

Influence of land development on heavy metal forms in the Bobrza River ecosystem (Świętokrzyskie Province, Poland)⁺

Research Article

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Abstract: Metals are perceived as pollutants but they are also natural substances found in the environment. The surface water environment is under the influence of continuing industrial pollution/effluents. Therefore it is necessary to determine various metal forms present in each component of the water ecosystem. The study presents analysis for Cd, Cu, Cr, Fe, Mn, Ni, Zn and Pb content in the Bobrza River bottom deposits and water. The analysis of water and sediment samples from the Bobrza River taken from the littoral zone at three sampling points: the riverhead, i.e. the natural environment; Białogon – the acidic environment; and Sitkówka-Nowiny – the alkaline environment, were analyzed. Sample quality indicators were defined with pH value, conductivity, heavy metal content for water and suspended matter samples. The metal forms in river sediment were also analyzed. The sediment samples were subjected to Tessier's five-stage sequential extraction procedure assisted by microwave radiation. Analyte concentration in water samples and in the extracts was determined with the use of F-AAS and GF-AAS techniques. The results obtained reveal a relationship between land development, the degree of metal bonding with suspended matter and metal forms found in river sediments.

Keywords: River • Suspended matter • Sediments • Heavy metals • Sequential extraction

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1. Introduction

Natural waters are the habitat of many plant and animal organisms. The chemical composition of the aqueous system is characterised by the presence and ratios of macro- and micro- elements. Metals, in general, are perceived as pollutants but they are also substances that occur naturally and found in the environment. Many elements reach the water environment from the atmosphere as a result of heavy rainfall or snowfall. They are often leached out from rocks or soils. Heavy metals are the stablest among pollutants. According to literature reports, their content in water environment vary considerably, the highest heavy metal contents are found in the suspension (about 80%), while the lowest – in the water [1]. The surface water environment is under the influence of continuing industrial demands/effluent. Therefore it is necessary to determine various metal forms present in each component of the water ecosystem.

Most of the reactions that happen in the water occur at the solid -solution interfaces. Some inorganic compounds, have strong adsorption properties therefore, are stopped at the interface, on the surface of particles and while in some they are found in the water. For this reason the quantity of metals decreases in chain of the suspension-sediment-water [2,3]. A significant role in pollution transport, metal transport included, is played by Suspended Particulate Matter (SPM), which constitutes a major component of surface waters [4-6].

The suspension comprises both organic and inorganic substances. The suspended matter also consists of particles of various sizes. However, only the fraction with the particle diameter < 1 µm remains in the suspended state and fosters long-distance adsorbed substance transport [6], while larger agglomerates – under favourable conditions – are subject to sedimentation or adsorption processes. Substance transport or sedimentation processes are therefore dependent on appropriate agglomerate size, water flow intensity, the presence of certain chemical compounds

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such as chlorides or sulphates [6], as well as chemical properties of the metal and associated compounds in their capacity for adsorption on solid particles and formation of hydrated ions, ion pairs, hydrolysed forms or complex compounds.

The form in which a given element occurs is also strongly dependent on physicochemical conditions of the water environment, such as temperature, the quantity of dissolved oxygen, pH, biological activity of organisms [7,8] and the basement complex type. In slightly alkaline solutions, for instance, with high oxygen content, metal ions pass into poorly soluble forms which have a tendency for adsorption on suspensions present in the water [8,9]. Consequently, a change of any factor may, to a greater or lesser extent, affect the speciation of substances which occur in a given environment. This is why it is important to distinguish individual entities in the state of dissolution, bonded to suspension particles and those found in shallow layers of bottom sediments [1].

2. Experimental Procedure

2.1. Research area

The research area covers the Bobrza River, which is a right inflow of the Czarna Nida River. This area is located in the western part of the Świętokrzyskie Mountains, in the Chęcińskie Hills. The sampling was conducted in three areas [1]:

- the riverhead of the Bobrza River (Point 1; reference point),
- Białogon – an acidic environment, impact of Kielce Pump Factory, Formaster Company and road transport (Point 2),
- Sitkowka-Nowiny – an alkaline environment, impact of Nowiny Cement Plant and Trzuskawica Cement and Lime Plant (Point 3) (Fig. 1, Table 1).

The Bobrza River is partially regulated with the use of fascine mats. Its depth ranges from 0.1 to 1 m, and width from 2 to 5 m. The river bottom is sandy, sandy-stony and stony; the banks are not high. Geologically and structurally, the area of the Bobrza River valley belongs to the Świętokrzyskie Foreland which determines a Mesozoic edge of Europe's oldest Świętokrzyskie Mountains, located on the Kielecko-Sandomierska Upland, and considered as low mountains. The most frequent in this region are lower- and middle-Devonian formations (sandstones, mudstones with admixture of loams and conglomerates) [1].

Between sampling Points 1 and 3, the Bobrza River crosses the E74 Kielce – Piotrków Trybunalski

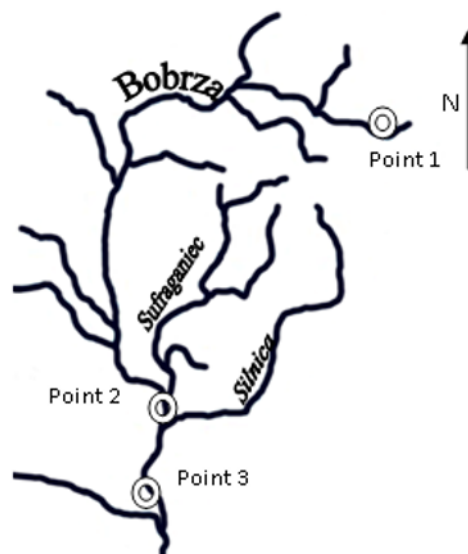


Figure 1. Sampling points in the Bobrza River system.

motorway and the E77 (7) Warszawa – Kielce – Kraków motorway. The road system is complete with a network of major and minor roads, as well as a Kielce – Kraków railroad, which runs along the river up to its mouth. Additionally, on the way, waters of the Bobrza River are supplied by several inflows such as the Babia, the Ciemnica, the Sufraganiec and the Silnica, which deliver additional organic and inorganic pollutants, coming *inter alia* from the municipal treatment plant.

