Original Research

Land Development and Forms of Heavy Metals Occurrence (Zn, Cd, Pb) in Polish Rivers

Jacek Namieśnik[1]*, Anna Rabajczyk[2]**

[1]Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland
[2]Independent Department of Environmental Protection and Modelling, Jan Kochanowski University of Humanities and Sciences in Kielce, Świętokrzyska 15 G, 25-406 Kielce, Poland

Received: 10 March 2010
Accepted: 9 August 2010

Abstract

Aquatic ecosystems are exposed to constant human pressure. The concentrations and species in which heavy metals occur are the basis for assessing the threats from secondary contamination of waters due to their toxicity, bioavailability, possible migration, accumulation, and biomagnification. Samples of soils, bottom sediment, and water were collected from a number of rivers in southern Świętokrzyskie province (Kielce region, Poland) that flow through areas with different types of land use. Tessier's sequential extraction technique was used, assisted with microwave radiation and ultrasound. The levels of Zn, Cd, and Pb in the various extracts were determined using F-AAS and GF-AAS.

Keywords: speciation, bottom sediment, soil, zinc, cadmium, lead

Introduction

Natural waters are a living environment for a great many plants and animals, and their chemical composition is characterized by the presence and quantitative interrelations of macro- and microcomponents. Whether the minerals and organic substances in water are present in dissolved, colloidal or suspended form is determined by the physical and chemical properties of the water.

Surface waters are subjected to constant human pressure. The contaminants in these waters, reaching aquatic ecosystems directly or indirectly, occur in different forms. The most stable of them are the heavy metals: their content in the different compartments of water bodies differs, but the largest quantities are found in suspended particulate matter, whereas the smallest are dissolved in the water itself [1-4].

By far the largest proportion of heavy metals discharged into rivers with sewage is transported with the sediments and accumulates in these on the river bed; when waters are high, the sediments also spill over onto the floodplain. Secondary mobilization of metals in sediments can be initiated by a change in pH or redox potential. Exposure of sediments to the air, and also the degradation of organic matter by micro-organisms can mobilize metals from sediments, which previously, in the river bed, were in a wholly or partially anoxic environment [5, 6]. The mobility of metals is additionally controlled by complexing agents like dissolved organic matter and inorganic anions [7, 8].

Fluvial processes, both in the river channel and on the floodplain, affect the magnitude and rate of accumulation of metal-contaminated sediments. In the channel of a continuously flowing river with a sandy bed, metal concentrations reach a maximum along the river bank, whereas in a river with a gravel bed, peak metal levels are found on midstream sandbanks [9, 10].

*e-mail: chemanal@pg.gda.pl
**e-mail: chromium@tlen.pl

Bottom sediments are an important element of aquatic ecosystems, since they provide unique niches for benthic animals and are a source of food for aquatic organisms like small invertebrates or protozoa. In order to evaluate the effect of contaminants on living organisms in an aquatic environment we need to investigate their sources and concentrations. Bottom sediments, acting like a sorption column, are thus a particularly useful study material for determining the main sources of contamination and supply significant information about what is actually going on in the water.

Research Area

Lying in the southern part of Świętokrzyskie province (Kielce region, Poland), the study area embraces two regions: the eastern part of the Pre-Carpathian Depression and the Nida Basin, through which flow the rivers Nida, Maskalis, Gorzyczanka, Bobrza, and Brzeźnica (Fig. 1). The Pre-Carpathian Depression makes up the southeastern part of the province, and its development is linked to the Alpine tectonic movements that caused the folding of the Carpathians. The Nida Basin lies in the southern and southwestern parts of the province.

Hydrographically, the study area lies in the catchment area of the Wisła River. All of the watercourses in question are directly or indirectly left-bank tributaries of the Wisła. The River Bobrza, a right-bank tributary of the Czarna Nida, flows north-south across the middle of the study area. This is situated in the western part of the Holy Cross Mountains mesoregion (Góry Świętokrzyskie), in the vicinity of the Chęcińskie Hills, which are built of mid-Devonian limestones and dolomites. The depression between Bolechowicki Ridge and the Zgórskie Range (Chęciński subregion) is filled with Pleistocene glaciofluvial deposits [11]. Factories and quarries associated with the cement-limestone industry are common in this area, and railway lines and arterial roads pass through it; all are sources of polluting dusts containing both metallic and non-metallic elements.

In contrast, the Gorzyczanka River flows through a countryside of farmland and orchards where pesticides and artificial fertilizers are used. These contain aromatic hydrocarbons, the salts of heavy metals (including Zn), acids, bases, and phenols [12].

The Nida, the longest river in Świętokrzyskie province that flows around the northeastern part of Jędrzejów district and drain the north-central parts of the Nida Basin, is a largely unregulated lowland river with a gentle gradient and numerous meanders. Two of its main tributaries are the Maskalis (left-bank) and the Brzeźnica (right-bank).

The rivers selected for this study flow through areas with different geochemical substrates and land uses, including mudstones ($CaSO_4$); claystones ($CaSO_4$, $CaCO_3$); quartzites $(Mg,Fe)_3Al_2[SiO_4]_3$ and $KAl_2[(OH,F)_2AlSi_3O_{10}]$; marls ($CaCO_3$, $CaMg(CO_3)_2$, and $FeCO_3$), aluminosilicates Al, Mg, and Fe; admixtures SiO_2, $CaCO_3$, $CaMg(CO_3)_2$, and $Fe(OH)_3$; loess formations (SiO_2 (60-70%), $mAl_2O_3{\cdot}nSiO_2$ (20-30%); MCO_3 (8-12%); $Fe(OH)_3$; and $Al(OH)_3$), as well as clay minerals on the geochemical background of the study area [13].

Human activities are an important factor shaping the natural environment. The dusts emitted by the 'Nowiny' cement works, located close to the Bobrza River, contain mostly CaO (41.26%), SiO_2 (15.32%), Al_2O_3 (4.21%), and K_2O (1.90%), and exhibit high pH_{KCl} values. The flue dusts also contain heavy metals, including Zn (173.0 $mg{\cdot}kg^{-1}$), Pb (140.0 $mg{\cdot}kg^{-1}$), and Cd (3.0 $mg{\cdot}kg^{-1}$) [14], which enrich the local soils and waters in the compounds of these metals.

