Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Limnologica 35 (2005) 185–198
LIMNOLOGICA
www.elsevier.de/limno

Distribution of trace metals in the Odra River system: Water–suspended matter–sediments

Edeltrauda Helios Rybicka*, Ewa Adamiec, Urszula Aleksander-Kwaterczak

University of Sciences and Technology in Krakow, Faculty of Geology, Geophysics and Environmental Protection, Al. Mickiewicza 30, 30-059 Krakow, Poland

Received 31 January 2005; accepted 29 April 2005

Abstract

Extensive investigations of trace metals concentrations in water, suspended particulate matter (SPM) and bottom sediments of the whole Odra River system were carried out over the years 1997–2000. The vertical distribution of selected metals and their mobility were also studied in the sediment cores from upper and middle river sections. Significant levels of metal contamination were found. Median concentrations (Cd, Pb, Cu, Zn and As) in the SPM and sediments were (mg kg^{-1}) 7.1 and 8.9 Cd, 128 and 146 Pb, 81 and 119 Cu, 1198 and 1204 Zn, 48 and 54 As, respectively. The highest metal pollution of the Odra River solids was found with cadmium, zinc, lead and arsenic, showing high similarity in their frequency distributions in both SPM and sediments. Cd, Zn and As appear to be of particular concern because of the high levels, that appear to be bioavailable, and their high mobility. The exchangeable and carbonate chemical forms of Cd and Zn reached up to 50% of their total amount. Besides the determination of total metal concentration, the metal chemical forms in river solids were investigated. The results of very wide studies of the Odra River system through 4 years suggest that metal pollution decreased, especially for Zn, Pb and Cu. Among all metals studied in the Odra River sediments, substantial reductions of Cd contamination were observed neither in the period after '97 flood, nor if compared with the earlier results obtained before '97. No essential differences of the metal contents were observed among the samples for the same river compartment, from the same locality, taken within the five sampling campaigns. The pattern of spatial and vertical metal distributions in the river solids indicates that a variety of sources might be responsible for the contamination; very intensive, historical and current mining and smelting activities probably are the most important ones.

Keywords: Trace metals; Water; Suspended matter; River sediments; Depth profile

Introduction

The Odra River catchment area is 136 528 km^2 and 84.9% of it lies in Poland, 10.4% in Germany and 4.7% in the Czech Republic. The extent and kind of the environmental problems at the Odra River catchment area are caused by geology and geomorphology, terrain configuration, agricultural and industrial activity and localisation of main industrial centres, which are: mining (coal, copper), metallurgy (non-ferrous), electroplating plants, pigments production, pesticides, anticorrosive materials, and power industry (Adamiec & Helios Rybicka, 2002a, b). In total, there are about 1700

*Corresponding author
E-mail address: helios@geol.agh.edu.pl (E. Helios Rybicka).

0075-9511/$ - see front matter © 2005 Elsevier GmbH. All rights reserved.
doi:10.1016/j.limno.2005.04.002

sources of pollutions at the Odra River catchment area, out of which 700 significantly influence the conditions of the river system.

The first studies of the Odra River in 1989–1993 showed that the bottom sediments were contaminated mainly with Zn, Cu, Pb and Cd. The highest contents of all studied metals were found at the Lubin–Legnica Cu-mining and smelting region, e.g. Cd up to 16, Pb up to 3954, Cu up to 1784 and Zn up to 6685 ($mg\,kg^{-1}$) (Helios Rybicka, 1996). The mean values of Zn and particularly of Pb and Cu in the $<63\,\mu m$ fraction of bottom sediments were significantly higher compared with the results obtained within the framework of National Environmental Monitoring, from 1990 to 1992 (Bojakowska & Sokołowska, 1993).

Investigations of the upper and middle Odra River system were carried out in the years 1997–2000 within the framework of the International Odra Project (Report IOP, 2002). Flood sediments collected immediately after the flood in August ’97, showed high metal content. The metal concentrations compared with bulk sediment samples varied in wide ranges and were significantly higher in the fraction $<20\,\mu m$. The median values were as high as ($mg\,kg^{-1}$): 1078 of Zn, 142 of Pb, 96 of Cu, 67 of Cr, 5.0 of Cd, 24 of Co, 43 of Ni and 1.1 of Hg. Obtained results have shown that in general, both the flood sediment bulk samples and their $<20\,\mu m$ size fraction contained high metal concentrations, but still lower ones if compared with the Odra River bottom sediments examined earlier (Helios Rybicka, 1996; Helios Rybicka & Strzebonska, 1999). However, high water flow could have caused dilution and resuspension effects in the river system.

