

Speciation Analysis of Lead, Zinc and Cadmium in River Bottom Deposits in Świętokrzyskie Region

A. Rabajczyk

Department of Management and Environmental Protection,
Jan Kochanowski University of Humanic and Natural Science in Kielce, Świętokrzyska Str. 15, 25-406 Kielce, Poland

Received: 20 December, 2007

Accepted: 2 June, 2008

Abstract

Bottom deposits of selected rivers in the Świętokrzyskie Region of Poland flowing through areas of various geological characteristics and land development were analyzed for the presence of cadmium, zinc and lead. Microwave-assisted 3-stage sequential extraction recommended by the European Union (EU) was applied for that purpose as well as a 5-stage extraction proposed by Tessier et al. Residues after sequential extraction were mineralized in concentrated nitric acid in order to check if applied sequential extraction procedures allowed extraction of total amounts of metals from bottom deposits. Metal contents were determined with F-AAS technique in particular extracts.

Keywords: Pb, Zn and Cd heavy metals, sediments, sequential extraction, F-AAS

Introduction

Pollution by heavy metals destroys plant and animal life in river ecosystems. Moreover, the influence of pollutants may become wider and extend water environment through the food chain. Heavy metals are the most widely known and tested pollutants transferred in the aquatic system. They are introduced into the environment as a result of natural processes and industrial and agricultural activity [1-3].

Most heavy metals disposed to rivers are bounded and transported with suspension with sediments in river to form bottom deposits. Concentration of pollutants in deposits varies from 26% to 47% of total load of pollutants transported by river [4], and according to other estimations it may amount even to 90% [5]. Heavy metals deposited with sediment are an important component of river channel building material and they may remain in this environment for a long period of time, especially in flatlands of low pace of environmental migration.

Erosion and water flow velocity related to river channel slope are the main factors affecting formation and properties

of deposits. Distribution of bottom deposits in river channel depends on many factors. Relationships between these factors are presented in Fig. 1.

Heavy metals such as Zn, Cd or Pb, are being deposited in bottom deposits during migration, where they are temporarily immobilized and may threaten biological life in a given water body. Heavy metals may be released from deposits to water and involved in food chain under favourable conditions, thus they participate in further stages of environmental cycle.

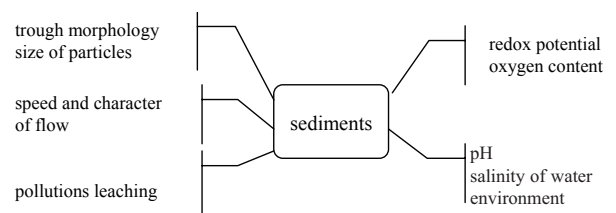


Fig. 1. Scheme of bottom deposit distribution dependent on external factors.

Flexibility of metals to be transferred to water depends on metal form in deposits [6]. Differentiation and quantitative determination of given element forms are of major importance for defining potential hazards to ecosystems caused by metals in the bottom deposit. However, metal forms in bottom deposits are defined in many ways:

- functional way, for example as forms accessible for plants, mobile forms, exchangeable cations,
- operational way that is applying procedures, reagents and extractants to isolate, identify and quantitatively determine metals,
- individual way, for example as particular chemical individuals, oxidation state of element [7].

In environmental or geochemical research, a determination of total amount of metals accumulated in bottom deposits does not give information on their mobility and accessibility for organisms. Information on what portion of total metal concentration is potentially available is actual toxicity factor. Using total concentration values to assess ecological hazard may overestimate real risk for environmental contamination [2].

Trace metals occur in different chemical forms and different types of bonds in bottom deposits. They can be found mainly in primordial minerals in relatively immobile forms in uncontaminated environments. In contaminated ecosystems heavy metals occur in more labile forms, which results from processes such as sorption, complex formation and coprecipitation with deposit particles. An amount of potentially bioavailable metal forms increases under specific physicochemical conditions in watercourse. Such factors as reaction of environment and redox potential value are of particular importance, at the same time low pH value favours metal migration.

Oxygenation rate and factors, which limit or prevent this compound from accessing the environment, are of huge importance because deficiency or especially permanent lack of oxygen changes metabolism from aerobic to anaerobic.