2.2. Materials and methods

The test material consisted of water and bottom sediment samples collected between April 2009 and April 2010. The material for research comprised samples of the Bobrza River water and bottom deposit collected at a depth down to 20 cm at three sample points located in the Bobrza River (Fig. 1). The water samples were taken only from the midstream sections of the rivers – possible effects due to foreign material from the river bank were thus avoided. The alluvial sediment samples were dredged from the river channels from spots where suspended particulate matter is deposited.

Minimum of three water samples were taken at each point. Water quality indicators were defined and included the pH value, conductivity, heavy metal content (Cd, Cu, Cr, Fe, Mn, Ni, Zn and Pb) in the water for both the suspended matter samples as well as sediments (Fig. 2). Sampling could thus be standardized, which eliminated accidental errors at this stage.

The pH value and conductivity were estimated by using CX-701 Elmetron. In the next phase of mineralisation of the samples was carried out by microwave radiation using Anton-Paar PE Multiwave

Table 1. Characteristics of environmental sampling points.

Sampling points	Characteristics
Point 1	Bobrza riverheads: ca. 0.5-1 km away from the riverheads runs E77 Warszawa – Kielce – Kraków road (7) and Kielce – Skarżysko-Kamienna – Warszawa railway line. The riverheads are separated from the road by a woodland stripe which on the one side provides a natural barrier to migration of road pollution, but on the other it is a major source of substances acidifying the environment; brown acidic soils deprived of calcium carbonate, formed out of Triassic sand and sandstone; large woodland areas, mostly composed of pine and fir tree stands.
Point 2	Bialogon, the southern quarter of Kielce: located in the impact zone of the Kielce Pump Factory and Formaster Company; the soil in the area is acidic and count among podsol soils, formed primarily out of accumulation of glacier formations or on non-carbonate Triassic sandstones. Typical rewashed water economy causes organic matter and fulvic acids, responsible for the podsolisation process, to migrate rapidly in the soil profile enriching the watercourse.
Point 3	South-eastern borders of Sitkówka-Nowiny: after the river has passed through the premises of Nowiny Cement Plant and Trzuskawica Cement and Lime Plant. Podsol and rusty soils which, due to the vicinity of cement and lime plants, have lost their natural physicochemical properties; the humic acids released are subject to complete neutralisation by active calcium present in the soil; hence increased C_{org} content in watercourses.

3000. Solutions were cooled and transferred to 100 mL volumetric flasks and diluted to the appropriate volume with ultrapure water. The water samples from the Bobrza River were filtered ($<0.45 \mu\text{m}$) and the particulate matter (SPM) was separated. Filtered materials obtained by filtering the water, were dried at 100°C to a constant dry weight and stored. SPM samples were digested with concentrated ultra pure nitric acid in a microwave oven (Anton-Paar PE Multiwave 3000) and stored until analysis. All reagents and acids were suprapure or of pro-analysis quality.

The sediment samples were sieved, then dried at a suitable temperature to prevent the growth of mould and micro-organisms which would redistribute chemical components, thus alter the composition of the material. After coning and quartering, the dried samples were ground in an automatic agate mortar to the grain size of $<100 \mu\text{m}$. This sediment material was digested with conc. HNO_3 in a microwave oven (Anton-Paar PE Multiwave 3000) and stored until analysis. In addition, one in ten samples was duplicated, so that analyses monitoring of the study could be carried out. Blank samples, making up $\geq 3\%$ of the total number of normal samples, were taken to determine the practical limit of detection.

Analyses of metals (Cd, Cu, Cr, Fe, Mn, Ni, Zn and Pb) were carried out with the use of F-AAS SavantAA Sigma or GF-AAS SavantAA Zeeman (made by GBC) with appropriately adjusted parameters. Analytical blanks were run in the same way as the samples and concentrations were determined with the use of standard solutions prepared in the same acid matrix.

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 two ways: 1) CRM sample assay, 2) samples + added standard assayed. 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. 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 salt was added to the sediment sample.

The reliability of the entire analytical procedure was monitored in two ways: by adding a standard to the assayed sample and by using CRM of bottom sediments (CMR 320).

3. Results and Discussion

The water samples were taken from the Bobrza River over one year (April 2009-April 2010) from three sampling points characterised by different land development.

The concentration of heavy metals was estimated and determined in all the samples from the Bobrza River after separating the SPM. The SPM consists of inorganic, organic and biological matter. The quantity of the suspended matter in the samples ranges from 24.24 to 56.88 mg dm^{-3} while the pH value oscillates between 5.5 and 8.7 (Table 2). Conductivity ranges from 32.0 to 677.0 $\mu\text{S cm}^{-1}$. Total heavy metal concentration in the Bobrza River water samples was measured with the wider-range scale mg dm^{-3} : from 0.10 to 1.64 for Cd; from 0.025 to 0.098 for Cu; from 2.67 to 8.55 for Cr; from 0.402 to 3.896 for Fe; from 0.034 to 0.158 for Mn; from 1.39 to 8.99 for Ni; from 6.62 to 30.11 for Pb and from 0.024 to 0.081 for Zn.