The objectives of this study were: (1) to establish the spatial variety in concentration of metals (Cd, Zn, Pb, Cu, Ni, Cr, Hg, Mn, Fe, As) in water, suspended particulate matter (SPM) and sediments of the Odra

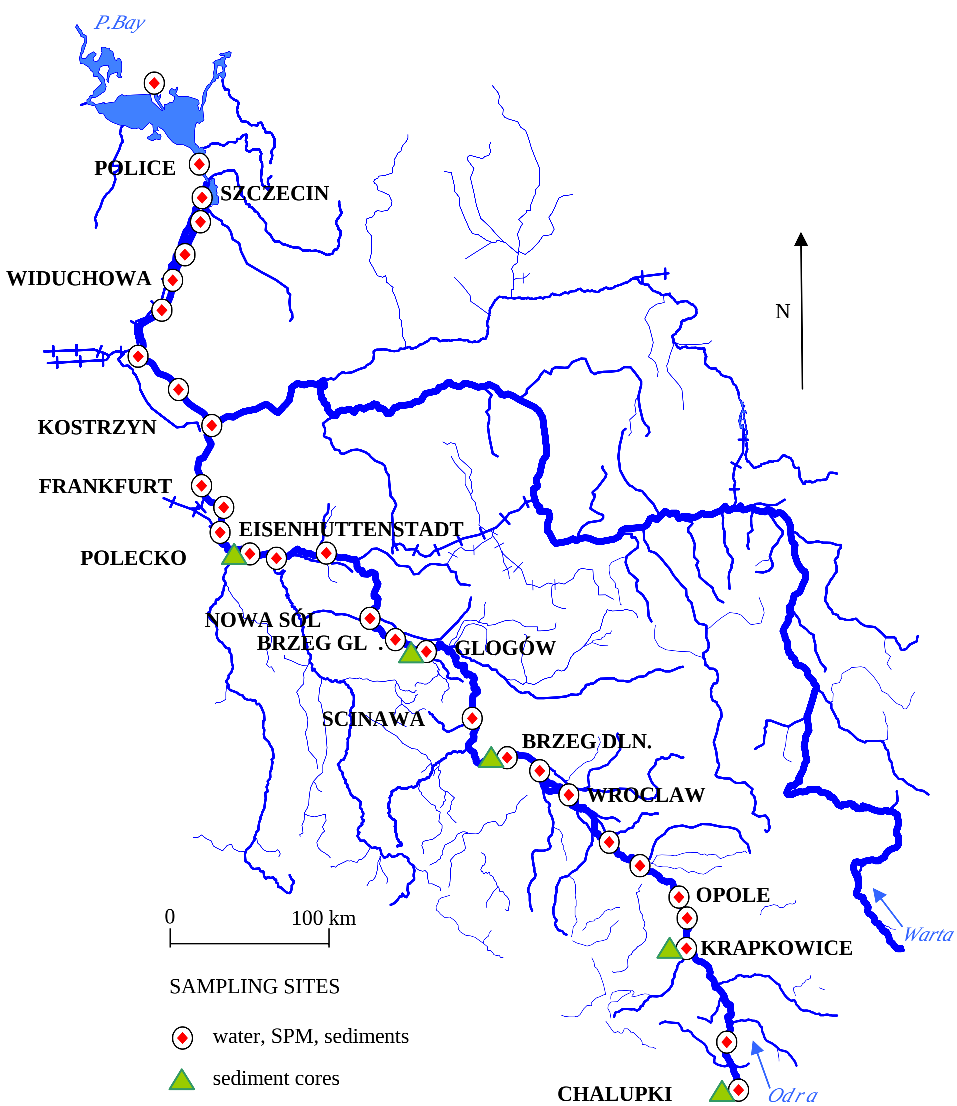

Fig 1. Sampling points in the Odra River system.

River, (2) to assess the level and extent of contamination by comparison with the river classification, and (3) to estimate the chemical forms of metals and their mobility in the river solids.

Sampling and methods

In order to estimate the level and spatial distribution of metals with its variability during different seasons over 3 years, about 50 samples of each component, i.e. water, suspended matter and bottom sediments were taken in each of five sampling campaigns: November 1997, May 1998, November 1998, June 1999 and May 2000. The samples were collected along the whole Odra River, from Olza town (close to the Czech Republic border) to Pomorska Bay (Fig. 1) (Report IOP, 2002).

The sediment depth profiles were taken from the river channel, along the upper and middle Odra River course in Chalupki (Ch), Krapkowice (Kr0, Kr1, Kr2), Brzeg Dolny (BD), Glogów (Gl1, Gl4) and Polencko (Po1) (Fig. 1). The sediment cores were sampled from the river channel and overbank at the depth from 25 to 150 cm, depending on the accessibility to the Odra River and kind of the riverbed. In the sediment cores hard ground was always reached, i.e. the layer of gravels or compacted mixture of clay and silt (Aleksander–Kwaterczak, 2004).

The Odra River water samples were filtered (<0.45 μm), particulate matter (SPM) was separated and its concentration was established. From the sediments, the grain size fractions <20 μm (fraction of bottom sediments recommended for IOP) or <63 μm (sediment depth profiles) were separated and their content calculated. The obtained SPM and sediment samples underwent an analytical procedure (extraction with aqua regia in a microwave oven) described earlier (Helios Rybicka & Strzebonska, 1999; Helios Rybicka & Knöchel, 2000). For the trace metal study on sediment depth profiles, the <63 μm fraction was separated and digested with conc. nitric acid, since in our wide investigations of river sediment cores this procedure has been used for longer time, allowing to compare the results (Helios Rybicka, 1996).

In order to assess the metal mobility in the selected suspended matter and sediment samples, the chemical forms of metals were determined using the sequential extraction method (Förstner, Ahlf, Calmano, & Kersten, 1990). Metal concentration was analysed by ICP-MS or ICP-ES and/or AAS methods.