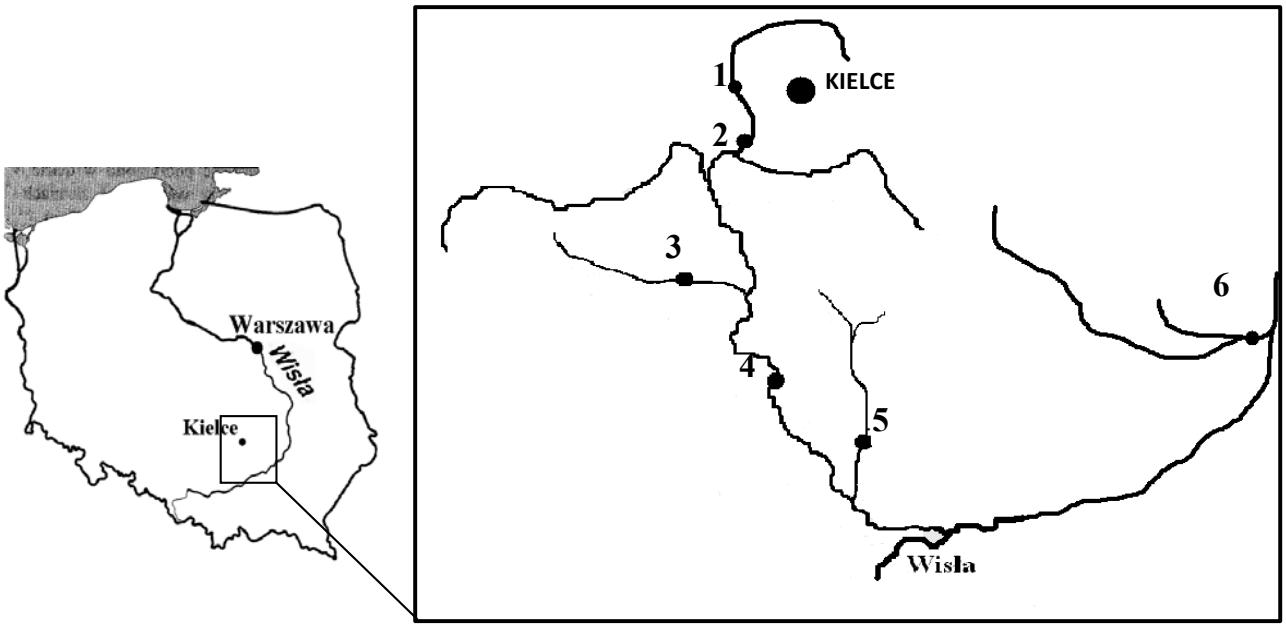

Fig. 1. Location of sampling points (SP) on the rivers Bobrza (SP1, SP2), Maskalis (SP3), Nida (SP4), Brzeźnica (SP5), and Gorzyczanka (SP6).

The chemical composition of these cement-limestone dusts is fairly constant and depends primarily on that of the raw materials used in the manufacturing method, clinker firing, and as cement additives [15].

Experimental Procedures

The test material consisted of water samples from the above-mentioned rivers and samples of bottom sediment from depths down to 20 cm taken at six sites in 2006-08 (Fig. 1) in accordance with the following standards:

- soil samples – PN-R-04031:1997
- bottom sediment samples – PN-ISO 5667-15:2004
- water samples – PN-ISO 5667-6:2003

Sampling could thus be standardized, thereby eliminating accidental errors at this step.

The water samples were taken only from the midstream sections of the rivers, thus avoiding possible effects due to foreign material from the river bank. The alluvial sediment samples were dredged from the river channels in those spots where suspended particulate matter is deposited. The soil samples were taken from sites 10-20 m from the river banks perpendicular to the water and sediment sampling points.

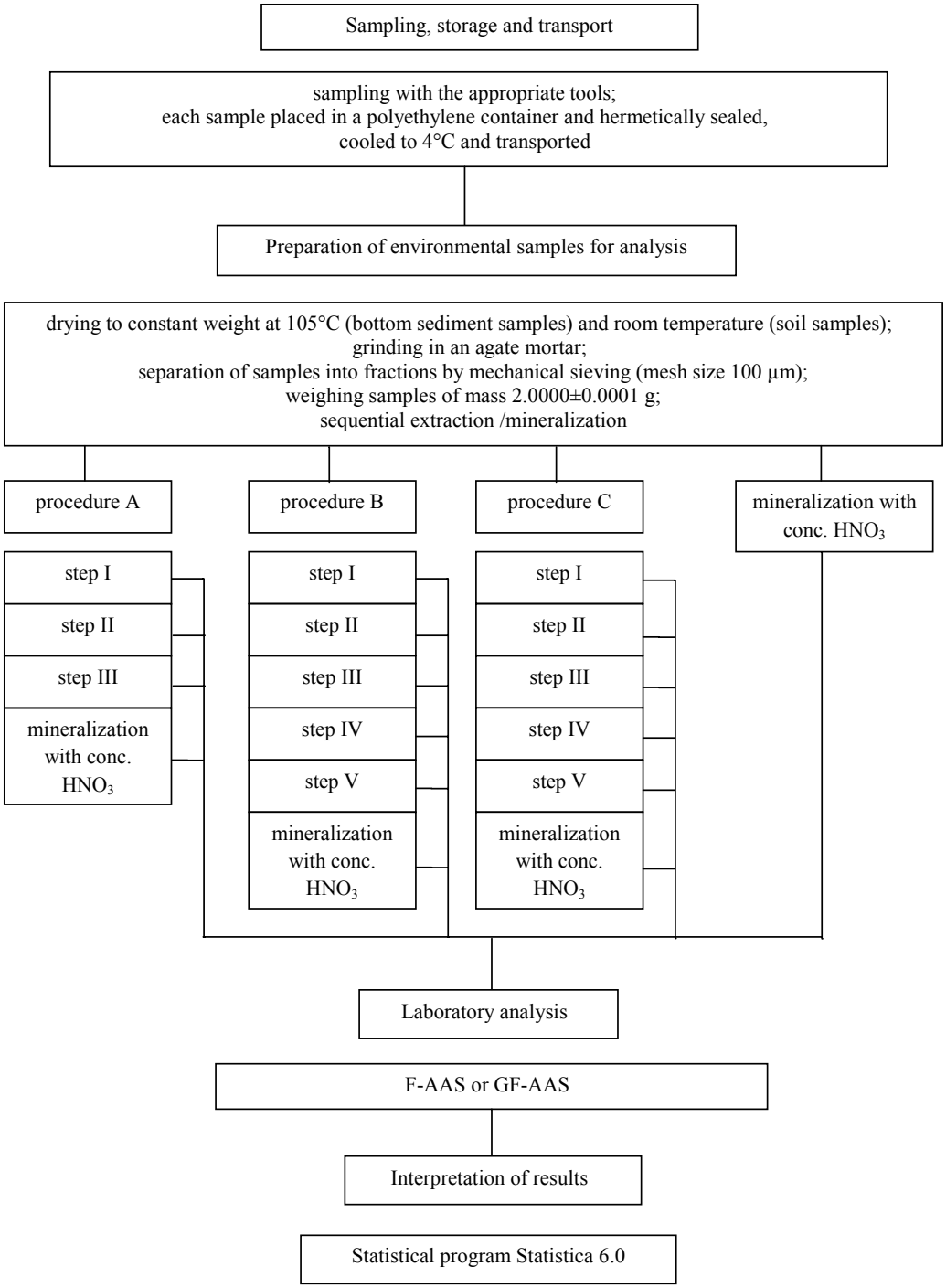

Fig. 2. Scheme showing the procedure for solid environmental samples.

Table 1. Sequential extraction procedure.

Step	Procedure A (microwave-assisted)	Procedure B (after Tessier)	Procedure C (ultrasound-assisted)
Soluble	0.11 mol·l^{-1} acetic acid (HOAc) step I: t_h: 600s, t_c: 300s, P_o: 45W, P: 17-23 atm., t_w: 300s step II: t_h: 600s, t_c: 300s, P_o: 115W, P: 21-25 atm., t_w: 300s step III: t_h: 300s, t_c: 300s, P_o: 150W, P: 25-30 atm., t_w: 300s	1.0 mol·l^{-1} magnesium chloride ($MgCl_2$) at pH 7 at room temperature for 1 h	1.0 mol l-1 magnesium chloride ($MgCl_2$) at pH 7 ultrasound for 60 min
Exchangeable			
Associated to Carbonates		1.0 mol·l^{-1} sodium acetate (NaOAc), acetic acid (HOAc) at pH 5 at room temperature for 3 h	1.0 mol·l^{-1} sodium acetate (NaOAc), acetic acid (HOAc) at pH 5 ultrasound for 60 min
Amorphous Fe oxyhydroxide	0.1 mol·l^{-1} hydroxylammonium chloride ($NH_2OH{\cdot}HCl$) at pH 2 step I: t_h: 60s, t_c: 60s, P_o: 39W, P: 23-25 atm., t_w: 300s	0.04 mol·l^{-1} hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), 25% (v/v) acetic acid (HOAc) at pH 2 at 96ºC with occasional agitation for 6 h	0.04 mol·l^{-1} hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), 25% (v/v) acetic acid (HOAc) at pH 2 ultrasound for 60 min
Crystalline Fe oxide			
Oxidizable associated with organic matter and sulphides	30% hydrogen peroxide (H_2O_2) step I: t_h: 60s, t_c: 60s, P_o: 117W, P: 23-25 atm., t_w: 300s 1.0 mol·l^{-1} ammonium acetate (NH_4OAc) at pH 2 step II: t_h: 60s, t_c: 60s, P_o: 117W, P: 23-25 atm., t_w: 300s	30% hydrogen peroxide (H_2O_2), 0.02 mol·l^{-1} nitric acid (HNO_3) at pH 2 at 85ºC for 5 h cooling 3.2 mol·l^{-1} ammonium acetate (NH_4OAc) in 20% (v/v) HNO_3 at room temperature for 30 minutes	30% hydrogen peroxide (H_2O_2), 0.02 mol·l^{-1} nitric acid (HNO_3) at pH 2 ultrasound for 30 min 3.2 mol·l^{-1} ammonium acetate (NH_4OAc) in 20% (v/v) HNO_3 ultrasound for 30 min
Residual and silicates		digestion with hydrofluoric acid (HF) + perchloric acid ($HClO_4$) (5:1) at room temperature for 5 h	digestion with hydrofluoric acid (HF) + perchloric acid ($HClO_4$) (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

