play important roles [18, 36, 40]. Speciation means occurrence of various physical and chemical forms of a given element in examined material, whereas, their identification and quantitative determination is a subject of speciation analysis [11, 14]. Fractionation is the process of classification of an analyte or a group of analytes into a certain matrix according to physical (size, solubility) or chemical (bonding, reactive) properties [45, 49]. Metal speciation, in this context, is taken as the fractionation of total metal concentrations into exchangeable forms (fraction I), metals bound to carbonates (fraction II), bound to hydrate iron and manganese oxides (fraction III), bound to organic matter (fraction IV) and residual forms (bound to clay mineral, fraction V) (Tab. 1) [46]. The proposed method enables to distinguish chemical forms of heavy metals in the sediment which may be released into solution in the conditions mentioned above. It should be also stressed that total content of heavy metals in sediment is the indicator of anthropogenic pollution of the water environment but does not provide useful information about risks of bioavailability, the capacity for remobilization and the behavior of the metals in aquatic system [11, 22, 33, 47, 48]. Only analysis of the concentration of heavy metals present in various forms reflects the multidirectional changes occurring in the water ecosystem and therefore it may have indicative values [27, 28, 36, 37].

Table 1. Heavy metal fractions in sediments [46]

Fraction I	Fraction II
Metals adsorbed on the surface of solid bodies during changes of water ion composition or balance shift in the system of sorption-desorption may pass to the solution	In consequence of pH value decrease a carbonate balance disorder may occur and this cause passing of metals into the solution
Fraction III	Fraction IV
In anaerobic condition (reducing) dissolving of sediment and metal passing into the solution may occur	Metals are immobilized in consequence of increasing mineralization of sediments, metals pass to one of other fraction or return to water
Fraction V	
Metals in permanent immobilization and in natural conditions are no threat to the water ecosystem	

The aim of the present study was to investigate, using a five-step sequential extraction procedure, the different forms of elements present in sediments of the two chosen small water reservoirs and to obtain information on mechanisms of metals behavior in the reservoirs sediments, by comparing the results.

## INVESTIGATION FIELDS AND METHODS

The examined sediments were sampled from small water reservoirs: at Kremna on the Wisłoka River and at Zesławice on the Dłubnia River (Tab. 2). The object at Kremna is located in the Subcarpathian region, 35 km southward of Jasło in the upper section of the Wisłoka River, on the 14.23 km of its course. The reservoir Zesławice is located in Little Poland region on the 9.03 km on the river course of the Dłubnia (within the administrative range of Krakow). A detailed characteristic of the two reservoirs is presented in the paper

[43, 44]. Utilization of the catchment area of the rivers on which the examined reservoirs are located is greatly diversified and may have some influence on chemical properties of sediments in these reservoirs. The territory of the catchment area of the Wisłoka River is of a mountainous character and is covered in 8% by forests (beech-fir woods and forest habitats with young pine forests are in majority). Green areas constitute 14% of the area and arable grounds only 5%. On the territory of the catchment area built mainly of sandstone-clayish Krosno layers, compact clayish-dusty and clayish-loamy soils prevail. In great majority these are solid brown leached soils and on lower levels humid soils are found [1, 43]. On the other hand, the catchment area of the Dłubnia River is an agricultural basin in 78% under cultivation; green areas constitute 1.6% and forest 9.5% of the total surface area. Almost the whole territory of the catchment area of the Dłubnia River is covered by a layer of loess whose depth on cretaceous formations reaches even 15 m. This layer is thicker in valleys than on the ridges, wherefrom the loess was partly or totally washed or blown off [2]. In none of these basins any bigger industrial object that could influence air, water or soil pollution is located.

Table 2. Chosen parameters of water reservoirs

Reservoir	Supplying river	Catchment area	Reservoir area	Reservoir capacity	Usage destination
Krempna	Wisłoka	165.3 km <sup>2</sup>	3.2 ha	119 000 m <sup>3</sup>	retention recreation
Zesławice	Dłubnia	218.1 km <sup>2</sup>	6 ha	228 000 m <sup>3</sup>	retention

Methods of sampling and the specialist measurement apparatus were described by Tarnawski [43], and the chemical composition of bottom sediments was presented in a former paper [15]. The upper sediment layer of 0–15 cm in depth was collected for investigations. The granulometric composition of the medium loam of the sediment from the water reservoir at Krempna was characterized by neutral reaction ( $\text{pH}_{\text{KCl}}$  7.13) and contained 3.25% of organic matter. The other sediment derived from the water reservoir at Zesławice and was classified as normal dust; it showed basic reaction ( $\text{pH}_{\text{KCl}}$  7.35) and contained 2.75% of organic matter.