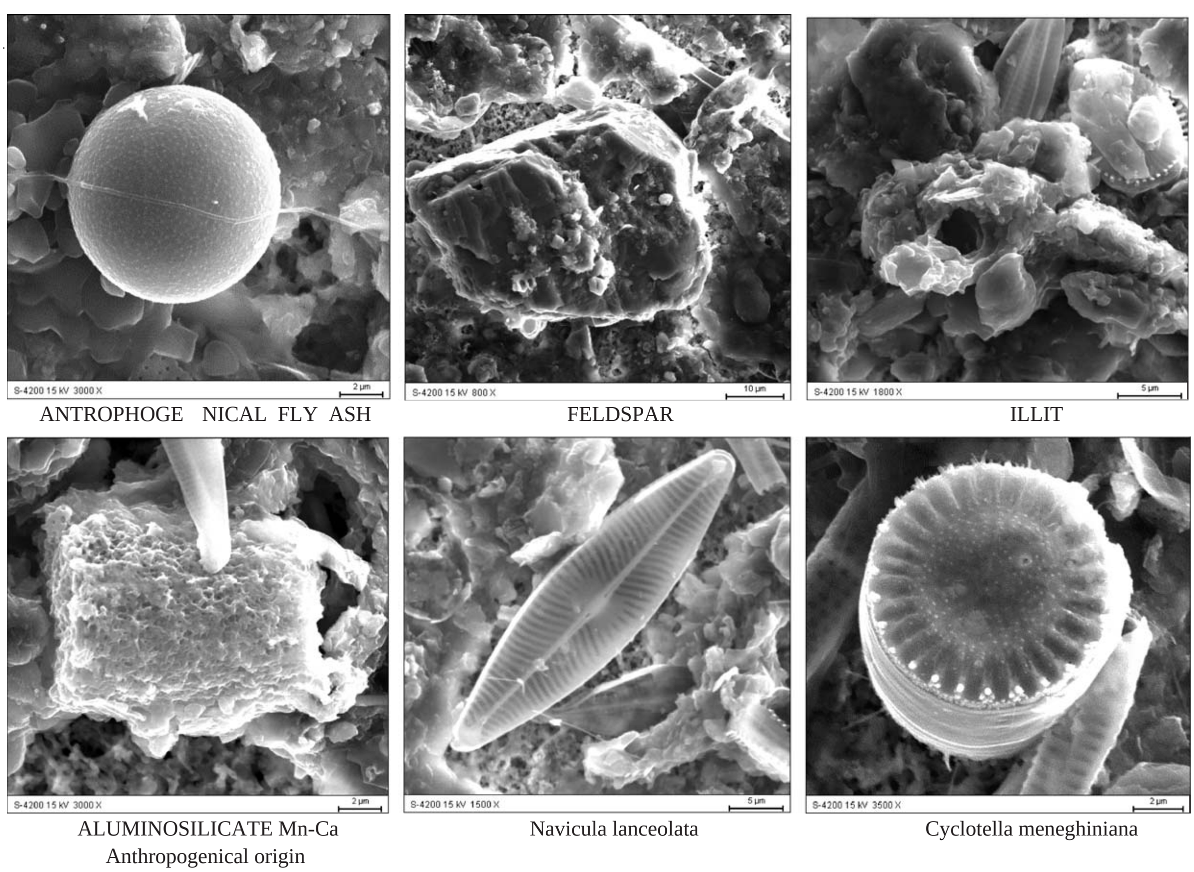

Fig. 2. SEM photos of the variety compounds in the Odra River suspended particulate matter (SPM).

Data quality control

The analyses were subject to sampling and analytical quality program to describe random errors by Robust Analysis of Variance, with ROB2 program application (Ramsay, 1993). During sampling in May 2000, the filed duplicates of water, SPM and sediment samples were taken. These samples were analysed twice as analytical duplicates. Robust analysis of variance was applied to estimate the precision (sampling and analytical variances) in comparison to geochemical variances.

Taking into consideration water samples data quality control was satisfying for most elements (except arsenic). The results of Cd, Ni, Cr and Cu measurements for suspended matter indicate the excellent precision. Percentage of the analytical and technical variances is below critical value of the total variances 4% and 20%, respectively, while analytical variance for Pb (5%) slightly exceeds this value. The analytical variance for Mn and Zn is 7% and 9%, respectively, accounted for As and Fe is not satisfactory enough. In both cases, sampling variances for all samples for suspended matter and sediments are satisfying and not exceed 16% of total variances. The analytical precision of sediments is satisfying for Cu, Zn, and Mn. For Fe and Cr analytical variance is 9% and 7%, respectively. The analytical precision for Cd, Pb and particularly for Ni is not enough satisfying.

In order to estimate accuracy of the analytical method, reagent blanks and certified reference materials (riverine water 1643d, Lake Sediment LSKD-4, River Sediment 1645, Sediment CRM 7002) were used to assure criteria related to quality of the analytical results. The results from ICP-MS technique were confirmed by TXRF in case of water and suspended matter, and for sediments with AAS measurements.