This change may cause the formation of compounds of higher metal mobility, bioavailability or solubility rate. It includes metals connected with Fe and Mn oxides and hydroxides under reduction conditions occurring at that time (Fig. 2). Metals eluted in that way may then enrich a fraction of easy exchangeable metals [8] and may be subject to migration and release to water. Toxic effects of metals in bottom deposits depend on concentration of potentially bioavailable metal forms of natural or anthropogenic origin [9].

Depending on type of organism exposed to heavy metals in bottom deposit and on physicochemical character of aquatic ecosystems, bioavailable metals may be bound to different components of deposit like organic matter, Fe-Mn oxides and hydroxides, carbonates or amorphous sulphides. Heavy metals may also be adsorbed on deposit particles as a result of physical sorption or chemisorption, forming a fraction of the most labile metals [2, 9, 10]. Toxic effects of metals in bottom deposits are conditioned by concentration of potentially bioavailable metal forms of natural or anthropogenic origin [9].

Research on deposits is important with regard to changing physicochemical conditions, which may cause compounds to change their forms in bottom deposit, which influences their mobility in bottom deposit-water-fauna and flora system and watercourse surroundings. Testing and monitoring river environment pollution is also important because of continuous flow of matter and its transport function.

Geochemical research on surface water bottom deposits are applied to evaluate pollution of lakes and rivers by noxious substances. They also aim to examine content of potentially noxious metals and metalloids and to trace changes of this content over time. Analysis of heavy metal general content in bottom deposits does not give complete insight into pollution of tested ecosystems and speciation analysis with regard to bioavailability of particular individuals is necessary.

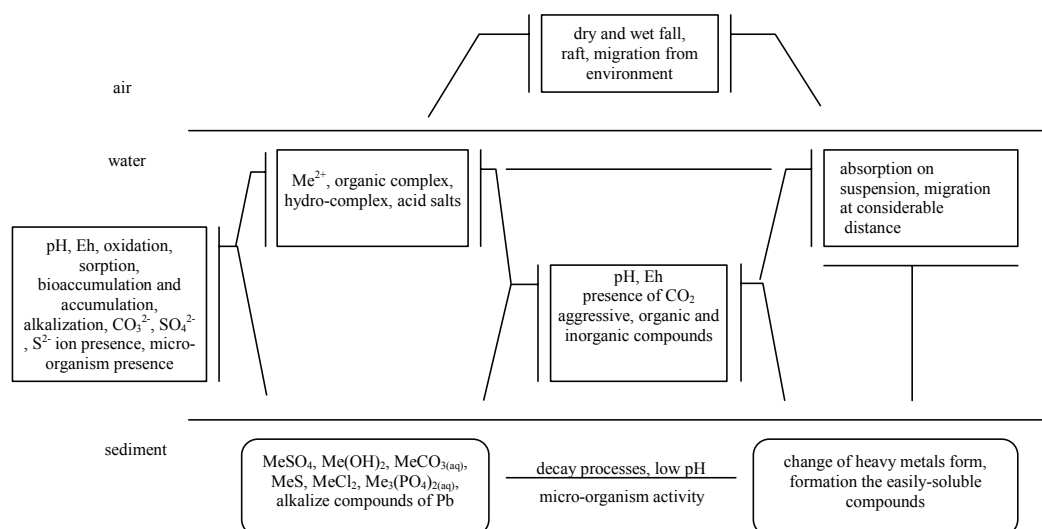


Fig. 2. Scheme of influence of several factors on metal migration in water-sediment system.

Table 1. Sequential extraction procedures.