The sediments were sampled with an Ekman-Birge grab, and the soils were taken from the surface layer down to a depth of ca 20 cm with a special soil sampler. Because of the frequent multicomponent determinations of trace elements on the same samples, stainless steel sampling tools and sieves, and polyethylene bags and bottles were used. In addition, one in ten samples was duplicated, so that analyses monitoring the study could be carried out. Blank samples, making up ≥ 3% of the total number of normal samples, were taken to determine the practical limit of detection.

The excess water was removed from the sediment samples to prevent the dissolution of some of the sediment components. The sediment and soil samples were sieved, then dried at a suitable temperature to prevent the growth of mould and micro-organisms that would redistribute chemical components, thus altering the composition of the material. After coning and quartering, the dried samples were ground in an automatic agate mortar to a grain size of < 100 μm. This soil and sediment material was then subjected to further preparatory processing – dissolution and extraction – in accordance with the scheme shown in Fig. 2. The pH and heavy metal contents of these samples were then determined.

Certified reference materials (CRM) – bottom sediments (CMR 320) and soils (BCR 142) – were used to establish the optimal parameters for procedures A and C. The reference method was Tessier's 5-step sequential extraction, a standard reference technique. The parameters for which the results were comparable in all three CRM procedures (Table 1) were then applied to the assay of the real environmental samples.

Each solution obtained after the various sequential extraction steps and also after mineralization with conc. HNO_3 was analyzed for its heavy metal content using F-AAS or GF-AAS, depending on the analyte concentration; the sediment was dried and weighed. In addition, to verify the efficacy of the sequential extractions, dessicated sediment and soil samples were mineralized with conc. HNO_3.

As part of the quality assurance system, the precision of the results was tracked and assessed by periodically assaying control samples. Accuracy was assessed in three ways:

1) CRM sample assay,
2) samples + added standard assayed,
3) comparison of the results of 2) with those obtained for the same sample using the Tessier reference method of sequential extraction.

Table 2. Species of zinc contained in the sediment samples [mg/kg dry matter] (mean and standard deviation).

Extraction procedure	Species					in HNO_3	Sum
	exchangeable	carbonate	oxide	organic/ organic and sulphide[A]	residue		
Bobrza River (SP1)							
A		41.31	20.03	6.81		1.60	69.75±13.23
B	8.98	30.04	25.98	11.45	4.50	0.13	81.08±10.31
C	3.55	12.32	22.76	3.40	3.66	21.95	67.64±12.27
in HNO_3						71.00	71.00±8.87
Bobrza River (SP2)							
A		31.16	23.86	15.43		3.55	74.00±11.65
B	8.64	29.34	25.17	14.01	5.23	0.01	82.40±10.31
C	2.02	6.22	7.29	2.43	2.37	35.30	55.63±9.61
in HNO_3						75.56	75.56±9.54
Maskalis River (SP3)							
A		18.81	22.76	33.64		3.95	79.16±7.44
B	8.48	20.70	18.02	17.05	5.13	2.86	72.24±9.15
C	3.04	11.23	8.42	5.01	2.08	32.21	61.99±9.83
in HNO_3						76.32	76.32±5.28
Nida River (SP4)							
A		34.37	23.87	34.17		4.35	96.76± 27.5
B	30.71	7.06	8.43	29.29	4.67	3.51	83.67± 8.26
C	11.98	3.42	2.44	7.84	2.11	34.99	62.78±15.50
in HNO_3						81.38	81.38±6.12
Brzeźnica River (SP5)							
A		44.85	28.34	25.29		2.25	100.73±19.14
B	24.82	24.76	23.70	18.23	2.51	4.40	98.42± 17.85
C	7.74	14.11	14.83	10.56	3.45	32.81	83.50±19.77
in HNO_3						93.75	93.75±15.45
Gorzyczanka River (SP6)							
A		0.18	0.19	1.19		1.37	2.93±0.98
B	0.15	0.21	1.45	1.77	0.07	0.06	3.71±0.73
C	0.07	0.17	0.26	0.07	0.39	1.29	2.25±0.62
in HNO_3						3.89	3.89±2.02

[A] organic – for 5-step extraction; organic and sulphide – for 3-step extraction

The reference method and the standard addition method were also used to determine and eliminate the variable systematic error. To this end a series of measurements was carried out for two solutions: the sample and the sample plus standard using the method under investigation, and a series of measurements for two standards using the reference method and the method under investigation. The correctness of the determinations was checked using the standard addition method; accuracies were ± 2.0, 4.0, and 3.2% for Cd, Zn, and Pb, respectively. The Statistica 6.0 statistical program was used for working up the results.

In order to assess the reproducibility of the results, given the impossibility of using reference materials, a known quantity of the solution of a metal (Cd, Zn, Pb) salt was added to the sediment sample. Analysis of the metal

Table 3. Species of cadmium contained in the sediment samples [mg/kg dry matter] (mean and standard deviation).

Extraction procedure	Species					in HNO_3	Sum
	exchangeable	carbonate	oxide	organic/ organic and sulphide[A]	Residue		
Bobrza River (SP1)							
A		1.05	1.01	0.92		0.04	3.02±1.02
B	0.39	0.78	0.75	0.55	0.92	0.01	3.40±1.25
C	0.11	0.22	0.21	0.30	0.45	1.26	2.55±1. 09
in HNO_3						2.22	2.22±0.40
Bobrza River (SP2)							
A		1.05	1.20	0.92		0.16	3.33±1.74
B	0.53	0.80	0.83	0.55	1.10	0.01	3.82±1.20
C	0.23	0.24	0.46	0.11	0.51	1.05	2.60±1.22
in HNO_3						2.73	2.73±0.40
Maskalis River (SP3)							
A		2.23	2.22	1.26		4.37	10.08±1.22
B	1.81	0.86	0.85	1.07	3.05	2.27	9.91±3.84
C	1.05	0.50	0.48	0.60	2.39	5.01	10.03±4.40
in HNO_3						9.42	9.42±1.52
Nida River (SP4)							
A		3.54	1.47	1.37		4.23	10.61±3.59
B	2.49	0.93	1.33	1.16	1.24	3.10	10.25±3.37
C	1.43	0.60	0.85	0.52	0.87	5.13	9.40±3.63
in HNO_3						7.50	7.50±3.49
Brzeźnica River (SP5)							
A		3.17	1.13	1.73		3.12	9.15±2.01
B	1.72	1.83	0.85	0.98	1.08	2.13	8.59±1.30
C	0.59	0.91	0.48	0.54	0.67	4.27	7.46±3.82
in HNO_3						8.02	8.02±2.48
Gorzyczanka River (SP6)							
A		1.28	1.23	0.88		0.34	3.73±2.16
B	0.29	0.79	1.30	0.87	0.40	0.15	3.80±2.36
C	0.19	0.31	0.52	0.62	0.23	1.17	3.04±2.15
in HNO_3						3.49	3.49±2.20

[A] organic – for 5-step extraction; organic and sulphide – for 3-step extraction

content in the extract of sediment with and without the addition of the relevant salt showed that 94% Cd, 91% Zn, and 89% Pb passed into the extract obtained after step I.