Table 1. Statistical parameters of metals concentration in water, suspended particulate matter and bottom sediments of the Odra River in the period from November 1997 to May 2000

Metals	Minimum	Maximum	Arth. mean	Median	S_d
Water ($\mu g\,L^{-1}$) $n = 115$					
As	0.10	8.75	1.90	1.80	1.24
Cd	0.002	1.09	0.13	0.09	0.18
Cr	n.d.	37.1	4.19	2.20	6.13
Cu	0.10	23.5	4.23	3.26	3.42
Ni	0.07	27.2	5.19	4.30	3.71
Pb	n.d.	10.9	1.18	0.68	1.65
Zn	1.26	202	32.1	27.3	29.1
Fe	2.00	1861	126	57.5	245
Mn	0.82	334	69.1	37.9	80.8
Suspended particulate matter ($mg\,kg^{-1}$) $n = 115$					
As	1.96	302	55.9	48.0	44.3
Cd	0.87	39.8	8.51	7.05	6.18
Cr	8.94	351	129	115	60.5
Cu	4.25	399	100	81.0	65.9
Ni	2.83	1287	103	60.5	152
Pb	9.37	1614	138	128	146
Zn	111	31 369	2027	1198	4113
Fe	1523	88 889	45 727	43 786	20 469
Mn	856	52 430	6323	5823	5352
Sediment ($mg\,kg^{-1}$) $n = 115$					
As	6.39	192	62.6	54.1	40.6
Cd	1.22	21.7	9.71	8.94	3.50
Cr	20.7	400	107	104	56.3
Cu	34.1	298	131	119	58.8
Ni	23.5	89.3	52.7	51.7	9.42
Pb	29.0	427	153	146	63.4
Zn	77.6	3113	1226	1204	451
Fe	16 690	79 464	45 908	44 963	9882
Mn	329	6020	2101	1760	1203
Hg[a]	0.65	9.41	2.16	1.65	1.59

Arth. mean – arithmetical mean, n.d. – not detected.
[a]$n = 33$.

Samples of all compartments (AQS-samples) were taken for the analytical quality control procedure and duplicates were analysed at the same time in six laboratories for comparison and confirmation (Report IOP, 2002).

Trace metals in the Odra River water

Trace metal concentrations in the Odra River were measured in all water samples (from the Czech Republic border to the Pomorska Bay for five sampling periods in 1997–2000) after separation of the SPM, which consist of an inorganic and organic-biological material (Fig. 2). Its concentration varied from 0.88 to 115 mg dm^{-3}.

Metal concentrations in the Odra River water varied in wide ranges (µg L^{-1}): 0.10–8.75 of As, 0.002–1.09 of Cd, up to 10.9 of Pb, 0.067–27.2 of Ni, up to 37.1 of Cr, 0.10–23.5 of Cu, 1.26–202 of Zn, 0.82–334 of Mn and 2.00–1861 of Fe. The statistical parameters of metal concentration in the water samples are shown in Table 1. Considering the median values of the metal contents, the regional differences are visible. While the soluble concentrations of Cd were approximately on similar levels in all examined samples along the whole Odra River course, the distribution of As showed higher content in the water samples from the upper Odra River section than in its middle and lower sections. The highest value 8.75 µg L^{-1} of As was stated in the upper Odra River at Krapkowice. In case of most other metals, water in the upper and middle Odra River was more polluted than in the lower Odra River.

In order to estimate the Odra River water pollution with trace metals, the obtained results were assessed by the LAWA classification (Irmer, 1997). Fig. 3 shows the frequency distribution of Cd, Zn, Cr, Cu, Ni and Pb in water samples from the whole Odra River expressed in numbers of samples in respective LAWA classes (Table 2).

Water samples were strongly contaminated with Cd, Cu and Zn. Their levels were found to exceed the

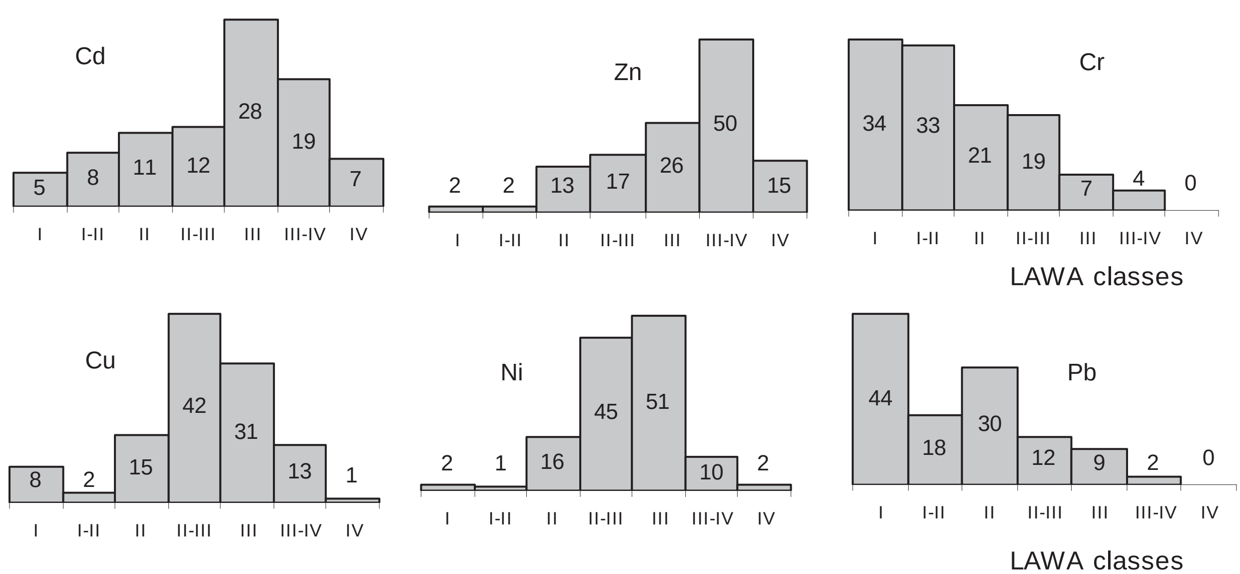

Fig. 3. Frequency distribution of Cd, Pb, Zn, Cu, Ni and Cr in water of the Odra River, expressed in numbers of samples in respective LAWA classes (see Table 2).