At sampling Point 1 (reference point), the Bobrza River water is slightly acidic and characterised by a small amount of the suspended matter and low conductivity therefore, consequently, also a small amount of

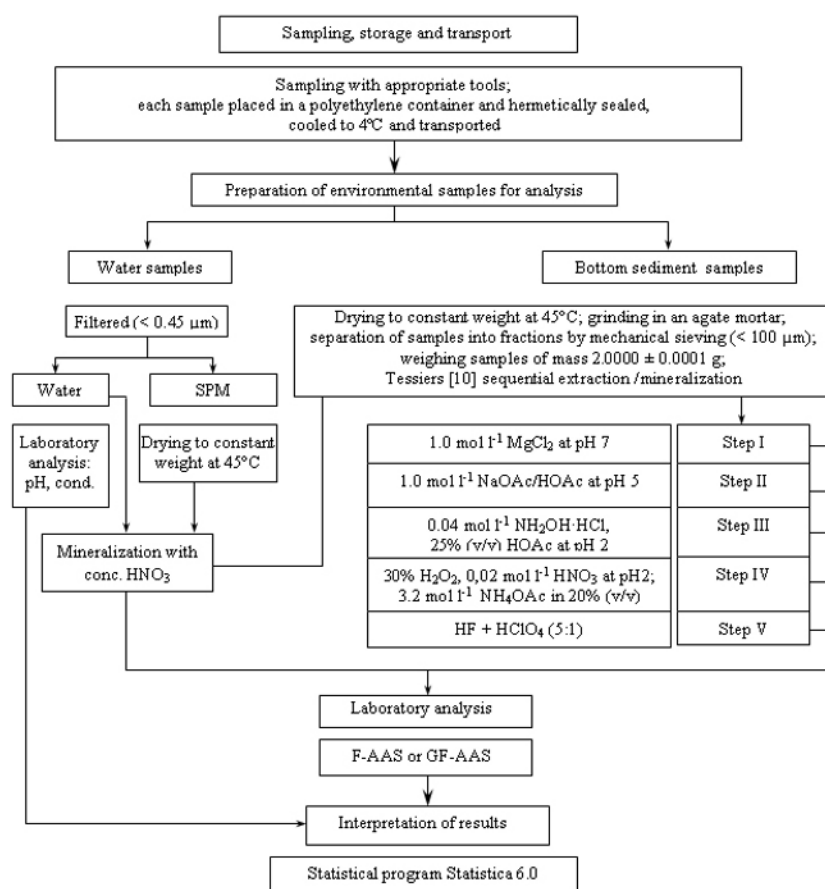


Figure 2. The procedure for environmental samples.

dissolved substances. Along the river course, the river stage increases and so does water flow intensity along with increasing impact of human activity, which may be observed in the results of water sample analyses. At the next sampling points, the river water displays a neutral reaction and is characterised by comparable mean conductivity and suspension values. An increased amount of pollutants, including suspension and dissolved substances, in the water samples analysed from the Bobrza River results from the following:

- the Babia water course entering the Bobrza (before Point 2, Fig. 1), carrying wastewater from household and industrial wastewater treatment plants,
- industry (mainly cement, lime and machine manufacturing plants) and agriculture,
- the vicinity to communications routes.

In the water environment, metal ions are co-ordinated by water molecules, hence the reactions of individual entities with organic donors and other ligand groups require the displacement of one or more water molecules, depending on the number of donor ligand groups. Humic substances (HS) which are components of the suspension display high exchange capacity. Yet

the capacity of humic substances to bond metals may be considerably affected by salt concentration in a solution. High salinity may make the process difficult. In addition, this kind of phenomenon is not the same for all metal cations, which is indicated by the following stability list of metal complexes with HS: $Pb^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+}$ [11]. In the case of interaction of HS with some metals, such as Fe, Al, Mn, Zn or Cu, the occurrence of various types of complexes has been found, including the "inter-humus" complexes of relatively high bond strength [12].

According to literature reports, a larger amount of the suspension adsorbs more of the metals and consequently only a small fraction remains in the form of free ions. This was the case with the Cu and Cr (average: ~63% and 51% respectively) at sampling Point 2, where the largest amount of the suspension was also observed (56.88 mg dm⁻³). In the case of Cd, Fe, Mn, Ni and Pb, the highest degree of bonding was observed at sampling Points 2 with an average: ~68%, 70%, 58%, 29% and 64% respectively, whilst for Zn – at the riverhead (~37%). The lowest bonding degree was observed for Fe, Ni, Pb at sampling Point 1 (average: ~50%, 19% and 29%

Table 2. Average (and min.–max.) values of analyses of the water samples in April 2009 – April 2010 ($n \geq 39$).