The microwave-assisted (150-300 W) mineralization of samples was carried out in a high-pressure (110 atm), high-temperature (250ºC) microwave mineralizer module (UniClever) with integral pressure control in the reaction vessel and temperature monitoring.

The ultrasound-assisted mineralization was performed in a SONICA ultrasound scrubber with an ultrasound generating power of 520 W and 45 kHz frequency.

Pb, Cd, and Zn contents in the solutions were analyzed using a flame (air-acetylene) AAS Savanta spectrometer (GBC) and a graphite cuvette with appropriately set parameters.

Quality assurance of analytical results was carried out by checking the reliability of the measuring instruments

Table 4. Species of lead contained in the sediment samples [mg/kg dry matter] (mean and standard deviation).

Extraction procedure	Species					in HNO_3	Sum
	exchangeable	carbonate	oxide	organic/ organic and sulphide[A]	residue		
Bobrza River (SP1)							
A		34.05	41.37	25.08		13.25	113.9±32.35
B	15.18	28.46	46.36	22.27	4.46	0.08	116.8±12.73
C	4.70	18.43	27.19	11.16	6.83	33.82	102.1±34.14
in HNO_3						102.9	102.9±16.33
Bobrza River (SP2)							
A		38.29	44.45	20.90		6.22	109.9±22.71
B	17.63	25.10	45.45	26.08	4.53	0.05	118.8±12.16
C	12.91	18.68	31.89	19.71	4.00	23.33	110.5±29.76
in HNO_3						107.1	107.1±13.87
Maskalis River (SP3)							
A		39.81	24.34	39.58		16.44	120.2±22.11
B	24.79	19.46	22.31	43.66	4.88	3.48	118.6±14.33
C	14.99	13.05	17.19	34.01	3.10	27.41	109.8±31.85
in HNO_3						113.4	113.4±23.30
Nida River (SP4)							
A		43.96	46.98	48.90		2.92	142.8±24.65
B	29.56	13.38	22.33	48.11	14.61	3.97	132.0±22.61
C	11.32	12.16	20.57	36.13	13.85	30.60	124.6±30.05
in HNO_3						126.7	126.7±27.7
Brzeźnica River (SP5)							
A		25.80	9.29	34.41		3.96	73.46±15.12
B	19.13	5.32	12.32	30.30	1.23	2.85	71.15±12.37
C	10.87	3.64	7.57	17.79	0.69	17.70	58.26±22.67
in HNO_3						67.27	67.27±26.16
Gorzyczanka River (SP6)							
A		0.769	1.977	3.202		0.027	5.975±2.006
B	0.065	1.18	9.27	0.320	0.370	0.050	11.26±2.840
C	0.012	0.070	0.560	0.055	0.217	4.60	5.514±0.169
in HNO_3						7.21	7.21±1.001

[A] organic – for 5-step extraction; organic and sulphide – for 3-step extraction

and the range of applicability of the analytical procedure, and also by calibrating the procedure periodically with the aid of mixtures of standards. The reliability of the entire analytical procedure was monitored in two ways: by adding a standard to the assayed sample and by using CRMs of bottom sediments (CMR 320) and soils (BCR 142).

Results

The samples of water, bottom sediments and soils were taken from rivers and their immediate vicinity in the southern part of Świętokrzyskie province in 2006-08. The samples were analyzed for their metal species content using sequential extraction (three procedures – see Table 1) and

Table 5. Species of zinc contained in the soil samples [mg/kg dry matter] (mean and standard deviation).

Extraction procedure	Species					in HNO_3	Sum
	exchangeable	carbonate	oxide	organic/ organic and sulphide[A]	residue		
Bobrza River (SP1)							
A		86.40	50.76	3.125		8.10	148.4±20.20
B	23.76	72.12	52.54	2.130	4.09	0.03	154.7 ±16.41
C	15.53	51.10	34.31	1.884	3.89	5.64	112.4±32.17
in HNO_3						145.9	145.9±12.51
Bobrza River (SP2)							
A		87.26	51.61	2.022		9.35	150.2±23.05
B	23.41	73.39	50.21	1.665	4.02	0.05	152.7 ±15.62
C	10.18	52.95	32.82	2.199	16.70	34.29	149.1±31.61
in HNO_3						149.2	149.2 ±15.63
Maskalis River (SP3)							
A		17.39	28.00	21.06		12.01	78.46±21.79
B	3.211	15.41	28.34	18.65	12.34	0.014	77.97±15.60
C	1.012	8.022	15.08	10.11	24.88	14.99	74.09±19.4
in HNO_3						73.03	73.03±1.53
Nida River (SP4)							
A		17.77	27.73	19.01		12.99	77.50±16.43
B	2.11	17.66	28.05	18.02	11.89	0.017	77.75±22.34
C	1.07	7.933	14.10	9.00	24.59	17.79	74.48±30.73
in HNO_3						73.27	73.27±1.25
Brzeźnica River (SP5)							
A		15.10	14.31	11.89		15.72	57.02±20.28
B	3.01	16.32	12.26	12.07	14.55	0.12	58.33±12.92
C	1.04	8.12	5.29	5.44	15.27	19.06	54.22±18.69
in HNO_3						52.93	52.93±2.20
Gorzyczanka River (SP6)							
A		0.343	0.530	2.646		1.062	4.581±0.726
B	0.164	0.360	0.566	2.268	1.110	0.019	4.487±0.938
C	0.138	0.376	0.343	0.563	0.061	2.036	3.517±0.872
in HNO_3						4.459	4.459±1.932

[A] organic – for 5-step extraction; organic and sulphide – for 3-step extraction

mineralization with concentrated HNO_3. The levels of zinc, cadmium and lead were assayed in all the solutions obtained (Tables 2-8).

Discussion of Results

The monitoring and analysis of the state of contamination of the rivers in the Wisła catchment area is of great significance as regards carrying out the tasks set out in the Framework Water Directive and the danger of flood hazard. That is why this study dealt with rivers in this catchment area. Samples for analysis were collected at six locations on the rivers Bobrza, Nida, Maskalis, Brzeźnica, and Gorzyczanka, and in their immediate vicinity in the south of Świętokrzyskie province. All these rivers are directly or indirectly left-bank tributaries of the Wisła.

Table 6. Species of cadmium contained in the soil samples [mg/kg dry matter] (mean and standard deviation).