Table 2. LAWA quality classess for river water (Irmer, 1997)

Metals (µg dm^{-3})	LAWA classes for river water						
	I	I–II	II	II–III	III	III–IV	IV
Pb	⩽0.4	⩽0.85	⩽1.7	⩽3.4	⩽6.8	⩽13.6	>13.6
Cd	⩽0.009	⩽0.017	⩽0.036	⩽0.072	⩽0.15	⩽0.28	>0.28
Cr	⩽1.3	⩽2.5	⩽5.0	⩽10	⩽20	⩽40	>40
Cu	⩽0.5	⩽1.0	⩽2.0	⩽4.0	⩽8.0	⩽16	>16
Ni	⩽0.6	⩽1.1	⩽2.2	⩽4.4	⩽8.8	⩽17.6	>17.6
Zn	⩽1.8	⩽3.5	⩽7.0	⩽14	⩽28	⩽56	>56

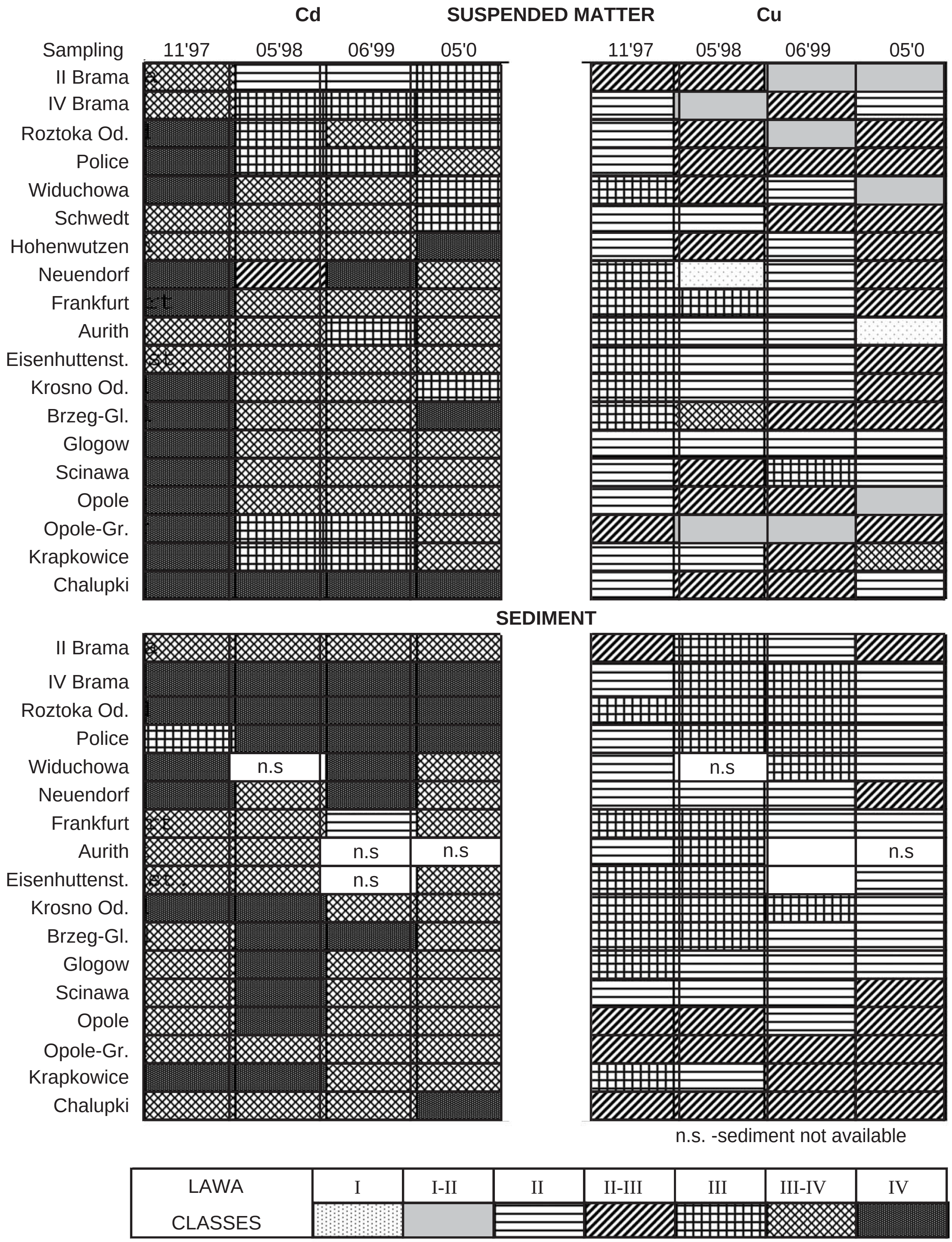

Fig. 4. Situation of pollution with Cd and Cu of the Odra River suspended particulate matter and sediments from November 1997 to May 2000 according to the LAWA classification (see Table 3).