Analysed		Unit	Sampling Point			S _D
			1	2	3	
pH		-	5.74 (4.86-6.84)	7.90 (7.03-8.76)	7.87 (6.94-8.58)	0.75
Cond.		[μS cm ⁻¹]	116.97 (32.300-149.25)	408.15 (318.10-609.00)	423.53 (184.87-677.00)	12.26
SPM		[mg dm ⁻³]	25.94 (24.24-29.34)	44.37 (36.31-56.88)	43.26 (35.76-53.99)	5.33
Cd	Soluble	[mg dm ⁻³]	0.36 (0.11-0.79)	0.51 (0.09-1.23)	0.32 (0.10-0.70)	0.63
	Total	[mg dm ⁻³]	0.532 (0.100-0.940)	0.805 (0.115-1.64)	0.571 (0.110-1.10)	0.34
	SPM	[mg kg ⁻¹]	10.19 (1.081-41.12)	6.743 (0.1054-12.81)	5.598 (0.1351-10.81)	3.22
	SPM	%	36.02 (9.195-60.26)	34.94 (3.70-64.71)	39.63 (9.09-68.18)	12.43
Cu	Soluble	[mg dm ⁻³]	0.017 (0.011-0.024)	0.018 (0.010-0.061)	0.048 (0.022-0.072)	0.033
	Total	[mg dm ⁻³]	0.031 (0.025-0.038)	0.073 (0.055-0.089)	0.083 (0.066-0.098)	0.021
	SPM	[mg kg ⁻¹]	0.493 (0.078-0.872)	1.22 (0.548-1.82)	0.802 (0.264-1.35)	0.210
	SPM	%	46.28 (22.58-66.67)	63.21 (9.20-92.00)	42.46 (12.66-69.89)	12.83
Cr	Soluble	[mg dm ⁻³]	2.31 (1.07-4.25)	3.05 (2.51-4.38)	5.81 (3.59-7.01)	1.20
	Total	[mg dm ⁻³]	3.80 (2.67-6.52)	6.65 (3.58-8.32)	7.33 (3.76-8.55)	1.40
	SPM	[mg kg ⁻¹]	54.90 (23.13-99.42)	82.87 (21.72-143.9)	34.52 (3.915-103.1)	8.56
	SPM	%	38.39 (14.22-61.49)	51.33 (25.51-66.17)	19.00 (2.82-48.52)	22.15
Fe	Soluble	[mg dm ⁻³]	0.716 (0.292-2.05)	0.298 (0.096-0.433)	0.280 (0.102-0.391)	0.022
	Total	[mg dm ⁻³]	1.41 (0.813-1.86)	0.952 (0.689-1.12)	0.672 (0.402-0.872)	0.42
	SPM	[mg kg ⁻¹]	27.08 (14.42-51.57)	15.17 (10.64-20.93)	9.137 (6.107-13.31)	3.18
	SPM	%	49.67 (22.05-69.85)	69.95 (58.08-86.07)	59.13 (48.62-74.63)	32.12
Mn	Soluble	[mg dm ⁻³]	0.031 (0.013-0.53)	0.087 (0.068-0.109)	0.063 (0.036-0.097)	0.011
	Total	[mg dm ⁻³]	0.065 (0.034-0.083)	0.126 (0.121-0.158)	0.147 (0.133-0.158)	0.031
	SPM	[mg kg ⁻¹]	1.402 (0.721-2.215)	1.156 (0.703-2.075)	2.006 (1.297-3.076)	0.621
	SPM	%	53.92 (36.14-83.33)	36.28 (26.85-51.77)	57.50 (38.21-75.34)	15.6
Ni	Soluble	[mg dm ⁻³]	4.52 (1.09-8.05)	3.09 (1.04-5.32)	4.39 (2.78-5.99)	1.51
	Total	[mg dm ⁻³]	5.407 (1.39-8.97)	3.898 (1.44-6.33)	6.342 (2.97-8.99)	1.22
	SPM	[mg kg ⁻¹]	34.33 (12.00-41.25)	18.85 (7.032-27.54)	44.45 (5.016-79.87)	16.7
	SPM	%	19.15 (8.46-33.23)	22.62 (15.82-39.77)	28.89 (6.40-48.62)	3.78
Pb	Soluble	[mg dm ⁻³]	5.82 (4.07-10.49)	8.28 (3.23-12.11)	5.74 (4.21-8.22)	0.34
	Total	[mg dm ⁻³]	8.00 (6.62-11.1)	21.8 (16.0-30.1)	17.0 (10.0-28.1)	1.71
	SPM	[mg kg ⁻¹]	84.47 (22.05-115.7)	306.4 (206.0-412.8)	255.4 (102.9-453.9)	34.55
	SPM	%	28.51 (5.15-42.43)	62.33 (49.58-80.10)	63.60 (38.92-75.54)	22.81
Zn	Soluble	[mg dm ⁻³]	0.022 (0.012-0.039)	0.042 (0.032-0.053)	0.038 (0.023-0.058)	0.011
	Total	[mg dm ⁻³]	0.034 (0.024-0.056)	0.060 (0.042-0.079)	0.060 (0.034-0.087)	0.011
	SPM	[mg kg ⁻¹]	0.466 (0.273-0.658)	0.413 (0.177-0.778)	0.497 (0.028-1.017)	0.098
	SPM	%	37.36 (19.51-50.00)	29.10 (18.97-44.12)	33.82 (2.78-60.26)	21.44

S_D - standard deviation

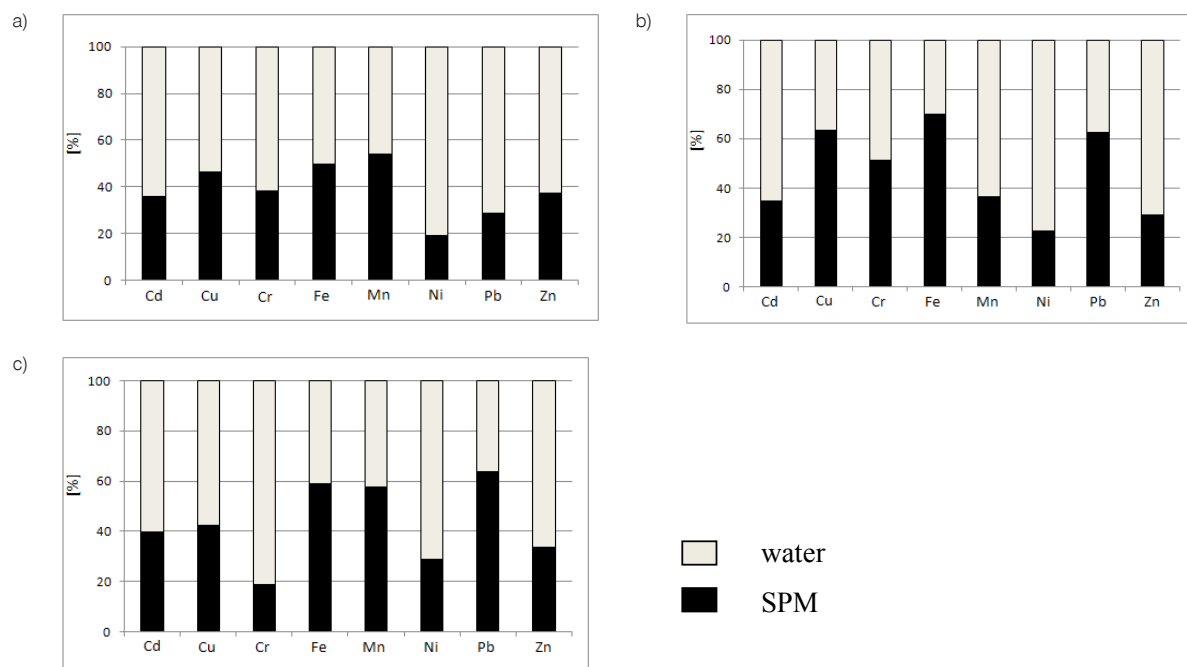


Figure 3. Portions of trace metals transported by the Bobrza River water and suspended particulate matter in 1st (a), 2nd (b) and 3rd (c) points of collecting water samples.

respectively), whereas for Cd, Mn and Zn at sampling Points 2 (average: ~35%, 36% and 29% respectively). For Cu and Cr - at sampling Point 3 (average: ~42% and 19% respectively) (Fig. 3).