Extraction procedure	Species					in HNO_3	Sum
	exchangeable	carbonate	oxide	organic/ organic and sulphide[A]	residue		
Bobrza River (SP1)							
A		4.22	3.61	0.23		2.65	10.71±3.48
B	1.18	5.38	4.36	0.10	0.14	0.04	11.20±4.32
C	0.24	0.73	1.78	0.11	0.51	6.37	9.74±5.55
in HNO_3						11.02	11.02±3.62
Bobrza River (SP2)							
A		5.57	4.38	0.14		0.85	10.94±4.33
B	1.15	5.35	4.36	0.10	0.10	0.10	11.16±4.31
C	0.15	0.86	0.60	0.11	0.11	7.78	9.61±5.52
in HNO_3						10.84	10.84±3.57
Maskalis River (SP3)							
A		0.102	0.093	0.063		0.122	0.380±0.27
B	0.102	0.069	0.117	0.062	0.014	0.019	0.383±0.31
C	0.054	0.046	0.069	0.037	0.020	0.147	0.373±0.29
in HNO_3						0.350	0.350±0.111
Nida River (SP4)							
A		0.171	0.083	0.071		0.056	0.381±0.25
B	0.107	0.090	0.082	0.058	0.034	0.016	0.387±0.26
C	0.042	0.055	0.037	0.020	0.010	0.205	0.369±0.29
in HNO_3						0.375	0.375±0.12
Brzeźnica River (SP5)							
A		0.323	0.108	0.051		0.050	0.532±0.28
B	0.243	0.135	0.077	0.041	0.021	0.020	0.537±0.38
C	0.096	0.092	0.043	0.020	0.035	0.201	0.487±0.34
in HNO_3						0.514	0.514±0.19
Gorzyczanka River (SP6)							
A		0.104	0.133	0.040		0.063	0.340±0.21
B	0.076	0.055	0.147	0.030	0.031	0.012	0.351±0.31
C	0.020	0.019	0.048	0.015	0.041	0.186	0.329±0.29
in HNO_3						0.304	0.304±0.19

[A] organic – for 5-step extraction; organic and sulphide – for 3-step extraction

The waters in these rivers have different pH values and heavy metal contents. The pH of the water samples varied from 6.11 (SP3) to 8.13 (SP6). Worth noting is the basic nature of the waters from the Gorzyczanka (pH=8.13) and Bobrza (pH = 7.27-7.98), high pH causes poorly soluble compounds to precipitate, including the carbonates and phosphates of Zn, Cd, and Pb, which reduces the concentrations of these analytes in the water. The levels of these metals were lowest in the Gorzyczanka, which had the highest pH, but were highest in the Nida, where the pH was ca 6.6. Determinations of Zn, Cd, and Pb levels in the water samples indicate that all the rivers sampled are strongly polluted. Only the waters of the Gorzyczanka can be put into category A1 with respect to their Zn level; where the Cd and Pb levels are concerned, however, these waters are non-classifiable. Generally speaking, the quality of the waters in these rivers is below that of good chemical status.

Table 7. Species of lead contained in the soil samples [mg/kg dry matter] (mean and standard deviation).

Extraction procedure	Species					in HNO_3	Sum
	exchangeable	carbonate	oxide	organic/ organic and sulphide[A]	residue		
Bobrza River (SP1)							
A		87.79	68.26	20.22		6.93	183.2±33.47
B	25.52	70.90	70.10	18.98	2.06	0.037	187.6±20.26
C	12.52	25.81	53.56	23.11	4.80	60.37	180.2±34.90
in HNO_3						171.3	171.3±22.76
Bobrza River (SP2)							
A		83.50	68.30	19.80		13.61	185.2±24.55
B	25.73	72.92	66.67	18.31	2.12	0.037	185.8±19.70
C	14.99	54.15	52.82	14.21	5.13	33.82	175.1±34.22
in HNO_3						168.2	168.2±20.56
Maskalis River (SP3)							
A		8.78	6.63	2.79		4.85	23.05±11.09
B	3.91	7.28	6.39	2.28	2.63	1.10	23.59±8.86
C	2.28	5.90	4.52	0.81	5.19	5.30	24.00±12.61
in HNO_3						22.54	22.54±15.25
Nida River (SP4)							
A		14.27	14.26	9.08		4.59	42.20±19.43
B	6.11	11.23	12.65	8.83	3.90	0.21	42.93±15.70
C	3.87	5.87	7.67	6.97	8.94	7.48	40.80±17.97
in HNO_3						39.18	39.18±4.49
Brzeźnica River (SP5)							
A		6.39	6.37	5.32		2.26	20.34±4.62
B	2.54	3.79	5.23	4.69	3.19	0.42	19.86±5.78
C	2.09	2.34	3.41	3.51	5.14	3.20	19.69±8.68
in HNO_3						16.77	16.77±3.64
Gorzyczanka River (SP6)							
A		0.550	4.689	3.47		0.553	9.26±1.14
B	0.722	0.343	8.94	0.211	0.480	0.036	10.73±2.19
C	0.526	0.362	6.51	0.026	0.071	1.73	9.23±1.60
in HNO_3						5.19	5.19±2.09

[A] organic – for 5-step extraction; organic and sulphide – for 3-step extraction

There are no natural sources of Zn, Cd, or Pb contamination due to the bedrock in the catchment areas of these rivers. The presence of heavy metals in these aquatic ecosystems is therefore solely the consequence of human activities. The chemical composition of the waters in the Bobrza and Nida is determined by the proximity of industrial plants (Sitkówka-Nowiny, Nida Gips). The discharge of flue dusts, containing not only Ca, Mg, and K, but also heavy metals like Zn, Pb, and Cd, means that the soils and waters in their vicinity are enriched in the compounds of these elements. The channels of the Brzeźnica and Gorzyczanka pass through farmland on which pesticides and synthetic fertilizers are used, which contain such compounds as the salts of heavy metals, acids, bases, and phenols. In contrast, the Maskalis flows through mixed deciduous woodland; the presence of these trees and the processes governing a woodland ecosystem influence the physicochemical nature of both water and bottom sediment.

Table 8. Cadmium, zinc, and lead content of water samples and the pH of the water, bottom sediment, and soil samples from the rivers (mean and standard deviation).

Sampling point	Concentration [ppb]			pH		
	Cd	Zn	Pb	Water	Bottom sediment	Soil
(SP1)	2.66±0.60	9.26±2.00	4.02±1.30	7.56	8.62	8.26
(SP2)	2.76±0.65	6.36±1.95	3.77±1.15	7.96	8.61	8.27
(SP3)	3.54±1.07	32.6±11.6	4.52±2.09	6.19	6.79	6.22
(SP4)	7.05±2.93	65.5±15.8	53.5±16.8	6.72	6.99	7.03
(SP5)	1.72±0.77	9.76±3.04	6.04±1.53	6.70	6.33	6.12
(SP6)	0.60±0.32	1.02±1.10	2.06±1.10	8.13	6.32	6.14

The acidic podzols of the woodland, and the sulphur and nitrogen compounds in the air blowing in from the nearby spa town, may lead to the acidification of surface waters, and in consequence cause poorly soluble compounds of metals to dissolve and be released into the water. A further important factor affecting water quality at the sampling points is the closeness of roads and the discharges of pollutants from communal and industrial sewage treatment plants.

Apart from defining the degree of contamination of these rivers and evaluating the effect of land use on their condition, this study also aimed to compare the efficacy of three sample preparation procedures:

1) an EU-recommended microwave-assisted 3-step sequential extraction (Procedure A),
2) Tessier's classical, routinely used, 5-step sequential extraction (Procedure B),
3) an ultrasound-assisted 5-step sequential extraction using the same reagents as in Tessier's method (Procedure C).

After each step in the three procedures the Zn, Cd, and Pb levels were assayed using AAS, depending on the concentrations of the analytes in the extracts.

Comparison of the results of speciation analysis obtained using these procedures and of the general analysis using mineralization with conc. HNO_3 (Tables 3-8) indicates that sequential extraction enables greater quantities of the analytes deposited in the sediment and soil to pass into the extract. In many cases, moreover, microwave-assisted extraction yields higher concentrations of analytes than traditional sequential extraction. The most effective procedures for the analysis of bottom sediment and soil samples are therefore A and B. With procedure C, on the other hand, analytes are leached out of solid samples in quantities greater than those obtained with HNO_3 in only 40% of samples.