LAWA target values, i.e. $0.072\,\mu g\,L^{-1}$ for Cd, $14\,\mu g\,L^{-1}$ for Zn, $4\,\mu g\,L^{-1}$ for Cu. In the case of Ni, about 30% of water samples contained higher amounts than the target value of $4.4\,\mu g\,L^{-1}$. For Cr and Pb, over 90% of the water samples did not exceed target levels, i.e. $10\,\mu g\,L^{-1}$ and $3.4\,\mu g\,L^{-1}$, respectively. No seasonal trends of metal

Table 3. LAWA quality classess for river SPM and sediments (Irmer, 1997)

Metals (mg kg^{-1})	LAWA classes for river solids						
	I	I–II	II	II–III	III	III–IV	IV
Pb	⩽25	⩽50	⩽100	⩽200	⩽400	⩽800	>800
Cd	⩽0.3	⩽0.6	⩽1.2	⩽2.4	⩽4.8	⩽9.6	>9.6
Cr	⩽80	⩽160	⩽320	⩽640	⩽1280	⩽2560	>2560
Cu	⩽20	⩽40	⩽80	⩽160	⩽320	⩽640	>640
Ni	⩽30	⩽60	⩽120	⩽240	⩽480	⩽960	>960
Zn	⩽100	⩽200	⩽400	⩽800	⩽1600	⩽3200	>3200

Table 4. Local geochemical background values for the sediment core samples of the Odra and Mala Panew Rivers

Sediment cores—localization	The local geochemical background values (mg kg^{-1})						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
Floodplain – Odra River (Nowa Sól)[a]	0.5	13	58	20	28	23	73
Floodplain – Mala Panew River (Krupski Młyn)[b]	0.4	5.1	37	5.6	11	76	130

[a]Aleksander-Kwaterczak (2004).
[b]Aleksander-Kwaterczak & Helios Rybicka (2004a, b).

concentrations in the Odra River water were observed. The metal processing activities in Ostrava and Legnica-Głogów caused the maximal amounts stated in the water samples, at the Czech border and in the river section below the Cu-industry areas, respectively.

Metals in the Odra River suspended particulate matter (SPM)

SPM samples from the Odra River were heavily contaminated with metals. Their contents varied in wide ranges (mg kg^{-1}): 1.96–302 As, 0.87–39.8 Cd, 9.37–1614 Pb, 2.83–1287 Ni, 8.94–412 Cr, 4.25–399 Cu, 111–31 369 Zn, 856–52 430 Mn and 1523–88 889 Fe (see Table 1). Taking into consideration the median values of metal content in SPM samples from the whole Odra River, the enrichment factor calculated according to the background values proposed by Turekian and Wedephol (1961) and by Martin and Meybeck (1979) for As, showed a general order:

$$28.4\ (\mathrm{Cd}) > 22.8\ (\mathrm{Zn}) > 11.2\ (\mathrm{As}) > 8.4\ (\mathrm{Pb}) > 2.2\ (\mathrm{Cu}) > 1.5\ (\mathrm{Ni}) > 1.3\ (\mathrm{Cr}).$$

The SPM samples were already strongly polluted with Cd and Zn (LAWA classes IV and II–IV) at the river section close to the Czech border. Contamination levels changed slightly up to Pomorska Bay, reaching III class (Fig. 4, Table 3). The concentrations of Cu and Pb in the upper river section correspond to classes II–III (moderately to strongly contaminated). At the Głogów-Legnica copper industry area, the increase of Cu was observed and classes III and III–IV prevailed. Lead concentration in SPM along the whole river course showed only slight changes, and classes II and II–III predominated. The highest concentration of Zn was found in SPM sample taken in November '98 from Szczecin Flood. The seasonal effects of metal contents were observed mainly in the lower Odra River; the SPM samples taken in November '98 showed higher concentrations of all metals compared with the results from May '98.

Metals in the Odra River sediments

The contents of the <20 μm size fraction in the Odra River sediments ranged from 2.2 to 63.8 wt%, and depended on the localisation and sampling season. The highest mean values were stated for the samples from November '98 and in November '97 (immediately after flood), i.e. 39.9% and 30.5%, respectively.

The metal pollution in the Odra River sediments (<20 μm) varied in wide ranges (mg kg^{-1}): 6.39–192 As, 1.22–21.7 Cd, 29–427 Pb, 23.5–89.3 Ni, 20.7–400 Cr, 34.1–298 Cu, 77.6–3113 Zn, 329–6020 Mn and 16 690–79 464 Fe (see Table 1). In the samples from May 2000 the highest contents 21.7 mg kg^{-1} of Cd and

Table 5. Statistical parameters of metals concentration in sediment cores from the upper and middle Odra River