In the sampling Point 1 higher metal concentrations (except for Cu and Fe) were recorded in May and June 2009 (Fig. 4). These months are characterised by lower rainfall and higher temperatures than April. Also in these months, higher quantities of suspended matter was found in samples of the Bobrza River waters at all sampling points studied. At the sampling Point 2 higher metal concentrations (except for Cu and Cr) were recorded in the period from July to October 2009. But in sampling Point 3 metal concentrations were different for each of metal. Seasonal trends can be seen in the concentration of Pb, Ni and Zn for the period from April to October 2009 that decreases in the subsequent months.

As for pH and conductivity, no seasonal correlations occur. Changes of these parameters are mostly the result of human activity in the areas and that explains the increase in pH and quantities of ionic substances and suspension with the course of the river. It was also observed that, local land use does not have the direct influence on the pH of water.

The metals analysed belong to the group of elements which are easily absorbed on suspensions, forming complexes with both, organic and inorganic compounds. However, it is not possible to unambiguously define which metal assimilates with the suspension matter more

easily, because of contributions from many environmental factors. A decrease in water flow intensity and bearing capacity may contribute to transport of metal sorbed on suspension particles to the sediment and sedimentation of fine particles carried with the water. In the case of cadmium, the presence of chloride and sulphate ions as well as high ionic strength is of additional importance, since under these conditions cadmium may be subject to desorption from the suspension [6].

Transport processes are determined not only by diffusion but also by the processes connected with the flow of the medium in which the chemical compound is found or by land development. While determining the role of the suspended matter in the transport of metals from a site with a higher concentration of the compound to another with a lower concentration, various processes must be taken into account, including sorption from water to the matter suspended in the water column and the opposite desorption, as well as sorption of a chemical compound from the water on the bottom sediment and the opposite desorption [13].

After being bonded with the suspension, metals move passively in the water environment, and under favourable hydrodynamic conditions they are subject to sedimentation processes due to which their quantities in water samples decrease. The transport of a chemical compound may also occur due to reasons unrelated to the presence of the substance in the transporting medium. These type of processes are exemplified by

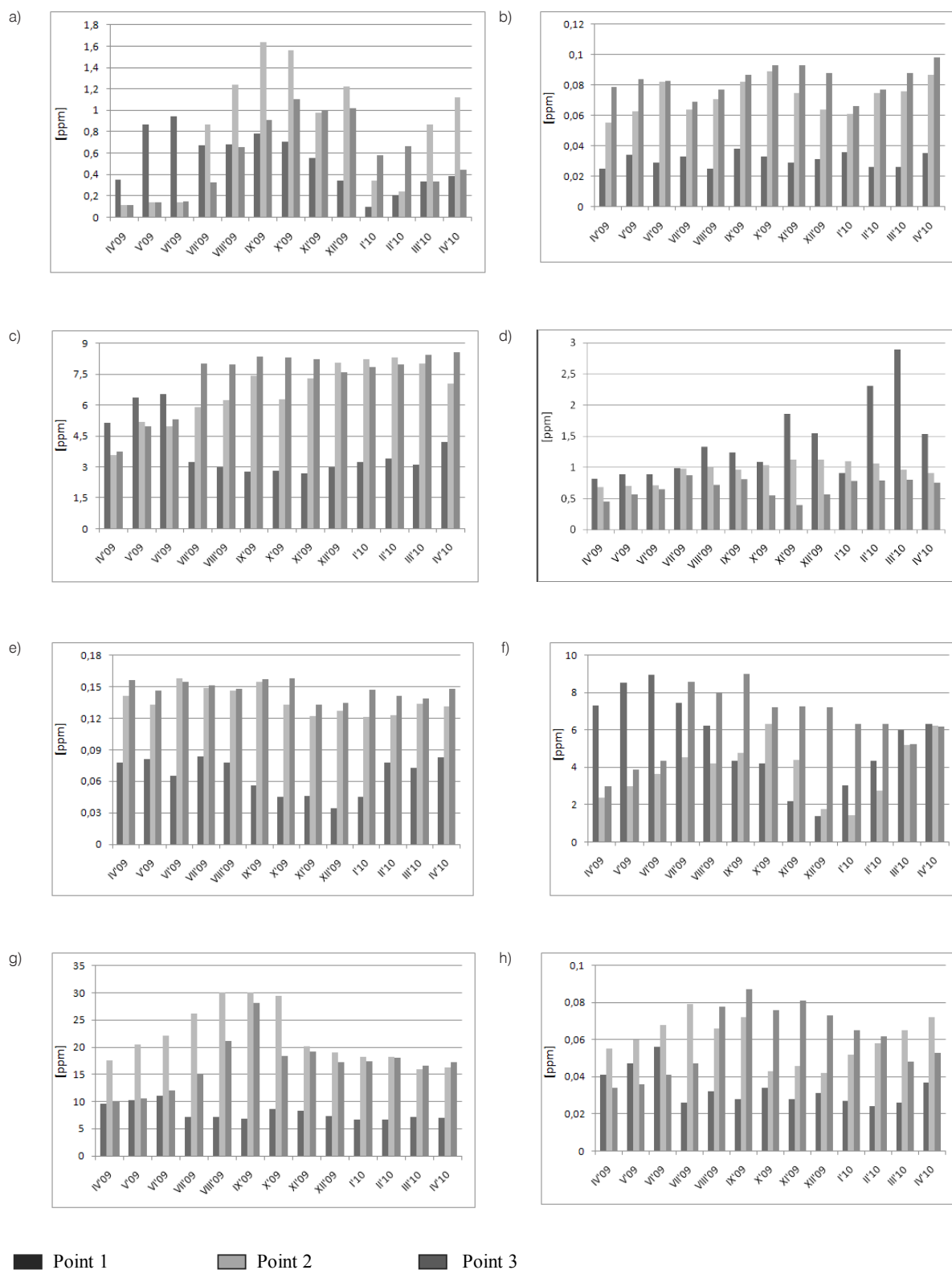


Figure 4. Total metal concentrations in individual sampling point, where: a) Cd, b) Cu, c) Cr, d) Fe, e) Mn, f) Ni, g) Pb and h) Zn.