Step	Method A	Method B
Soluble	0.11 mol l ⁻¹ acetic acid (HOAc)	1.0 mol l ⁻¹ magnesium chloride (MgCl ₂) at pH 7
Exchangeable	I step: t_h : 600s, t_c : 300s, P_o : 45W, P : 17-23 atm., t_w : 300s	at room temperature for 1 h
Associated to carbonates	II step: t_h : 600s, t_c : 300s, P_o : 115W, P : 21-25 atm., t_w : 300s III step: t_h : 300s, t_c : 300s, P_o : 150W, P : 25-30 atm., t_w : 300s	1.0 mol l ⁻¹ sodium acetate (NaOAc), acetic acid (HOAc) at pH 5 at room temperature for 3 h
Amorphous Fe oxyhydroxide	0.1 mol l ⁻¹ hydroxylammonium chloride (NH ₂ OH·HCl) at pH 2	0.04 mol l ⁻¹ hydroxylamine hydrochloride (NH ₂ OH·HCl), 25% (v/v) acetic acid (HOAc) at pH 2
Crystalline Fe oxide	I step: t_h : 60s, t_c : 60s, P_o : 39W, P : 23-25 atm., t_w : 300s	at 96°C with occasional agitation for 6 hrs
Oxidisable/ Associated to organic matter and sulphides	30% hydrogen peroxide (H ₂ O ₂) I step: t_h : 60s, t_c : 60s, P_o : 117W, P : 23-25 atm., t_w : 300s 1.0 mol l ⁻¹ ammonium acetate (NH ₄ OAc) at pH 2 I step: t_h : 60s, t_c : 60s, P_o : 117W, P : 23-25 atm., t_w : 300s	30% hydrogen peroxide (H ₂ O ₂), 0.02 mol l ⁻¹ nitric acid (HNO ₃) at pH 2 at 85°C for 5 h cool 3.2 mol l ⁻¹ ammonium acetate (NH ₄ OAc) in 20% (v/v) HNO ₃ at room temperature 30 minutes
Residual and silicates		hydrofluoric acid (HF), perchloric acid (HClO ₄), digestion with 5:1 at room temperature for 5 h

t_h - heating time, t_c - cooling time, t_w - waiting time, P_o - power, P - pressure.

European Union (EU) recommendations include 3-stage sequential extraction, assuming that metal compounds left in deposits after extraction are harmless because they are not transferred to hydrosphere and biosphere at normal biological conditions. However, changeability of physicochemical and biological parameters in water, as a result of human activity, may be a reason for arising conditions that influence migration of particular individuals in water – bottom deposit – vegetation system. A 5-stage speciation analysis proposed by Tessier et al. and associates allows us to determine five metal fractions, including those exchangeable and bound to carbonates, hydrated iron and manganese oxides, organic matter and other metals permanently bounded to minerals.

Research Area

Research was conducted on river bottom deposits in Świętokrzyskie Region of similar basement complex and different land development. Nida is the longest river in the Świętokrzyskie Region, flowing north-east of Jędrzejowice Powiat and draining middle north of Niecka Nidziańska. It is the lowland river of medium slope and it meanders. It is regulated to a lower extent. Maskalis River is one of the main left-bank tributaries of Nida River, and Brzeźnica

River is one of the major right-bank tributaries. Brzeźnica is the river flowing over Jędrzejowice Powiat only. It is 16.8 km long, it empties into Nida River at 80 km and it drains an area of 98 km². Channels of these rivers are formed of marls, limestones, gypsum deposits, postglacial sands, boulder clays of various sand ratios and deposits of different depths lying on limestone deposits.



Fig. 3. Bottom deposit sampling points in Maskalis (1), Nida (2) and Brzeźnica (3) Rivers (physico-geographical regions according to J. Kondracki).

Table 2. Zinc content in individual forms [mg/kg dry matter] (mean and standard deviation).

Method extraction	No.	Form					Mineralization in HNO ₃	Sum
		exchangeable	carbonate	oxide	organic/ organic and sulphide*	residue		
Maskalis River								
A	I		28.9 ± 4.8	28.0 ± 3.7	27.4 ± 4.1		4.5 ± 0.8	88.8 ± 7.4
	II		34.7 ± 5.2	17.4 ± 2.9	39.8 ± 4.4		3.4 ± 0.8	95.3 ± 7.4
B	I	14.6 ± 1.2	22.1 ± 1.2	17.5 ± 1.1	16.9 ± 1.3	4.9 ± 0.8	3.0 ± 0.2	79.0 ± 2.5
	II	21.3 ± 3.4	19.2 ± 2.9	18.5 ± 2.6	17.2 ± 2.2	5.3 ± 0.9	2.7 ± 0.7	84.2 ± 5.7
Mineralization in HNO ₃	I						71.2 ± 5.4	71.2 ± 5.4
	II						81.3 ± 5.1	81.3 ± 5.1
Nida River								
A	I		38.2 ± 3.6	23.2 ± 2.8	35.9 ± 5.2		3.0 ± 0.6	100.3 ± 6.9
	II		30.5 ± 6.1	24.5 ± 3.5	32.4 ± 3.8		5.7 ± 1.1	93.1 ± 8.1
B	I	32.5 ± 6.1	6.1 ± 1.1	7.4 ± 1.2	29.7 ± 3.3	4.1 ± 1.2	3.8 ± 0.7	83.6 ± 7.3
	II	28.9 ± 4.7	8.0 ± 1.3	9.5 ± 1.2	28.9 ± 2.2	5.2 ± 0.6	3.2 ± 0.5	83.7 ± 5.5
Mineralization in HNO ₃	I						80.8 ± 6.7	80.8 ± 6.7
	II						81.9 ± 5.5	81.9 ± 5.5
Brzeźnica River								
A	I		42.9 ± 6.4	28.9 ± 5.1	27.5 ± 4.8		2.0 ± 0.4	101.3 ± 9.5
	II		46.8 ± 5.7	27.8 ± 5.3	23.0 ± 3.8		2.5 ± 0.6	100.1 ± 8.7
B	I	28.7 ± 3.9	23.8 ± 3.5	25.1 ± 2.7	15.3 ± 2.9	2.9 ± 0.4	2.9 ± 0.9	98.7 ± 6.6
	II	20.9 ± 4.2	25.7 ± 5.3	22.3 ± 5.2	21.2 ± 2.9	2.1 ± 0.6	5.9 ± 0.8	98.1 ± 9.1
Mineralization in HNO ₃	I						93.5 ± 15.6	93.5 ± 15.6
	II						93.9 ± 15.3	93.9 ± 15.3