The methods for the quantitative determination of different forms of the heavy metals in sediments contain sequential extraction procedures (Tab. 3) Extraction of 1 g samples of sediment was carried out in 50 cm<sup>3</sup> polyethylene centrifuge tubes. Following each extraction, the mixtures were centrifuged at 3000 rpm for 30 min at room temperature. The residue was washed with 8 ml of deionized water and centrifuged as mentioned above. The supernatant was removed and discarded. This procedure consisted in multi repeated extraction of the sample sediment by use of reagents of increasing aggression specific for a given fraction [19]. The reagents used at the extraction stages are illustrated in Table 3. The last stage of extraction is a total digestion of the sediment which plays a control part respectively to determined total concentration of the given element in the examined material. The total concentration was determined after a former mineralization in a muffle furnace and then in a mixture of  $\text{HNO}_3$  and  $\text{HClO}_4$  (2:1). High purity reagents and double distilled deionized water were used in all the analyses. In the obtained solutions the heavy metals concentration was determined by the use of the technique of flame atomic absorption spectrometry FAAS (SOLLAR M6 Mk2 Dual, UNICAM). The fol-

lowing wavelengths (nm) were used for the determination of the analyses: Zn 213.9, Cu 324.8, Ni 232.0, Pb 283.3. The detection limits of metals investigated for all the extraction steps are presented in Table 5. The values changed from 0.01 to 0.07 mg·kg<sup>-1</sup> [41].

Table 3. Scheme of five-step sequential extraction

Fraction	Extraction solution	Temperature	Time
I	1 MgCl <sub>2</sub> (pH 7)	room temperature	1 hour (shaking)
II	1 M CH <sub>3</sub> COONa acidified to pH 5 CH <sub>3</sub> COOH	room temperature	5 hours (shaking)
III	0.04 M NH <sub>2</sub> OH·HCl in 25% (v/v) CH <sub>3</sub> COOH	96°C	5 hours (extraction)
IV	0.02 M HNO <sub>3</sub> , 30% H <sub>2</sub> O <sub>2</sub> , 30% H <sub>2</sub> O <sub>2</sub> 3.2 M CH <sub>3</sub> COONH <sub>4</sub> in 20% (v/v) HNO <sub>3</sub>	85°C	2 hours (extraction)
		85°C	3 hours (extraction)
V	HF, HClO <sub>4</sub> the residue was dissolved in HCl 1:1	room temperature	0.5 hour (shaking)

## RESULTS AND DISCUSSION

The total content of heavy metals in bottom sediment is approximate to values given by Tarnawski [43]. Comparing the total content in sediments between Krempna and Zesławice reservoirs (Tab. 4), we concluded that the content of metal in sediments of the Krempna is considerably higher. Average metals content in sediments at Krempna reservoir decreases in order Zn > Ni > Cu > Pb, whereas at Zesławice reservoir Zn > Pb > Cu > Ni. Taking into account the geochemical background, geocumulative index and the IUNG scale, the investigated sediments showed natural concentration of heavy metals (Tab. 4) [3, 4, 16, 17].

Table 4. Total content of heavy metals in bottom sediments

Sediment	Zn	Cu	Ni	Pb	
	[mg·kg <sup>-1</sup> d.m.]				
Krempna	97.44	40.74	46.53	20.23	
Zesławice	76.31	12.23	11.00	12.85	
Geochemical background	10–120	2–60	5–90	3–40	
<sup>1</sup> IUNG Criterion	< 100	< 40	< 50	< 70	
<sup>2</sup> I <sub>geo</sub>	Krempna	-0.62	-0.56	-0.98	-0.64
	Zesławice	-0.25	-1.91	-2.92	-0.80

<sup>1</sup> Institute of Soil Science and Plant Cultivation, <sup>2</sup> Geochemical index