Table 3. Average content (and min-max) of heavy metals (Fe, Mn, Cd, Pb, Zn, Cr, Cu, Ni) in Bobrza River sediment samples, and its distribution in particular fractions between April 2009 and April 2010 at particular sites [mg kg⁻¹ dry matter] ($n \geq 39$).

Sampling point	Exchangeable F1	Carbonate F2	Fractions Oxide F3 Cd	Organic F4	Residue F5	Sum $\pm S_D$
1	0.005 (n.d.-0.012)	0.010 (0.002-0.021)	0.015 (0.008-0.022)	0.020 (0.010-0.028)	0.003 (n.d.-0.010)	0.054 $\pm$ 0.022 (0.017-0.066)
2	0.011 (0.007-0.022)	0.076 (0.033-0.102)	0.090 (0.045-0.128)	0.210 (0.128-0.331)	0.004 (0.001-0.010)	0.392 $\pm$ 0.051 (0.134-0.433)
3	0.022 (0.015-0.041)	0.102 (0.078-0.199)	0.143 (0.102-0.189)	0.181 (0.144-0.214)	0.025 (0.012-0.038)	0.473 $\pm$ 0.101 (0.377-0.522)
Cu						
1	0.003 (n.d.-0.011)	0.026 (0.015-0.046)	0.031 (0.020-0.057)	0.052 (0.023-0.077)	0.021 (0.011-0.038)	0.133 $\pm$ 0.022 (0.117-0.151)
2	0.32 (0.08-0.55)	2.21 (1.77-2.63)	3.32 (2.18-3.98)	1.01 (0.82-1.33)	0.20 (0.09-0.31)	7.06 $\pm$ 0.73 (5.66-7.83)
3	0.44 (0.16-0.63)	3.54 (1.87-4.33)	3.25 (1.75-3.99)	2.18 (1.23-3.09)	0.59 (0.15-0.83)	10.0 $\pm$ 0.98 (8.44-12.89)
Cr						
1	0.06 (n.d.-0.12)	0.78 (0.33-1.08)	1.13 (0.83-1.54)	1.07 (0.77-1.49)	0.82 (0.55-1.32)	3.86 $\pm$ 0.92 (3.57-4.22)
2	3.22 (2.83-3.92)	12.43 (8.81-15.67)	14.21 (9.91-19.66)	20.01 (16.07-29.33)	5.63 (3.07-7.22)	55.5 $\pm$ 3.22 (51.2-62.8)
3	18.33 (11.72-26.11)	17.32 (15.88-26.03)	20.54 (15.07-33.76)	15.22 (11.41-23.62)	1.49 (0.95-1.88)	72.9 $\pm$ 6.81 (61.8-85.3)
Fe						
1	3.21 (2.66-4.07)	2.87 (1.35-3.29)	47.22 (37.22-61.21)	38.28 (26.34-52.66)	6.56 (1.89-7.88)	98.14 $\pm$ 10.19 (82.55-118.4)
2	14.76 (9.73-19.05)	56.34 (47.11-72.21)	320.9 (278.1-385.3)	206.8 (192.1-227.0)	56.33 (22.71-61.50)	655.1 $\pm$ 32.81 (611.7-693.8)
3	33.69 (11.8-47.6)	98.76 (82.11-119.2)	433.4 (399.1-476.5)	248.2 (202.1-299.3)	22.15 (15.33-34.87)	836.2 $\pm$ 46.22 (783.1-869.2)
Mn						
1	2.87 (1.53-3.87)	15.22 (10.12-26.81)	54.22 (41.88-71.23)	11.06 (6.03-19.22)	2.83 (1.42-4.68)	86.20 $\pm$ 12.43 (77.21-95.33)
2	23.11 (15.02-41.88)	97.98 (77.03-116.3)	268.8 (244.7-298.3)	120.59 (101.3-139.7)	54.32 (43.78-66.21)	564.8 $\pm$ 46.77 (522.7-593.9)
3	20.54 (5.77-31.53)	102.3 (79.31-128.3)	344.2 (300.9-365.8)	123.5 (111.8-147.3)	76.76 (62.91-92.05)	667.3 $\pm$ 32.33 (623.7-695.1)
Ni						
1	0.79 (0.31-1.09)	1.22 (0.98-1.45)	1.22 (1.03-1.39)	2.58 (2.01-2.63)	0.32 (0.17-0.48)	6.13 $\pm$ 0.88 (5.84-6.52)
2	15.32 (10.21-27.31)	10.02 (5.29-20.11)	28.86 (16.33-41.76)	8.26 (3.22-15.23)	1.34 (0.89-1.73)	63.8 $\pm$ 8.21 (47.32-75.29)
3	19.22 (8.37-30.94)	13.19 (6.99-28.33)	27.03 (16.91-40.25)	7.45 (3.01-16.22)	2.11 (1.06-3.65)	69.0 $\pm$ 11.0 (55.21-83.36)
Pb						
1	6.22 (3.29-9.11)	14.09 (9.37-21.81)	11.34 (7.30-18.99)	15.29 (9.02-23.55)	1.16 (0.82-1.33)	48.1 $\pm$ 12.1 (40.11-53.27)
2	27.03 (19.05-39.34)	56.12 (42.38-71.08)	154.6 (104-188.2)	103.5 (88.92-121.6)	87.45 (73.22-95.37)	428.7 $\pm$ 45.8 (401.6-463.8)
3	57.43 (49.33-69.82)	59.69 (47.90-71.04)	155.2 (133.2-169.5)	106.4 (93.71-121.5)	87.58 (72.33-98.06)	466.3 $\pm$ 42.2 (439.9-483.2)
Zn						
1	4.25 (n.d.-5.99)	4.32 (3.29-5.21)	7.53 (5.98-8.66)	7.81 (5.53-9.28)	3.29 (2.77-4.23)	27.2 $\pm$ 9.71 (21.33-38.41)
2	19.76 (8.58-27.75)	33.75 (25.66-42.17)	28.60 (19.32-41.33)	22.07 (16.98-25.33)	7.32 (4.28-9.08)	111.5 $\pm$ 23.88 (101.4-119.2)
3	32.82 (26.43-39.82)	41.16 (36.22-49.95)	31.29 (23.28-39.44)	18.32 (10.03-24.77)	19.01 (10.22-27.60)	142.6 $\pm$ 31.12 (139.3-155.2)