* organic – for 5-stage extraction; organic and sulphide – for 3-stage extraction

Bottom deposits were collected from areas of different land development (Fig. 3).

On Brzeźnica River a sampling point was located in a section located among ploughlands, on Maskalis River another point was located in mixed forest area with a predominance of deciduous trees, and on Nida River a point was placed near the “Nida Gips” factory and a heavy traffic road. The sampling points are therefore of similar geological structure, but they are exposed to different types of pollutants resulting from land development, which influences a balance of metals in water-bottom deposit system and metal forms in separate parts of ecosystem.

Experimental Procedures

Bottom deposit samples collected at a depth of 0-20 cm twice in June and October 2006 from 3 points placed in Maskalis, Nida and Brzeźnica Rivers were the materials for research. A layer of the bottom sediment was collected by

an Ekman-Birge apparatus. In the bottom sediments from all sites a percentage content of water, loss of ignition and the content of chosen metals were determined.

Crushed deposit samples were dried at 105°C to reach constant mass, then ground in agate mortar and sieved to reach fraction of ≤100 μm grain diameter. 3 samples of 2 g in weight were taken for mineralization from representative and homogeneous portions of material and they underwent sequential extraction using two methods (Table 1):

- microwave-assisted sequential extraction according to BCR procedure (3-stages) – Method A,
- Tessier sequential extraction (5-stages) – Method B.

Dried bottom deposit samples and residues after sequential extractions were mineralized with concentrated HNO₃. Content of metals in the bottom sediment was determined by means of atomic absorption spectrophotometry using a Perkin-Elmer model 3100 atomic absorption spectrophotometer at appropriate parameters. Correctness of determinations was checked out by applying a benchmark addition method.

Table 3. Cadmium content in individual forms [mg/kg dry matter] (mean and standard deviation).