Metals (mg/kg)	Minimum	Maximum	Arth. mean	Median	S_d
Chalupki (Ch) /river channel/$n = 9$					
fr.< 63 μm (wt%)	20.0	64.2	36.9	36.5	12.0
Cd	1.32	3.73	2.51	2.35	0.82
Cu	34.7	84.2	61.2	61.6	18.3
Pb	69.4	96.6	79.5	74.9	9.41
Zn	507	1936	1258	1261	497
Krapkowice (Kr1&Kr2) /river channel/$n = 39$					
fr.< 63 μm (wt%)	1.76	85.2	32.6	24.2	28.8
Cd	1.70	14.3	3.30	2.71	2.27
Cu	31.7	64.8	44.4	44.8	7.81
Pb	50.3	112	78.4	79.7	15.9
Zn	398	886	599	581	135
Krapkowice (Kr0) /overbank/$n = 7$					
fr.< 63 μm (wt.%)	8.19	21.3	13.7	13.5	3.95
Cd	1.72	2.95	2.20	2.40	0.46
Cu	45.7	122	73.1	64.9	22.9
Pb	96.5	167	124	137	29.0
Zn	505	771	636	655	101
Brzeg Dolny (BD) /river channel/$n = 23$					
fr.< 63 μm (wt%)	1.25	7.19	3.10	2.99	1.19
Cd	1.85	3.88	2.84	2.82	0.55
Cu	39.7	73.2	49.0	45.8	9.64
Pb	51.8	129	105	110	17.0
Zn	524	1657	1024	1004	223
Glogow (Gl1&Gl4) /river channel/$n = 23$					
fr.< 63 μm (wt%)	0.01	3.45	0.78	0.49	0.86
Cd	3.33	10.8	6.38	5.61	2.40
Cu	144	766	326	293	155
Pb	143	802	377	389	166
Zn	788	3691	1866	1526	873
Polecko (Po1) /river channel/$n = 22$					
fr.< 63 μm (wt%)	0.10	1.65	0.32	0.18	0.42
Cd	0.11	4.76	0.96	0.61	1.07
Cu	22.1	135	51.1	38.5	35.1
Pb	35.7	310	101	54.4	84.6
Zn	216	1025	475	462	212

192 mg kg^{-1} of As were found. In the sediment samples from the lower Odra River, the content of Cu and Cr was higher compared with the upper and middle Odra River. The highest content of Zn, As and Hg was observed in the sediments from the upper and middle Odra River, while of Pb in the lower Odra River.

Generally, the sediment samples taken in the spring period exhibited the highest degree of contamination. Taking into consideration the median values of metal contents in sediment samples from the whole Odra River, an enrichment factor calculated according to the geochemical background values (Turekian and Wedephol, 1961) showed, similar as in SPM given above, a general order:

$$32.7\ (\text{Cd}) > 12.9\ (\text{Zn}) > 12.6\ (\text{As}) > 10.8\ (\text{Hg}) > 7.6\ (\text{Pb}) > 2.9\ (\text{Cu}) > 1.1\ (\text{Cr}) > 0.8\ (\text{Ni}).$$

The metal contents in the sediment samples were expressed in terms of the LAWA classification (Table 3). The obtained results showed that the strong to very strong contamination (classes III/IV and IV) with Cd was typical for almost all samples along the Odra River (Fig. 4). Generally, the Odra River sediments are unpolluted to moderately polluted with Cu, moderately to strongly contaminated with Pb and strongly to very strongly with Zn.