 S_D - standard deviation, n.d. - not detection

the deposition of a chemical compounds bonded with the suspended matter which falls to the bottom of the water column, or recurrent formation of the suspension. Since substance transport and sedimentation processes are conditioned by the presence of appropriately-sized agglomerates, water flow intensity and chemical compounds such as chlorides or sulphates, both the quantity and forms in which the analysed metals occur at particular sampling points vary.

The formation and properties of bottom sediments in a river are governed principally by the intensity of erosion, and also by 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. The extremely rich diversity of physicochemical and biological processes taking place at surface water means that precipitation and sedimentation are usually the dominant processes, causing heavy metals to accumulate in bottom sediments. Sorption diminishes the content of organic and inorganic compounds in the water. Metal contamination in the Bobrza River sediments has been determined for Cd, Fe, Cu, Mn, Ni, Zn, Cr and Pb. Mean heavy metal concentration levels in sediments at all the locations are higher than background values. Total heavy metal concentration in sediment samples from the Bobrza River was measured in a wider- scale range mg kg^{-1} : from 0.017 to 0.522 for Cd; from 0.117 to 12.89 for Cu; from 3.57 to 85.3 for Cr; from 82.55 to 869.2 for Fe; from 77.21 to 695.1 for Mn; from 5.84 to 83.36 for Ni; from 40.11 to 483.2 for Pb and from 21.33 to 155.2 for Zn (Table 3).

The total metal content in the bottom sediment constitutes evidence for the deposition of anthropogenic loads of metals in it. The slightly basic pH of the water (at sampling Points 2 and 3) may reduce the solubility of the relevant metal compounds, therefore, 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, acid rains and surface run-off, which may increase the acidity of the river water, and consequently the solubility of metals compounds bound up in the sediment.

Metal compounds contained in the bottom sediments are released, mainly in soluble forms. Since this also lowers the soil pH, there is a considerable increase in metal solubility (additionally affected by the redox potential). The migration of mobile forms of Cd, Cr, Cu,

Fe, Mn, Ni, Zn and Pb into the water-bearing layer is also enhanced. Migration of these metals from the bottom sediment to the water therefore causes secondary contamination and increases their concentrations in the aquatic ecosystem. Metals that form readily soluble compounds are more mobile and are more easily assimilated by aquatic organisms, which may well be the reason that it accumulates in the organisms.

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 5-step sequential extraction method used here, yielded information on the occurrence and bioavailability of various forms of metals in the bottom sediments of the area under study.

While comparing analyte quantity in samples of bottom sediments, it is observed that the largest amounts of metals found at sampling Points 1 and 2 are in the form:

- bound to iron and manganese hydrated oxides (F3). The metals adsorb on the developed surface of precipitated iron and hydrated manganese oxides. The deposit may be solubilized and the adsorbed metals may be transferred to water as a result of reduction of iron and manganese under anaerobic/reducing conditions,
- bound to organic matter (F4). The metals adsorbed on surface of organic matter or bound to the organic matter includes zinc, cadmium and lead and they are temporarily immobilized as a result of natural deposit mineralization, they may transfer to one of the other fractions or to water,
- metals are bound to carbonates (F2) (only Zn in sampling Point 2). The metals occur as carbonates or are coprecipitated with carbonates. If the pH value decreases in the bottom zone, the carbonate balance may be disturbed and metal carbonates metal or metals coprecipitated with carbonates may be transferred to water (Fig. 5).

Definitely lower analyte quantities are adsorbed on the surface of solid bodies which may pass into the pelagic zone as a result of changes in the ion composition of the water or balance shift in the sorption-desorption system (exchangeable metals).

While comparing analyte quantity in samples, it was observed that the largest amounts of metals found at sampling Point 3 are in the form of precipitating hydrated iron and manganese oxides (F3), except of the zinc which creates the metals bounded to carbonates (F2). The lowest amounts of metals in sampling Point 3 are in turn found in the fraction permanently bonded with minerals (residue).

Comparison of the assay of analytes in the sediments from the sampling Points 1, 2 and 3 shows that the