Chemical analysis of forms of Zn, Cu, Ni and Pb binding in sediment samples showed diversification of metal concentrations in particular fractions (Tab. 5). For a better illustration of metal distribution between fractions their percentage participation was presented in a graphical form (Fig. 1). In soils and water sediments zinc is bound first of all by soil minerals, hydrated Fe and Mn oxides and organic matter [5, 16]. In the examined sediments this metal was mainly bound unexchangeable with minerals (62%, 35% respectively for reservoirs Krempna and Zesławice), hydrated Fe, Mn oxides (14%, 24%)

organic mater (15%, 9%) In the sediment of the reservoir at Zesławice special attention should be drawn to a relatively big amount of Zn bound with fraction II (carbonates), comparable to the amount of Zn bound with fraction V in this sediment. Whereas, in the sediment of the reservoir at Krempana fraction V distinctly dominated in binding Zn, and fraction II constituted about 8% of the sum amount of this element. The results confirming the thesis of considerable role of hydrated Fe, Mn oxides in binding of Zn are confirmed by investigations of sediments from the Lake Gorecki and the Middle Odra River [12, 51]. Also in sediments from reservoirs at Goczałkowice, Rapel (Chile) and from eleven lakes in the Area of Wielkopolski National Park most Zn bound with hydrated Fe and Mn oxides was found [20, 30, 40]. To sum up, for Zn the slope decreased in the order of residual > hydrated Fe, Mn oxides > organic matter > carbonate > exchangeable fraction in sediment at reservoir Krempana (Tab. 5). Similar patterns were obtained in the investigation of river and harbor sediments in Lake Balaton in which most of Zn was concentrated in V fraction and approximately 20% was associated with the organic mater (fraction V) [49]. The increasing order of fraction of Zn in sediment at reservoir Zesławice is exchangeable < organic matter < hydrated Fe, Mn oxides < carbonate < residual fraction (Tab. 5). Comparable results were given by Korfali, and Davies [18] who

Table 5. Concentration of Zn, Cu, Ni and Pb in different fractions of sediments

Element	Fraction	Detection Limit	Reservoir Krempana	Reservoir Zesławice
		[mg·kg <sup>-1</sup> d.m.]		
Zn	I	0.08	0.35 ± 0.02	0.47 ± 0.06
	II	0.08	7.27 ± 0.06	24.75 ± 1.19
	III	0.002	11.95 ± 1.10	18.51 ± 0.69
	IV	0.14	13.02 ± 0.79	6.58 ± 0.23
	V	0.25	54.06 ± 1.20	26.78 ± 0.06
	Σ of fraction		86.65 ± 3.05	77.09 ± 1.85
Cu	I	0.26	0.47 ± 0.02	0.31 ± 0.02
	II	0.26	4.07 ± 0.35	0.89 ± 0.03
	III	0.005	0.90 ± 0.12	0.87 ± 0.02
	IV	0.46	16.55 ± 0.69	4.01 ± 0.15
	V	0.82	18.75 ± 0.99	6.15 ± 0.17
	Σ of fraction		40.74 ± 2.18	12.23 ± 1.64
Ni	I	0.40	0.52 ± 0.05	BDL
	II	0.40	4.14 ± 0.06	2.05 ± 0.11
	III	0.008	6.01 ± 0.19	2.23 ± 0.16
	IV	1.25	7.11 ± 0.23	1.50 ± 0.02
	V	1.58	28.76 ± 2.81	5.27 ± 0.12
	Σ of fraction		46.54 ± 0.28	11.15 ± 0.20
Pb	I	0.56	<sup>1</sup> BDL	BDL
	II	0.56	2.02 ± 0.23	1.70 ± 0.10
	III	0.011	4.55 ± 0.30	3.26 ± 0.14
	IV	0.98	4.92 ± 0.12	3.35 ± 0.30
	V	1.75	8.73 ± 0.23	4.46 ± 0.27
	Σ of fraction		2.21 ± 0.63	12.77 ± 0.10

Mean ± standard deviation (n = 3), <sup>1</sup>BDL – below detection limit

analyzed speciation of Zn and other metals in sediment and water in a river underlined by limestone in which, the highest Zn sediment content was in residual fraction (29–40%), and next in the carbonate fraction (24–27%). Relatively high content of Zn in the mobile fraction II (carbonate bound) (Fig. 1) of the sediment at Zesławice reservoir may be explained by the effect of decreased reaction in consequence of which zinc is released into the aquatic ecosystem. In this condition Zn is more available to aquatic life.