Method extraction	No.	Form					Mineralization in HNO ₃	Sum
		exchangeable	carbonate	oxide	organic/ organic and sulphide*	residue		
Maskalis River								
A	I		2.2 ± 0.4	2.2 ± 0.3	1.2 ± 0.5		3.8 ± 0.8	9.4 ± 1.1
	II		2.2 ± 0.4	2.2 ± 0.3	1.2 ± 0.5		4.9 ± 1.1	10.5 ± 1.3
B	I	1.7 ± 0.2	0.8 ± 0.2	0.8 ± 0.2	1.0 ± 0.3	2.9 ± 0.5	2.0 ± 0.3	9.2 ± 0.7
	II	1.9 ± 0.3	0.9 ± 0.2	0.9 ± 0.2	1.1 ± 0.3	3.2 ± 0.4	2.5 ± 0.6	10.5 ± 0.9
Mineralization in HNO ₃	I						8.1 ± 1.3	8.1 ± 1.3
	II						8.8 ± 1.7	8.8 ± 1.7
Nida River								
A	I		3.3 ± 1.2	0.9 ± 0.2	1.2 ± 0.3		4.1 ± 1.9	9.5 ± 2.3
	II		3.7 ± 2.1	1.9 ± 0.7	1.4 ± 0.4		4.3 ± 1.7	11.3 ± 2.8
B	I	2.1 ± 0.6	0.8 ± 0.2	0.8 ± 0.2	1.0 ± 0.4	1.3 ± 0.7	2.9 ± 1.4	8.9 ± 1.7
	II	2.9 ± 0.5	1.0 ± 0.3	1.8 ± 0.5	1.3 ± 0.2	1.2 ± 0.2	3.2 ± 1.8	11.4 ± 2.0
Mineralization in HNO ₃	I						7.0 ± 3.1	7.0 ± 3.1
	II						8.0 ± 3.8	8.0 ± 3.8
Brzeźnica River								
A	I		3,2 ± 1,5	1.1 ± 0.3	1.7 ± 0.6		3.0 ± 0.8	9.0 ± 1.8
	II		3,2 ± 1,4	1.2 ± 0.6	1.8 ± 0.4		3.2 ± 1.5	9.4 ± 2.2
B	I	1.6 ± 0.6	1,9 ± 0,4	0.9 ± 0.2	1.0 ± 0.3	1.1 ± 0.6	2.0 ± 0.4	8.5 ± 1.1
	II	1.8 ± 0.5	1,8 ± 0,4	0.8 ± 0.2	0.9 ± 0.2	1.1 ± 0.4	2.2 ± 1.3	8,6 ± 1,5
Mineralization in HNO ₃	I						7.3 ± 1.8	7.3 ± 1.8
	II						8.7 ± 3.1	8.7 ± 3.1

* organic – for 5-stage extraction; organic and sulphide – for 3-stage extraction

Microwave mineralization of deposit samples was conducted in high-pressure (110 atm), high-temperature (250°C). UniClever module microwave mineralizer, with integral control of pressure in reaction vessel and with monitoring of temperature. Mineralization was conducted in the range of 150-300 W microwave energy.

Results

Analysis of bottom deposits was conducted with microwave assisted 3-stage sequential extraction and with 5-stage mineralization using concentrated HNO₃ for defined sampling points. Zinc, cadmium and lead were determined in obtained solutions (Tables 2-4).

Discussion of Results

A different analytical approach is applied to determine bioavailable concentrations of heavy metals in deposits, but

the following methods are taken into account: single extraction with one extractant and sequential extraction aimed at determining fractions of trace metals in deposits which may react on natural environmental condition changes that are specific for each fraction [2, 9-11]. Modification and development of extraction methods aims to use fewer amounts and less aggressive extractants because metals eluted under less drastic conditions are more correlated with their bioavailability [12-15].

Methods of sequential extraction (3-stage and 5-stage) applied allowed obtaining information on various forms and bioavailability of tested metals in bottom deposits of Maskalis, Nida and Brzeźnica Rivers. Extraction of analytes from bottom deposit of tested rivers carried out according to BCR procedure gave information on Zn, Cd and Pb in carbonate, oxide, organic and sulphide form, while Tessier extraction gave information on metals in forms:

- exchangeable metals – adsorbed on surface of solids, which may transfer to water as a result of changes in

Table 4. Lead content in individual forms [mg/kg dry matter] (mean and standard deviation).