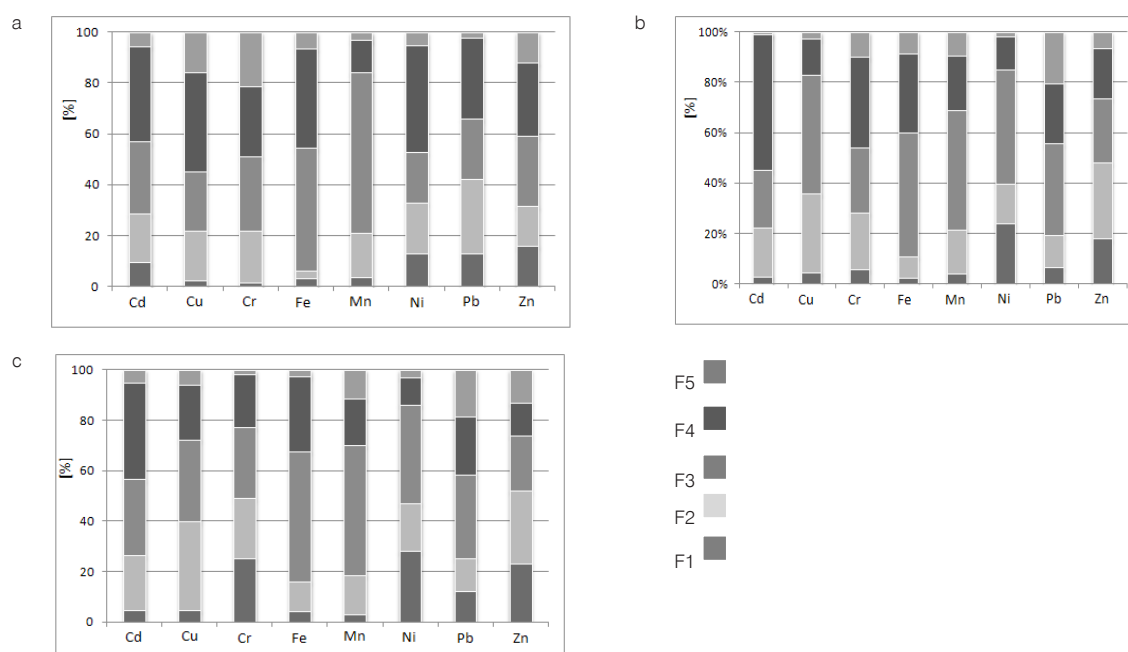


Figure 5. Percentage of analysed metals forms in particular fractions of the Bobrza River in sampling Points 1 (a), 2 (b) and 3 (c) of collecting water samples.

material sampled from the last sampling point contained the highest concentration of the metals. This may be due to the proximity to farmLand and the zinc-containing pesticides applied there. In the case of the sampling Point 3, the quality of the ecosystem is governed by the nearby Nowiny Cement Plant and Trzuskawica Cement and Lime Plant and the adjacent highway, which carries quite heavy traffic. The quantity and quality of the analytes from the Bobrza samples are determined by the mixed-deciduous woodland through which the river flows; this is the reason for the large amounts of metals in organic and exchangeable forms.

The presence of high metal content in bottom sediments in the form of carbonate and oxide fractions is the result of environmental alkalisation and deposition of dusts containing alkaline metal oxides together with non-ferrous metal oxides. It should be noted that the content of the metals analysed increases in bottom sediments at sampling Points 2 and 3. Moreover, while comparing the analysis results, it may be observed that bottom sediments are very susceptible to change. This may be connected with the enormous dynamics of processes which shape the water environment, such as migration of compounds of varying acid and alkali characteristics from the area under investigation.

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 [15].

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 [16]. 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 [17]. 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. The higher level of metals may enable sediment layers to be distinguished from those that were deposited before and after a pollution source came into existence.

4. Conclusions

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

1. In the river system, water and suspended matter are responsible for metal transport. It is evident from our calculations that Cr, Zn, Ni, Mn and Cd were mainly

transported by river water, while Pb, Cu and Fe – by the river's suspended matter.

2. A larger amount of the suspension adsorbs more of the metals and consequently only small amount remains in the form of free ions as was seen for Pb, Cu and Zn.

3. Heavy metal contents at Points 2 and 3 of the Bobrza river (water, SPM and sediment) were slightly higher as compared to heavy metal contents at Point 1.

4. The various bonding degrees between particular metals, suspended matter and sediments depend not only on the quantity of the suspended matter but also on the pH value of the environment, salinity and heavy metal properties, as well as land development.

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References

- [1] A. Rabajczyk, E. Sykała, Humic Substances in Ecosystems 8, 134 (2009)
- [2] J.D. Luck, S.R. Workman, M.S. Coyne, S.F. Higgins, Biosystem Engineering 100(3), 401 (2008)
- [3] M. Saeedi, S.H. Daneshvar, A.R. Karbassi, International Journal of Environmental Science & Technology 1(2), 135 (2004)
- [4] Y. Ding, R. Dresnack, P. C. Chan, Internal Report: Assessment of High-Rate Sedimentation Processes: Microcarrier Weighted Coagulation Jar Tests (EPA/600/X-99/033), New Jersey (1999)
- [5] G. Blo, C. Contado, C. Conato, F. Dondi, Separation and Elemental Characterization of water born particles. In: J. Namieśnik, W. Chrzanowski, P. Szpinek (Eds.), New Horizons and Challenges in Environmental Analysis and Monitoring (Centre of Excellence in Environmental Analysis and Monitoring, Gdańsk, 2003)
- [6] R.M. Cenci, J.-M. Martin, Science of the Total Environment 332, 167 (2004)
- [7] Ch. Horng, Sh. Wang, I. Cheng, J. of Experimental Marine Biology and Ecology 371, 68 (2009)
- [8] J.J. Vicente-Martorell, M.D. Galindo-Riano, M. Garcia-Vargas, M.D. Granado-Castro, J. Hazard. Mat. 162, 823 (2009)
- [9] V.K. Gaur, S.K. Gupta, S.D. Pandey, K. Gopal, V. Misra, Environ. Monit. Assess. 102, 419 (2005)
- [10] A. Tessier, P. Campbell, M. Bisson, Anal. Chem. 51(7), 844 (1979)
- [11] H. Irving, R.J.P. Williams, Nature 162, 746 (1948)
- [12] F.H. Frimmel, Vom Wasser, 53, 243 (1979)
- [13] B. Żukowska, J. Pacyna, J. Namieśnik, Ecol. Chem. Eng., 14(S4), 199 (2007)
- [14] S.E. Manahan, Toxicological chemistry and biochemistry (Lewis Publishers, CRC Press Company, Boca Raton-London-New York-Washington, 2003)
- [15] M.G. Macklin, In: M.G. Anderson, D.E. Walling, P. Bates (Eds.), Floodplain Processes (Chichester, Wiley, 1996)
- [16] J. Lewin, M.G. Macklin, In: V. Gardiner (Ed.), Metal mining and floodplain sedimentation in Britain. First International Conference on Geomorphology, Manchester, United Kingdom, 1985 (Wiley, Chichester, 1986) 1009-1027
- [17] P.A. Brewer, M.P. Taylor, Catena 30, 229 (1997)