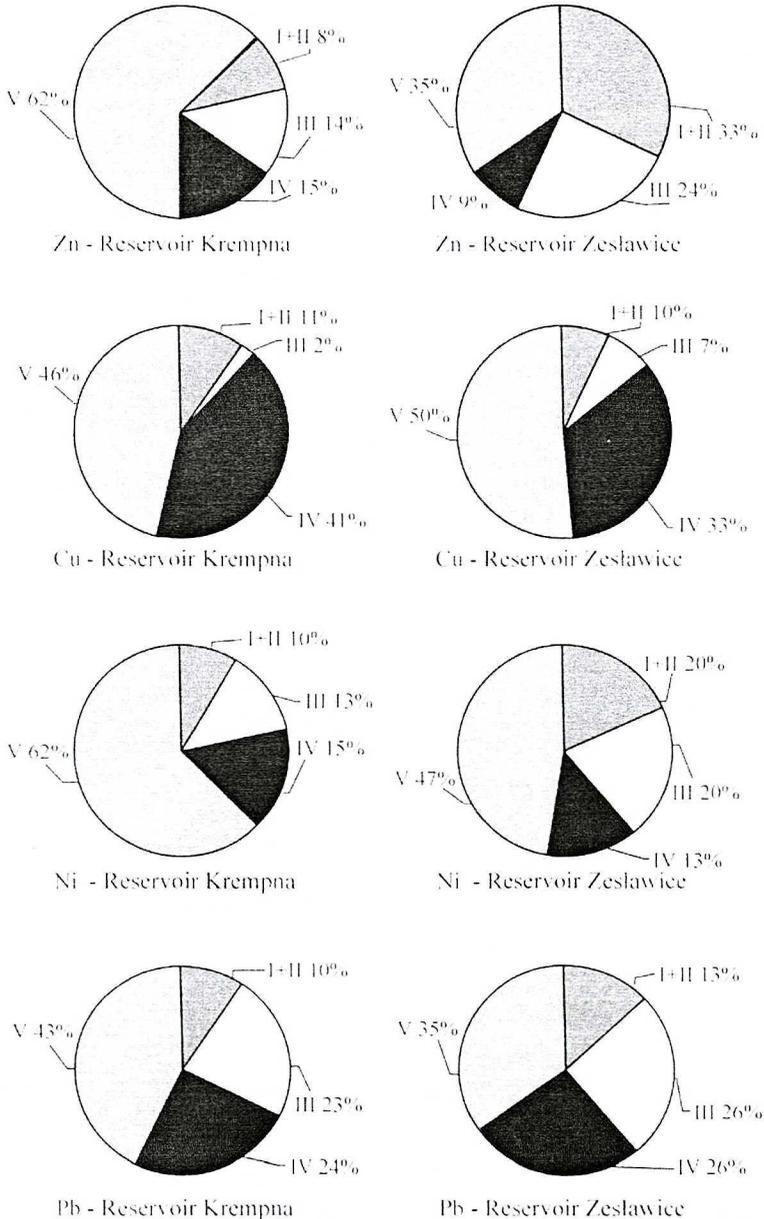


Fig. 1. The concentrations in percent [%] of metals determined at each extraction step in the sediments samples