The results also indicate that one-step mineralization is insufficient. That is why the expression 'total content' used in the discussion of results obtained in this way is a misrepresentation. Also not to be forgotten is the fact that one-step mineralization does not tell us anything about the forms of occurrence of the various metals, or about their quantities deposited in the bottom sediment or soil – information that is critical, for example, in the context of decisions on whether or not to recultivate aquatic ecosystems. By defining the threats to the environment from potential secondary contamination by metals or the possible uptake of metals by aquatic organisms like macrolites or molluscs, we can perform effectively the tasks set out in the Framework Water Directive, including those relating to the conservation of Baltic Sea waters. Therefore, further discussion on the extent of contamination of the rivers covered by this study is based on the results obtained using procedures A and B only.

The largest amounts of Zn were found in the bottom sediment samples from the rivers Nida (SP4) and Brzeźnica (SP5), while the greatest quantities of Cd and Pb were in the sediments from the Maskalis (SP3) and Nida (SP4), the respective levels of these metals being 100, 10.5, and 140 ppm. In contrast, the smallest quantities of metals were found in the sediments from the Gorzyczanka (Zn = ca 3.5 ppm, Pb = ca 11 ppm) and Bobrza at both measurement points (Cd = ca 3.5 ppm). In the case of soils sampled 10-20 m from the river banks perpendicular to the water and sediment sampling points, the maximum and minimum amounts of the analytes fluctuated around different values. The highest amounts of Zn, Cd, and Pb (ca 154, 11, and 186 ppm, respectively) were recorded in the soils at both SPs by the Bobrza, whereas the lowest quantities were found near the Gorzyczanka (ca 4,7 ppm Zn, 0.35 ppm Cd, and 10.5 ppm Pb) and the Maskalis (ca 3.5 ppm Cd).

The bottom sediments of these rivers are therefore scarcely contaminated with Zn, slightly contaminated with Pb, but contaminated with Cd. Seen from the point of view of soil quality standards (Table 9), the soil samples can be classified in group A (from near the Maskalis, Brzeźnica, and Gorzyczanka with respect to their Cd, Pb, and Zn levels), group B (the Bobrza at both SPs with respect to the Zn level) and group C (the Bobrza at both SPs with respect to the Cd and Pb levels). The worst polluted rivers are therefore the Bobrza, Maskalis, Nida, and Brzeźnica, whereas the Gorzyczanka and the adjacent terrain is the least contaminated.

The total metal content in the bottom sediment constitutes evidence for the deposition of anthropogenic loads of Zn, Cd, and Pb in it. The slightly basic pH of the water (at

Table 9. Geochemical background and permissible levels of Cd, Pb, and Zn for bottom sediments and soils [ppm] [16].

Metal	Geochemical background		Sediments			Soil[A]		
	sediment	soil	scarcely contaminated	slightly contaminated	contaminated	Group A	Group B	Group C
Cd	< 0.5	< 0.5	1	5	20	1	4	15
Pb	15	26 – 34	50	200	500	50	100	600
Zn	73	37 – 64	200	1000	2000	100	300	1000

[A]Permissible levels for samples taken from depths down to 30 cm

SP1, 2, and 6) may reduce the solubility of the relevant metal compounds, which will limit their ability to pass into the aqueous phase. However, the rate of metal migration to the water may rise in the presence of organic compounds or carbonates, or when high temperatures prevail. The invariable functioning of the ecosystem may be additionally threatened by the discharge of sewage, as well as acid rains and surface run-off that might increase the acidity of the river water, and consequently the solubility of Zn, Cd, and Pb compounds bound up in the sediment.

Metal compounds contained in the soil are released, mainly in general and soluble forms. Since this also lowers soil pH, there is a considerable increase in metal solubility (additionally affected by the redox potential), and migration of mobile forms of Cd, Zn, and Pb into the water-bearing layer is enhanced. Migration of these metals from the soil and bottom sediment to the water therefore causes secondary contamination and increases their concentrations in the aquatic ecosystem. Metals forming readily soluble compounds are more mobile and are more easily assimilated by aquatic organisms, which may well be why they accumulate in them.

A suite of different analytical approaches are applied to prepare samples for determining the levels of the bioavailable species of heavy metals they contain. The usual procedures, however, involve sequential extraction, the aim of which is to determine the fractions of trace metals present in sediment or soil, which can respond, each in its own specific way, to changes in the environment. The modification and development of extraction techniques is moving toward using smaller quantities of less aggressive extractants, since metals leached under less aggressive conditions are better correlated with their bioavailability.

The sequential extraction methods used here, whether 3-step or 5-step, yielded information on the various forms of occurrence and bioavailability of Zn, Cd, and Pb in the bottom sediments and soils in the study area. BCR extraction of analytes from sediments and soils provided information about the amounts of Zn, Cd, and Pb in carbonate, oxide, organic and sulphide form, whereas Tessier's method yielded information on these metals in the individual forms (Tables 2-7).

The 3-step sequential extraction yields information on the most bioavailable fractions and on the fractions able to migrate between phases in response to environmental changes in pH or redox potential. This EU-recommended procedure does not, however, give any information about metals bound to organic matter (fraction IV in Tessier's method) or metals permanently bound to the soil, usually to its mineral components (fraction V in Tessier's method). Fraction IV consists of metal compounds that are usually inaccessible to non-aggressive solutions for a certain period. But as time passes, aerobic or anaerobic decomposition of the organic matrix enables metals to pass into solution or other fractions, thereby becoming a source of secondary contamination in waters. The analytes contained in Tessier's fraction V are practically immobile and their compounds are chemically passive and biologically unavailable; but given favourable changes in the environment, even they can migrate to other fractions, thus posing a threat to ecosystems. Modification of this technique therefore appears indispensable. If the maximum information is to be acquired about all the fractions in which a given analyte is present, even those posing the smallest possible threat to the environment.

The results indicate that, with the procedures applied here, the analyte cannot be extracted in its entirety. The total metal concentrations obtained show, moreover, that the external factors invoked in Tessier's [17] procedure, such as the duration of the procedure and the temperature, are in many cases insufficient to extract an analyte in its entirety from solid matter. But in contrast to the 3-step procedure, only trace amounts of metals remain unaccounted for.

The respective pH ranges of the sediment and soil samples analyzed in this work are 6.20-8.80 and 6.10-8.31 (Table 10). The occurrence of soils and bottom sediments with high pH values (SP 1 and 2) is due principally to their content of grains and particles of limestone and the deposition of cement-limestone dusts. The basicity of the soil, as well as the bottom sediments and water of the Bobrza, may be the reason why metals are immobilized there. This is confirmed by the total metal contents in the soil and sediment samples from these two SPs, which are indicative of elevated concentrations of Zn, Cd, and Pb.

The bottom sediments of the Bobrza and the soils in its immediate vicinity are similar with respect to the contents of the various fractions of Zn, Cd, and Pb. From a comparison of the analyte quantities in the solid samples it emerges that both in soils and sediments, most of the Zn, Cd, and Pb occurs in the form of carbonates or is co-precipitated with carbonates, and is also adsorbed on the extended surface area of precipitated hydrated oxides of iron and manganese. Far smaller quantities of these analytes are adsorbed on the surface of solid bodies, and can pass into the water as a con-

sequence of a change in the ionic composition of the water or a shift in the sorption-desorption equilibrium (exchangeable metals), or are absorbed on or bound to organic matter. The smallest amounts of Zn and Pb are found in the fraction permanently bound to minerals (residue), while those of Cd are in the exchangeable fraction.

The distribution of metals in the various bottom sediment and soil fractions at the other sampling points is different:

- zinc: carbonate and oxide (SP3), exchangeable and oxide (SP4), exchangeable and carbonate (SP5), and organic (SP6);
- cadmium: permanently bound (residue) and oxide (SP3), exchangeable (SP4), carbonate (SP5), and oxide (SP6);
- lead: organic and carbonate (SP3), organic and oxide (SP4 and SP5), and oxide (SP6).