Method extraction	No.	Form					Mineralization in HNO ₃	Sum
		exchangeable	carbonate	oxide	organic/ organic and sulphide*	residue		
Maskalis River								
A	I		39.0 ± 15.3	21.2 ± 7.7	41.4 ± 18.4		15.8 ± 2.6	117.4 ± 25.3
	II		40.6 ± 12.4	27.5 ± 9.3	37.8 ± 10.1		17.0 ± 3.8	122.9 ± 18.9
B	I	21.7 ± 8.2	19.9 ± 4.6	22.3 ± 5.2	45.1 ± 11.7	4.9 ± 1.1	3.0 ± 0.5	116.8 ± 15.9
	II	27.9 ± 7.4	19.0 ± 3.6	22.3 ± 4.9	42.2 ± 8.3	4.9 ± 1.6	3.9 ± 1.1	120.2 ± 12.8
Mineralization in HNO ₃	I						111.8 ± 21.2	111.8 ± 21.2
	II						114.9 ± 25.3	114.9 ± 25.3
Nida River								
A	I		41.4 ± 18.3	45.5 ± 13.2	48.1 ± 15.5		3.0 ± 0.4	138.0 ± 27.4
	II		46.5 ± 12.1	48.5 ± 14.1	49.7 ± 11.6		2.8 ± 0.4	147.5 ± 21.9
B	I	30.2 ± 11.7	10.5 ± 3.4	22.3 ± 9.3	47.6 ± 16.9	14.0 ± 3.6	4.7 ± 1.2	129.3 ± 23.1
	II	28.9 ± 11.1	16.3 ± 4.5	22.3 ± 5.7	48.7 ± 17.4	15.2 ± 3.3	3.2 ± 0.6	134.6 ± 22.1
Mineralization in HNO ₃	I						124.1 ± 28.5	124.1 ± 28.5
	II						129.2 ± 26.9	129.2 ± 26.9
Brzeźnica River								
A	I		24.5 ± 9.2	9.5 ± 3.1	35.7 ± 14.6		3.9 ± 1.2	73.6 ± 17.6
	II		27.1 ± 6.5	9.1 ± 2.6	33.1 ± 10.5		4.0 ± 0.8	73.3 ± 12.6
B	I	18.0 ± 3.2	4.8 ± 1.1	12.3 ± 4.2	31.3 ± 10.8	1.4 ± 0.3	2.8 ± 0.5	70.6 ± 12.1
	II	20.2 ± 9.2	5.9 ± 1.3	12.3 ± 3.4	29.3 ± 7.7	1.1 ± 0.4	2.9 ± 0.7	71.7 ± 12.6
Mineralization in HNO ₃	I						65.6 ± 28.2	65.6 ± 28.2
	II						68.9 ± 24.1	68.9 ± 24.1

* organic - for 5-stage extraction; organic and sulphide – for 3-stage extraction

water ionic content and displacement of equilibrium in sorption-desorption system,

- metals bound to carbonates – occurring in carbonate forms or coprecipitated with carbonates; if pH value decreases in bottom zone, carbonate balance may be disturbed and carbonate metal forms or metals coprecipitated with carbonates may be transferred to water,
- metals bound to iron and manganese hydrated oxides – adsorbed on developed surface of precipitated iron and manganese hydrated oxides; deposit may be solubilized and adsorbed zinc, cadmium and lead may be transferred to water as a result of reduction of iron and manganese under anaerobic that is reducing conditions,
- metals bound to organic matter – adsorbed on surface of organic matter or bound to this matter; zinc, cadmium and lead are temporarily immobilized and, as a result of natural deposit mineralization, they may transfer to one of the other fractions or to water,
- permanently bound to minerals (residue) – zinc, cadmium and lead built in crystal lattice of natural and

secondary minerals, do not transfer to water under natural conditions and in predictable time because they are permanently immobilized; that is why they should not be a real hazard to ecosystems, but they must not be ignored because change of conditions may favour them to transfer to other fractions, and consequently to water.

Additionally, residues after extraction underwent mineralization with concentrated HNO₃ in order to detect the amount of analytes unextracted during conducted procedures. The results prove that applied procedures do not allow extraction of the total amount of analyte. Total values show that external factors such as process duration and temperature applied in Tessier et al. procedure [16] are not sufficient to extract total amount of analyte from tested solid material. Microwave assisted 3-stage procedure combined with mineralization of residues with concentrated HNO₃ applied to lead and zinc analysis allowed extraction of higher amount of analyte from tested material, but for cadmium both methods gave comparable results. Total metal content

in bottom deposit signifies that Zn, Cd and Pb in bottom deposits originate from anthropogenic sources.

Based on 5-stage speciation analysis it can be stated that dominant forms of analytes in individual river deposits were:

- for zinc: exchangeable and organic form (Nida), exchangeable and carbonate form (Maskalis and Brzeźnica),
- for cadmium: exchangeable form (Nida, Brzeźnica), permanently bounded, or residue form (Maskalis),
- for lead: organic form (Nida, Maskalis, Brzeźnica).

Large amount of exchangeable metal forms (20-40% of total content in deposits) may indicate environmental acidification. In research on bottom deposits conducted by some authors [17-20] content of zinc, for example exchangeable form, was low and it did not exceed 2-3% of total amount of this element in deposit. Low mobility of this element might result from pH value of tested environments which amounted to 8.7 while zinc precipitates from water at $\text{pH} > 8$ [21].