The basic role in copper binding in soils is played by organic matter [16]. The fluvic and humic acids and other sources of organic matter with complexant properties explain the high concentration level of Cu associated with this fraction [28]. In the examined sediments Cu was bound first of all, to minerals (about 50%) and organic matter (41% and 33% respectively for the reservoir at Kremrna and Zesławice (Fig. 1)). The participation of copper bound with other fractions constituted, as a whole, less than 20%. Higher concentration of copper bound with fraction IV in the sediment from the reservoir of Kremrna may result from a higher organic matter content in this sediment as compared with the sediment from the water reservoir of Zesławice. Additionally, in both examined sediments significant positive correlation between the total content of copper and the amount of organic matter was found; this is confirmed by correlations equaling respectively 0.98 (reservoir Kremrna) and 0.96 (reservoir Zesławice) at  $p \leq 0.05$  [15]. A dominating form of organic matter in Cu binding was stated also by Segarra *et al.* [35], Fytianos, Lourantou [11], Wenhong Fan *et al.* [50], and Pizarro *et al.* [30]. Whereas, in the bottom sediment of Lake Gorecki, copper was found mainly in fraction V (83%) and considerably smaller amount of this element (16%) [51] was bound with organic matter. To sum up, the fraction generally did not vary from higher to lower concentration for copper in the following order: residual > organic matter > carbonates > hydrated Fe, Mn oxides > exchangeable fraction for the Kremrna Reservoir whereas, in sediment reservoir at Zesławice residual > organic > carbonates  $\approx$  hydrated Fe, Mn oxides > exchangeable fraction (Tab. 5).

Constant forms connected with minerals (fraction V) practically totally not available (Tab. 5) were the dominating fraction of nickel. The above mentioned Ni fraction constituted 62% in the sediment from the reservoir at Kremrna and 47% in the sediment of the reservoir at Zesławice. Participation of Ni fraction bound with organic matter, hydrated Fe and Mn oxides and carbonates was as follows: 15%, 13%, and 9% in sediments from the reservoir at Kremrna and respectively 13%, 20%, 18% in sediments from the reservoir at Zesławice (Fig. 1). In sediments from lakes of Wielkopolski National Park and reservoir at Goczałkowice, nickel (Ni) similarly as in the presented investigations was connected mainly with fraction V [20, 40, 51]. In bottom sediment from the Middle Odra River, Ni was dominant in bound to hydrated Fe and Mn oxides [12]. Dissimilar results were given also by Tokalioğlu *et al.* [47] analyzing speciation of heavy metals sediments from lakes of water-laden area of Sultanazlıği, Kayseri (Turkey) in which, the 50% of the total Ni concentration was the obtained organic fraction. In summary the fractions generally vary from higher to lower concentration for nickel in the following order: residual > organic matter > hydrate Fe-Mn oxide > carbonate > exchangeable fraction in sediment reservoir at Kremrna and residual > hydrate Fe-Mn oxide > carbonate > organic matter > exchangeable fraction in sediment in Zesławice Reservoir (Tab. 5).

Residual fraction is the predominant form on Pb in the examined sediments (Tab. 5). Participation of Pb bound with minerals constituted 43% in reservoir at Kremrna and 35% in reservoir at Zesławice. Particular attention should be given to an equalized distribution of Pb between fractions III, IV in sediments of the two reservoirs (Fig. 1). Participation of Pb connected exchangeably in sediments from the reservoirs was very small and did not exceed 0.1% (Fig. 1). Similar results were obtained by Kwapuliński and Wiechuła [20] from examinations of sediments of Goczałkowicki Reservoir in which Pb was mainly bound with fraction V and subsequently with fraction III and IV. Whereas, in sediments

of the lakes of Wielkopolski National Park heavily polluted with Pb (almost 2 times more than total Pb) the majority was constituted by the fraction connected with hydrated Fe, Mn oxides (respectively 50%) [40]. Also in sediments of the Lake Gorecki a major part of lead was bound with fraction III (34%), fraction V (34%) and fraction II (21%) [51]. Other results were obtained by Dobicki *et al.* [7] examining the sediments of Chańcza Lake. In the sediments of this lake participation of lead bound with carbonates (35%) and with organic matter (30%) was the highest. Also in sediments from a contaminated bay of northern China mostly Pb bound with hydrated Fe and Mn oxides and carbonate were found [50]. According to these results, the distribution of lead (Pb) among particular sediment fractions from the two reservoirs showed an increasing tendency from exchangeable < carbonates < hydrate Fe-Mn oxide  $\approx$  organic matter < residual fraction (Fig. 1).