These data indicate that Zn, Cd, and Pb in the soil samples are predominantly bound to carbonate and to the hydrated oxides of Fe and Mn. The smallest quantities of these metals were measured in the exchangeable metal, organic-bound and mineral-bound (residue) fractions. The largest amounts of Zn, Cd, and Pb in the bottom sediment samples, however, were present in the carbonate and organic matter fractions, whereas the smallest quantities were in the fraction containing metals permanently bound to minerals.

In soils and hypergenic environments, zinc forms complex ions like $[ZnOH]^+$, $[ZnHCO_3]^+$, $[Zn(OH)_3]^-$, and $[ZnO_2]^-$ [18]. In these soil and sediment samples it is strongly bound by Fe and Mn oxides, a typical feature in environments into which large loads of pollutants are discharged. Zinc is also bound to carbonate; in this form it complements exchangeable zinc and is therefore a danger to the environment. This kind of situation is due to the sensitivity of the carbonate form to changes in pH and the reduction in carbonate solubility with increasing environmental pH [18]. Zinc is sorbed in the presence of organic compounds, although this process, too, is governed by the pH of the medium: at pH 5.8, 60% of the cationic concentration of zinc is bound by humic acids, whereas at lower values, sorption is practically non-existent. Despite the alkalization of the environment, the amount of Zn bound up in the organic fraction is small, making up only ca 1.3% of all the forms determined in the soil samples. The bottom sediments contained more Zn in the organic fraction: ca 21% in 2007 and 11% in 2008 in relation to the overall content of this element in the study material. The mobility of Zn is therefore controlled by its bond to the oxide fraction and the high Ca:Zn ratio [18], which is the effect of an annual Ca deposition of ca 3 $mg \cdot m^{-2}$ in this area [14].

The geochemical properties of cadmium are similar to those of zinc. Found mostly in the divalent form, Cd participates in various complex ions like $[CdOH]^+$, $[CdHCO_3]^-$, $[CdCl]^-$, $[Cd(OH)_4]^{2-}$, and organic chelates. Soil analyses showed that in an alkaline environment, Cd precipitates in carbonate form which, along with cadmium phosphates, are poorly soluble compounds. In view of the nature of the soils in the study area, Cd is easily mobilized by weathering, after which it is bound by the clay minerals of iron hydroxide [19]; this statement is endorsed by the results of the present study. The situation with the sediment samples is different, however; there, the highest levels of Cd were found in the oxide fraction and the residue. This is probably due to the diverse factors governing water quality in rivers, e.g. the inflow of contaminants from lands upstream of the study area.

Lead migrates around the environment far less intensively than cadmium or zinc because of the poor solubility of the minerals in which it occurs. Pb in the form of a finely-dispersed suspension or bound to a low-molecular-weight organic fraction can persist for a long time in water and be transported over considerable distances; on reaching an alkaline environment, it is precipitated in the form of poorly soluble salts. Lead accumulates in both plants and in bottom sediments. This is probably the reason for the low overall lead content in the water samples analyzed here. Presumably, then, its levels in the solid samples are linked directly not only with their mineralogical and granulometric composition, but also with the origin of the bedrock, gaseous emissions from road vehicles, and industry.

The largest amounts of Pb in the soil and sediment samples were found in the oxide and carbonate fractions: this is an effect of the considerable environmental pollution in this part of Poland, and also of an elevated pH. Already at pH > 6.5, the mobility of Pb in the substrate is seriously limited, which is due to the precipitation of lead in the form of carbonates and phosphates [20-22].

The presence of large concentrations of metals in soils and bottom sediments in the carbonate and oxide fractions at SP 1, 2, and 4 is a consequence of the alkalization of the environment and the deposition of dusts containing the oxides of alkali metals and non-ferrous metals (Zn, Cd, and Pb). The levels of these latter metals are higher in the soil than in the bottom sediments. Such a situation may be due to the dynamics of the processes governing the aquatic environment, such as the migration of compounds with different acid-basic properties from terrain upstream of the study area. This also affects the stability of the amounts of Zn, Cd, and Pb in the various sediment and soil fractions during the year. Comparison of the analytical results indicates that the bottom sediment is the most sensitive to changes. The slight differences in the assayed amounts of heavy metals contained in the various fractions of the soil samples during the year highlight the slowness of the processes shaping the soil environment.

The large quantities of metals in exchangeable form (ca 20% of the total content in the sediments) at SP4 and 5 indicate acidification of the environment; this observation is corroborated by the assays of the water samples taken at these sampling points. Analysis of the bottom sediments at the other SPs showed that quantities of exchangeable zinc were low and did not exceed 2-3% of the total content of this metal in the sediment. Its minimal mobility in these environments could have been due to the pH of ca 8.7, since at pH > 8 zinc precipitates out of the water.

The mean levels of the second, highly bioavailable, form of occurrence, (i.e. of metals adsorbed on the extended surface of precipitated Fe and Mn oxides and hydroxides), were 19% for Zn, 14% for Cd, and 18% for Pb in the sediments. The proportion of metal carbonates in the bottom sediments, however, was the lowest in the River Nida (8% Zn, 12% Cd, and 11% Pb), and the highest in the Brzeźnica in the case of Zn and Cd (26%) and in the Maskalis in the case of Pb (17%). The level of metals occurring in the form of organic compounds was highest for lead (av. 40%), and lowest for cadmium (16%), which may be evidence for environmental alkalization, a process during which lead is converted to organometallic compounds.

The last of the forms of occurrence of the metals analyzed in this study include analytes incorporated into the crystal lattice of the primary and secondary mineral components of the bottom sediments. The metals contained in this fraction are practically immobile, and their compounds are chemically passive and biologically unavailable. The proportion of residue in the overall contents of zinc and lead was quite small (2-11%), but made up to 40% of the sediment taken from the Maskalis River.

Comparison of the assayed quantities of analytes in the sediments from the Maskalis, Nida, and Brzeźnica shows that the material sampled from the last-named river contained the least Cd and Pb, but the most Zn. This may be due to the proximity of farmland and the zinc-containing pesticides applied there. In the case of the Nida, the quality of the ecosystem is governed by the nearby 'Nida Gips' factory and the adjacent highway, which carries heavy traffic. The quantity and quality of the analytes from the Maskalis samples are determined by the mixed-deciduous woodland through which the river flows; this is the reason for the large amounts of Zn, Cd, and Pb in organic and exchangeable forms.

Conclusions

The formation and properties of bottom sediments in a river are governed principally by the intensity of erosion, and also the rate of flow of the water, which is a consequence of the river channel's gradient. The distribution of bottom sediments in the channel also depends on other factors, for example the bedrock, the proximity of sources of contamination, environmental pH, and land use.

Heavy metals accumulated in sediments are mobilized not only by the chemically controlled processes of dissolution and leaching, but also as a consequence of the erosion of anthropogenically contaminated layers. At the present time we are witnessing the mobilization of heavy metals accumulated in historical times in floodplain sediments and the secondary contamination of rivers by them as a result of the joint action of erosion and leaching [23].

The heavy metal content in soils and surface waters therefore depends not only on the bedrock, synergic weathering processes, leaching, and accumulation, but also on the quality of atmospheric fallout. The soils of the study area include podzols formed from sandstone rocks [14], which usually contain smaller amounts of elements in comparison to rocks enriched with clay fractions [19]. From the total amount of dusts deposited and their chemical composition, it is clear that the total annual deposition of macro- and microelements is large.