Content of the second form of significant bioavailability i.e. metals adsorbed on developed surface of precipitated Fe and Mn oxides and hydroxides amounted to 19% for Zn, 14% for Cd and 18% for Pb on average in tested deposits. The percentage of carbonate bonds of metals in bottom deposits was the lowest for the Nida River (8% Zn, 12% Cd and 11% Pb), while the highest percentage was for Zn and Cd in the Brzeźnica River (26%) and for Pb in the Maskalis River (17%). Content of organic bonds was the highest for lead (40% on average), and it was the lowest for cadmium (16%), which among other things may indicate alkalinisation processes in environment. Lead undergoes these processes and it is transformed into organometallic compounds.

The last tested form of metals included analytes built in crystal lattice of primordial and secondary minerals in deposit. Metals in this fraction are practically immobile and their chemical compounds are passive and biologically unavailable. The percentage of residue fraction in total zinc and lead amount was insignificant (2-11%) while it amounted to 40% for cadmium in deposit collected from the Maskalis River.

In the 5-stage sequential extraction procedure proposed by Tessier et al. (1979) the residual fraction was extracted with the mixture of $\text{HF}:\text{HClO}_4$. Afterwards, the residues after sequential extractions were mineralized with concentrated HNO_3 . In this case the samples were extracted twice the strong acid extraction to the residual phase of the samples, in contrast to the microwave-assisted sequential extraction according to BCR procedure (3-stage sequential extraction). So, although the application of strong mixtures to residual phase in the 5-stage extraction procedure, the ratios of the sum of metal contents of sequential extraction stages to the total metal content obtained with concentrated HNO_3 are quite different from each other for both sequential extraction procedures (Table 5).

The ratios for the 3-stage extraction procedure are generally higher than those of the 5-stage procedure, except analyze: Pb and Cd in Maskalis River samples (I and II respectively), Cd and Pb analyse in Nida River samples (II).

Nevertheless, the differences between the ratios for 3-stage extraction procedure and the ratios for 5-stage extraction procedure are from 0.00% (for Cd, II sample of Maskalis River) to 16.6% (for Zn, I sample of Nida River). I think this problem issue from sediment sample preparation for speciation of heavy metals. Efficiency and repeatability of multistage extraction techniques directly depend on elements such as:

- working conditions: extractant pH and concentration, leaching time, mass ratio of solid to solution, extraction temperature, atmosphere type above solution (air, nitrogen), phase separation method (influence of centrifugation velocity and time, type of filters, etc.),
- decomposition using microwaves in 3-stage extraction procedure,
- a number of stages used for sequential extraction procedures.

“Wet” decomposition with microwaves may proceed both in open and closed system. At the same time, closed system is highly recommended for trace element analysis because it avoids loss of analytes and secondary sample contamination.

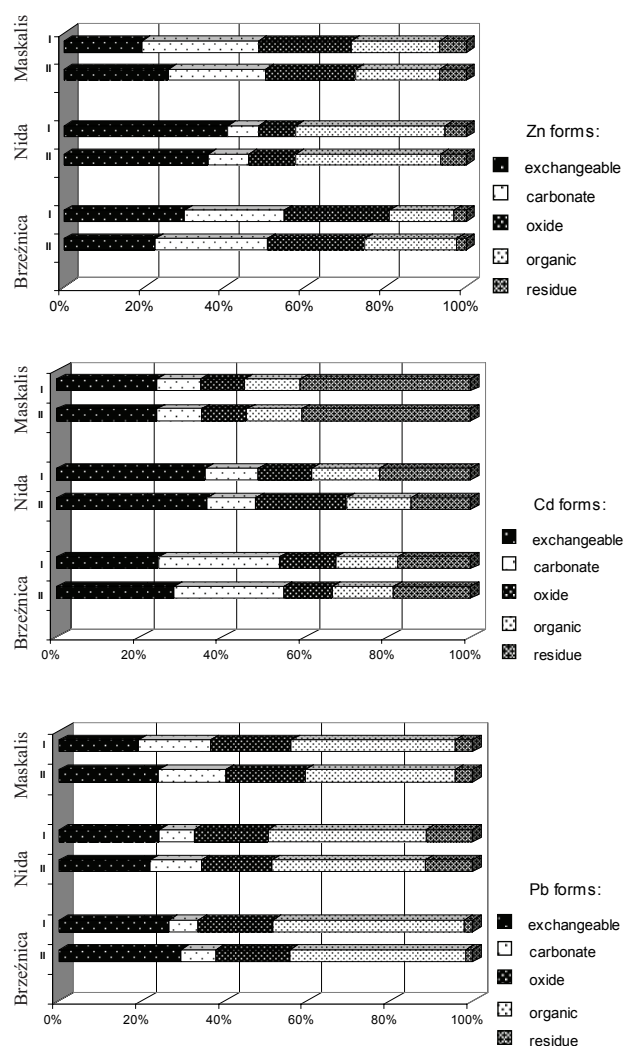


Fig. 4. Percentage of Zn, Cd and Pb forms in particular fractions of tested rivers of Świętokrzyskie Region.