When analyzing the obtained results it was stated that the distribution of investigated metals between particular fractions in sediment of both reservoirs showed similar tendencies. Predominately the amounts of Zn, Cu, Ni and Pb were constantly bound with minerals (fraction V). This is very significant information since it may be assumed that this part of metals is not available to living organisms and in the nearest future will not be activated. The smallest amount of all the metals occurred in forms easily available to live organisms in fraction I which included the mentioned metals easily released into the water. Participation of Zn, Ni and Pb in this fraction was approximately 1%. Only Cu participation in fraction I was higher and equaled 3% in reservoir at Zesławice. According to many authors the reaction influences the highest degree mobility of heavy metals: the lower the pH value the greater solubility of particular metals [13, 34]. With regard to the neutral and alkaline reaction of the examined sediments they may play a role of a trap for heavy metals. In the presented investigations medium quantities of metals were bound with hydrated Fe, Mn oxides (fraction III) and with organic matter (fraction IV). These are averagely mobile fractions however, metals connected with organic matter can undergo transition into one of the other forms in consequence of the naturally proceeding mineralization. Metals bound with hydrate Fe, Mn oxides, on the other hand, can be again released into water in the case of highly reducing conditions occurring in the zone above the bottom [38]. Different analytical data were treated to sum the results from the first, second and third fractions to get the bioavailable fraction and from the fourth and fifth ones to obtain a non-bioavailable fraction [21, 29].

In the investigated sediments a potential risk of reoccurrence of water pollution with zinc may take place at change of oxidizing-reducing conditions, and pollution with Cu and Ni during mineralization of organic matter. On the basis of the carried out fractionation of heavy metal in sediments, a low threat caused by heavy metal release in result of changes of chemical content of water in the two reservoirs was stated.

Summing up, fractionation of heavy metals in bottom sediment is of great importance in recognition of chemical and biochemical processes occurring in the water environment and allows for appraise of real threat to aquatic life on the part of various types of pollution. Sequential extraction analysis is a technique developed for the overall assessment of speciation and potential mobility of metals in sediments [6].

## CONCLUSIONS

1. Relatively dominant participation of heavy metals connected with minerals (fraction V) and an alkaline or neutral reaction of sediments may be evidence of a potentially small threat on the part of released trace elements in the case of chemical composition of water changes in the two reservoirs.
2. Based on fractionation studies of the metals in sediments and their mobility and bioavailability, the elements presented below can be arranged as follows (from more bioavailable to less bioavailable):  $Pb > Ni > Zn > Cu$  (reservoir Krempna) and  $Zn > Pb \approx Ni > Cu$  (reservoir Zesławice).
3. Generally, bottom sediments of small water reservoir do not contain a significant amount of heavy metals. After removal, these sediments may be utilized in nature. It is contrary to sediments of other water reservoirs, mentioned in publications, located in urbanized territories under distinct influence of industry and this may exert a harmful effect on sediment quantity. In order to confirm the thesis, investigations of heavy metal fraction in sediments of other small reservoirs of small water retention, should be extended.

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#### FRAKCYJONOWANIE WYBRANYCH METALI CIĘŻKICH W OSADACH DENNYCH MAŁYCH ZBIORNIKÓW WODNYCH

Celem badań było frakcjonowanie Zn, Cu, Ni i Pb w osadach dennych dwóch zbiorników małej retencji wodnej: w Krempnej na rzece Wisłocy oraz w Zesławicach na rzece Dłubni. Podział metali pomiędzy różne frakcje wykonano stosując ekstrakcję sekwencyjną wg Tessiera i in. Wyodrębniono 5 frakcji metali: wymienne (frakcja I), związane z węglanami (frakcja II), z uwodnionymi tlenkami Fe i Mn (frakcja III), z materią organiczną (frakcja IV) oraz trwale związane z minerałami (frakcja V). Największe ilości metali były związane z frakcją V, najmniejsze zaś występowały w formach najłatwiej dostępnych dla organizmów żywych we frakcji I. Udziały Zn, Ni i Pb w tej frakcji kształtowały się poniżej 1%. Również metale w formie związanej z frakcją II były stosunkowo niskie, z wyjątkiem Zn w osadzie Zesławice. Udział Zn związanego z węglanami stanowił 33%. Pośrednie ilości metali były związane z uwodnionymi tlenkami Fe i Mn (frakcją III) oraz z materią organiczną (frakcją IV). Stosunkowo wysoki udział metali we frakcji V, śladowe ilości metali we frakcji I oraz zasadowy i obojętny odczyn osadów może świadczyć o potencjalnie niskim zagrożeniu ich uwolnienia w przypadku wystąpienia zmian chemizmu wód obu zbiorników.