If a river channel migrates laterally across an alluvial plain, maximum concentrations may occur even at greater distances from the channel, in sediments accumulated during the maximum contamination of the river [24]. Once the discharges of large quantities of contaminated sediments have ceased, thin layers of sediments containing heavy metals, accumulated under high water conditions, form on terraces along sections of the channel incised into the valley bottom [25]. It is often the case that metal levels vary significantly from one layer of sediment to another, reflecting historical changes in the contamination of a river [9]. The higher level of metals may enable sediment layers to be distinguished that were deposited before and after a pollution source came into existence.

The results of this study indicate that a 5-step procedure is needed to extract the various forms of metals from a sample in order to obtain information on the quantities of analyte bound up in the five bottom sediment fractions. This is important with regard to the development of aquatic organisms and for evaluating the potential threat of secondary contamination by elements in aquatic ecosystems.

On the basis of the results of this study, we can state that:

- the 5-step sequential extraction according to Tessier is a useful tool for obtaining information on metal concentrations in bottom sediments and soils;
- the 5-step ultrasound-assisted sequential extraction procedure requires refining if the quantities of metals recovered are to be comparable with those obtained by other methods;
- the 3-step microwave assisted extraction may be an alternative method for 5-step sequential extraction, but incomplete information is obtained about the occurrence forms of heavy metals in environmental samples;
- a standardized sequential extraction procedure should be worked out, enabling the forms of occurrence of metals in bottom sediment samples to be defined;
- the study area is seriously contaminated by the metals assayed;
- the metals accumulated in the bottom sediments are a potential source of secondary contamination of the rivers in the southern part of Świętokrzyskie province;
- metals were bound to different extents in the various fractions in the water, bottom sediment, and soil samples taken from the study area;
- the sediment levels of all the forms of occurrence of Zn, Cd, and Pb varied exception to this rule were the metals incorporated in minerals, i.e. the residue;
- land use has a significant impact on the forms of occurrence of heavy metals in solid environmental samples due to the different types of land use and the transport of contaminants by their tributaries.

References

1. ADAMIEC E., HELIOS-RYBICKA E. Distribution of pollutants in the Odra river system. Part V. Assessment of total and mobile heavy metals content in the suspended matter and sediments of the Odra river system and recommendations for river chemical monitoring, Polish Journal of Environmental Studies, **11**, (6), 675, **2002**.
2. ALEKSANDER-KWATERCZAK U., HELIOS-RYBICKA E. Mobility of heavy metals in the Mala Panew River sediment depth profiles and their migration in to groundwater system. In: 11th Magdeburg seminar Waters in Central and Eastern Europe: assessment, protection, management: proceedings of the international conference (Eds. W. Geller et al.), (UFZ Centre for Environmental Research Leipzig-Halle. Department Inland Water Research, UFZ-Bericht, No 18/2004). pp. 199-200, **2004**
3. HELIOS-RYBICKA E., ADAMIEC E., ALEKSANDER-KWATERCZAK U. Distribution of trace metals in the Odra River system: Water-suspended matter-sediments, Limnologica **35**, 85, **2005**.
4. LUCK J.D., WORKMAN S.R., COYNE M.S., HIGGINS S.F. Solid material retention and nutrient reduction properties of pervious concrete mixtures, Biosystem Engineering **100**, 401, **2008**.
5. HUDSON-EDWARDS K.A., MACKLIN M.G., CURTIS C.D., VAUGHAN D.J. Chemical remobilization of contaminant within floodplain sediments in an incising river system: implications for dating and chemostratigraphy, Earth Surface Processes and Land-forms **23**, (8), 671, **1998**.
6. ZOUMIS T., SCHMIDT A., GRIGOROVA L., CALMANO W. Contaminants in sediments: remobilization and demobilization, The Science of the Total Environment **266**, (1), 195, **2001**.
7. BUDEK L., WARDAS M. Contamination of Serafa and Malinówka Rivers (Kraków area) by heavy metals — changes after the flood of 1997, 8th Scientific Confer. Metal Ions and Other Abiotic Factors in the Environment, Agricultural University of Krakow at Department of Agricultural Environment Protection, Krakow, **2003**.
8. SALOMONS W. Environmental impact of metals derived from mining activities: Processes, predictions, prevention, Journal of Geochemical Exploration **52**, 5, **1995**.
9. CISZEWSKI D. Channel processes as a factor controlling accumulation of heavy metals in river bottom sediments: consequences for pollution monitoring (Upper Silesia, Poland), Environmental Geology **36**, 45, **1998**.
10. LADD S.C., MARCUS W.A., CHERRY S. Differences in trace metal concentrations among fluvial morphologic units and implications for sampling, Environmental Geology **36**, 259, **1998**.
11. URBAN J., WRÓBLEWSKI T. Chęciny-Kielce Landscape Park – an example of officially not proclaimed geopark, Polish Geolgical Institute, Special Papers **13**, 131, **2004**.
12. European and Mediterranean Plant Protection Organization, Normes OEPP. EPPO Standards Good plant protection practice. Bonne pratique phytosanitaire. PP 2/33 OEPP/EPPO, Bulletin OEPP/EPPO 34, pp. 425-426, **2004**.
13. DROZD J., LICZNAR M., LICZNAR S.E., WEBER J. Pedology – A Handbook with Elements of Mineralogy and Petrography, Wyd. AR Wroclaw, **1997** [In Polish].
14. ŚWIERCZ A. Analysis of soil processes and vegetation transformations in the alkalized forestial habitats in the świętokrzyski region, Committee 'Man and the Environment' under the Presidium of the Polish Academy of Science 39 Warszawa – Kielce, **2005** [In Polish].
15. Poland's Report on Demonstrable Progress under the Kyoto Protocol, Ministry of the Environment, Warsaw, **2006**.
16. Directive of the Ministry for the Environment of 9 September 2002 with respect to soil quality standards and land quality standards, J.L.02.165.1359 of 4 October **2002**.
17. TESSIER A., CAMPBELL P.G.C., BISSON M. Sequential extraction procedure for the speciation of particulate trace metals, Analytical Chemistry **51**, (7), 844, **1979**.
18. DZIADEK K., WACŁAWEK W. Metals in the environment. Part I. Heavy metals (Zn, Cu, Ni, Pb, Cd) in the soil environment, Chemistry-Didactics-Ecology-Metrology **10**, (1-2), 33, **2005**.
19. KABATA-PENDIAS A., PENDIAS H. Trace Elements in Soils and Plants. CRC Press LLC. Boca Raton, London, New York, Washington, D.C., **2000**.
20. BERTSCH P.M., SEAMAN J.C. Characterization of complex mineral assemblages: Implications for contaminant transport and environmental remediation. Proceedings of the National Academy of Sciences **96**, 3350, **1999**.
21. TEMPLETON A.S., TRAINOR T.P., TRAINA S.J., SPORMANN A.M., BROWN Jr. G.E. Pb(II) distributions at biofilm-metal oxide interfaces. Proceedings of the National Academy of Sciences **98**, (21), 11897, **2001**.
22. TRAINA S.J., LAPERCHE V. Contaminant bioavailability in soils, sediments, and aquatic environments. Proceedings of the National Academy of Sciences **96**, 3365, **1999**.
23. MACKLIN M.G. Fluxes and storage of sediment-associated metals in floodplain systems: assessment and river basin management issues at a time of rapid environmental change. in: Anderson M.G., Walling D.E., Bates P. (Eds.) Floodplain Processes, Chichester, Wiley, pp. 441-460, **1996**.
24. LEWIN J., MACKLIN M.G. Metal mining and floodplain sedimentation in Britain. in: Gardiner V. (Ed) First International Conference on Geomorphology 1986, Chichester, Wiley, pp. 1009-1027, **1987**.
25. BREWER P.A., TAYLOR M.P. The spatial distribution of heavy metal contaminated sediment across terraced floodplains, Catena **30**, 229, **1997**.