Table 5. The ratios of the sum of metal contents of sequential extraction stages to the total metal content obtained with concentrated HNO₃ for both used sequential extraction procedures.

No.	Method extraction	$\frac{\sum_{i=1}^{n-stage} C_i}{C_{tot.}} \cdot 100$ [%]			The difference between the ratios [%]		
		Zn	Cd	Pb	Zn	Cd	Pb
Maskalis River							
I	A	124.7	116.0	105.0	10.9	2,1	0.48
	B	111.0	113.6	104.5			
II	A	117.2	119.3	107.0	11.6	0.00	2.24
	B	103.6	119.3	104.6			
Nida River							
I	A	124.1	135.7	111.2	16.6	5.85	6.29
	B	103.5	127.1	104.2			
II	A	113.7	141.2	114.2	10.1	0.92	8.76
	B	102.2	142.5	104.2			
Brzeźnica River							
I	A	108.3	123.3	112.2	2.49	5.6	4.10
	B	105.6	116.4	107.6			
II	A	106.6	108.0	106.4	1.97	8.42	2.16
	B	104.5	98.9	104.1			

$$\frac{\sum_{i=1}^{n-stage} C_i}{C_{tot.}} - \text{sum of metal contents of sequential extraction stages.}$$

$C_{tot.}$ - total metal content obtained with concentrated HNO₃.

A presence of organisms, their life-processes and climatic conditions which influence changes in processes forming bottom deposits are also essential in analysis of water ecosystem cleanliness state. Bottom deposit samples were collected at the beginning and at the end of summer. Results prove that qualitative and quantitative changes of analytes proceed in environment. All forms of Zn, Cd and Pb in deposits were characterized by different concentrations dependant on time of sampling except of metals built in minerals or so-called residue.

When comparing analyte amounts in tested bottom deposit from Maskalis, Nida and Brzeźnica Rivers, we noticed that samples from the Brzeźnica River contain the fewest amounts of cadmium and lead and the amount of zinc is the highest. It may result from very close location of ploughlands on which plant protection chemicals containing zinc are used. The closeness of "Nida Gips" industrial plant and high traffic road to Nida River may be a reason for the highest amount of lead in bottom deposit in comparison with those of all analyzed rivers. The lowest amounts of zinc was found in deposits collected from the Maskalis River. But a mixed forest area with a predominance of deciduous trees surrounding the river might be a reason for high amounts of organic and exchangeable forms of Zn, Cd and Pb.

Conclusions

Obtained results indicate if a 5-stage extraction is necessary to get information on the amount of analyte bounded in five fractions in bottom deposits, which is important for development of aquatic organisms and for defining a hazard and a possibility for secondary pollution of water ecosystems by elements.

Bottom deposits of tested watercourses are characterized by high diversity of occurrence and content of individual fractions of analyzed heavy metals. Among others, it is a result of different land development and possibility for inflow of pollutants from tributaries. Moreover, diversified surface features and lithology of bedrock in Nida River catchment significantly contributes to permeability of surface deposits and water quality.

A 5-stage sequential extraction procedure should be applied to precisely determine pollution rate and potential sources of secondary contamination of aquatic ecosystems as well as mobility and bioavailability of heavy metals. It appears to be necessary to develop unified procedure of sequential extraction, which will allow us to determine metal forms in bottom deposit samples and which will enable us to compare cleanliness of water ecosystems and to trace changes in catchment.

Analysis of ground, land development and organisms is a valuable complement of physicochemical research on collected material. Such an approach allows us to isolate potential pollution sources of rivers and their participation in total qualitative and quantitative balance. It also allows us to isolate areas of various environmental hazard rates with regard to mobility and potential bioavailability of heavy metals in bottom deposits.

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