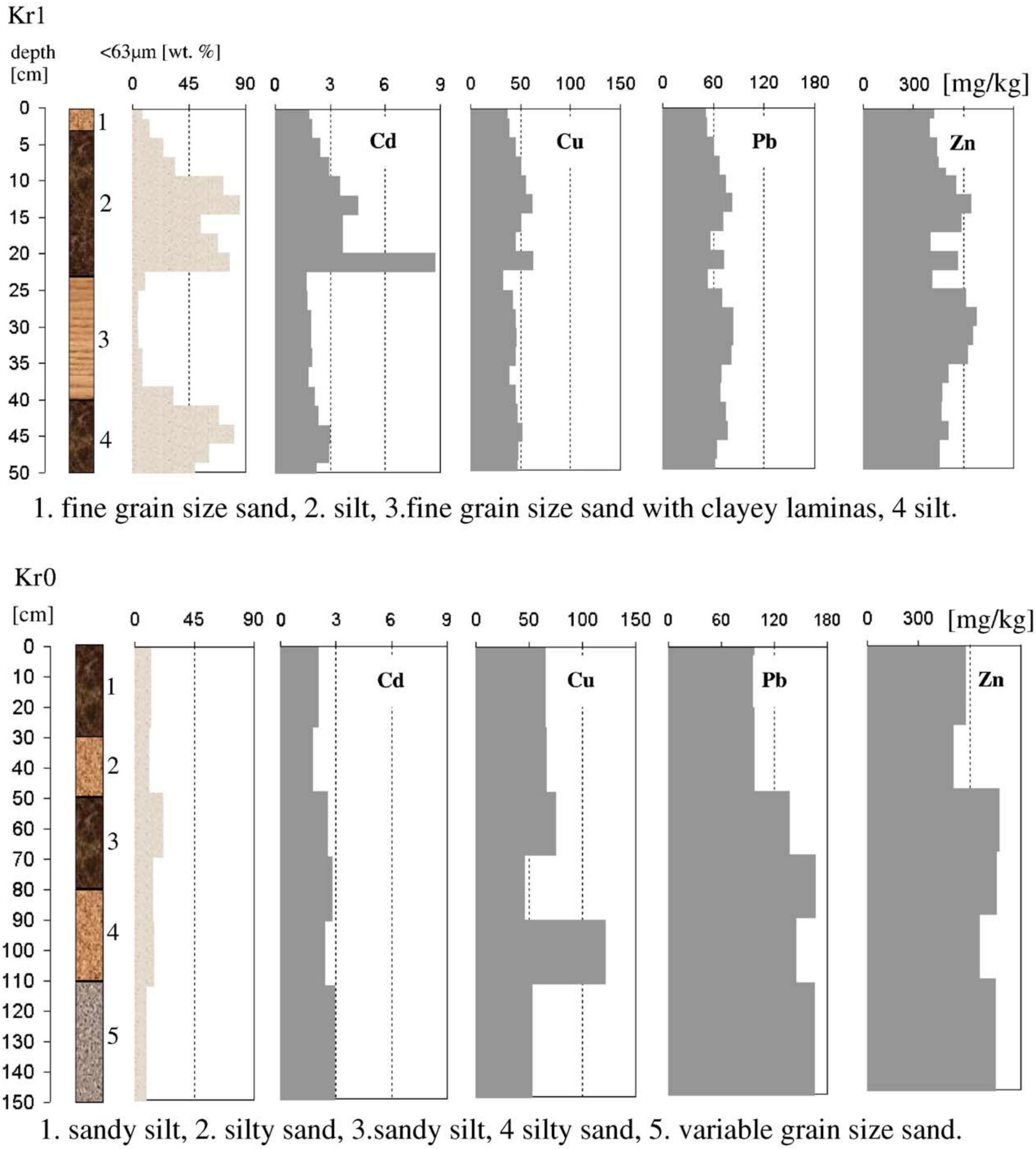

Fig. 5. Vertical distribution of the $<63\,\mu m$ sediment fraction and Cd, Cu, Pb and Zn contents in the Odra River sediment cores from Krapkowice.

Metals in the sediment depth profiles

In order to estimate trace metal contaminations and the quality classes of sediments, the local geochemical background for the Odra River sediment core from Nowa Sól was investigated, and the obtained values are ($mg\,kg^{-1}$): 0.5 Cd, 13 Co, 58 Cr, 20 Cu, 28 Ni, 23 Pb and 73 Zn (Aleksander-Kwaterczak, 2004). The age of analysed sediment was studied and assessed at above 150 years by Ciszewski (2003). Additionally, the local geochemical background was studied for the Mala Panew River (tributary of the Odra River) sediment core and the results are shown in Table 4 (Aleksander-Kwaterczak & Helios Rybicka, 2004a, b).

The contamination levels of the sediment cores (fraction <63 μm) were found to exceed the geochemical background values, both local (Table 4) and proposed by Turekian and Wedephol (1961), especially for Cd, Cu, Pb and Zn. Their amounts ranged ($mg\,kg^{-1}$) (Table 5): Cd 0.11 (Po1)–14.3 (Kr2), Cu 22.1 (Po1)–766 (Gl4), Pb 35.7 (Po1)–802 (Gł4), Zn 216 (Po1)–3691 (Gł4).

In the sediment core from Chalupki the highest contents of Cd, Cu, Pb and Zn were found in the layer below the depth of 17.5 cm and were as high as: 3.73, 84, 96 and 1936 $mg\,kg^{-1}$, respectively.

The sediment core samples from Krapkowice showed high contents of all metals in the profile Kr0 (150 cm depth) taken from flooded land. At the depth below 70 cm, the maximal contents of Cd, Cu, Pb and Zn were found: 2.95, 122, 167 and 771 $mg\,kg^{-1}$, respectively (Fig. 5). In sediment core Kr0 contamination with metals, except Cu, increased with depth.

The representative sediment samples were taken from eight sections (selected according to lithology) of the Krapkowice core (Kr1). The metal speciations were studied in the size fraction <63 μm, using the sequential extraction procedure mentioned above. The results are shown in Fig. 6. Cadmium was the most mobile and its relative portions ranged from 37% to 65% of exchangeable fraction and from 22% to 30% of carbonate fraction. The highest relative portions of easy and moderately reducible fractions were stated for Cu (up to 75%), Pb (almost 90%) and Zn (60%). Considering the vertical distribution of chemical speciation for each metal no significant changes are visible.

The sediment core from Brzeg Dolny (BD) showed the highest amounts of Cd 3.9, Cu 73, Pb 129 and Zn 1657 $mg\,kg^{-1}$ in the sediment layer at the depth of 40–50 cm. The elevated amounts of Zn and Pb were stated at the depths 7.7–17.5 and 25–30 cm.

Among all investigated sediment depth profiles of the Odra River, the most contaminated with Cd, Cu, Zn and Pb were the cores from Glogów at the region of Cu industry. The highest contents of about 10 $mg\,kg^{-1}$ of Cd, 766 $mg\,kg^{-1}$ of Cu and up to 3690 $mg\,kg^{-1}$ of Zn were found in the core (Gl4) at a depth of 30–40 cm, while up to 630 $mg\,kg^{-1}$ of Pb at 15–35 cm depth (Fig. 7).

Sediment core from Polencko (Po1), located about 130 km away from the Glogów–Lubin Cu-mining and smelting region, showed less contamination with metals if compared with cores from Glogów. Median values of Cd, Cu, Pb and Zn (Table 5) were the lowest from all obtained, i.e. ($mg\,kg^{-1}$): 0.61, 38.5, 54.4, 462, respectively.

Quality assessment of the Odra River system

Metal concentrations in the Odra River water were relatively low, and classified as class I. Generally, metal concentrations in water were lower than the admissible values for drinking water in Poland (Adamiec & Helios Rybicka, 2002a, b).

The metal contents in the SPM and sediment samples expressed in terms of the LAWA classification showed

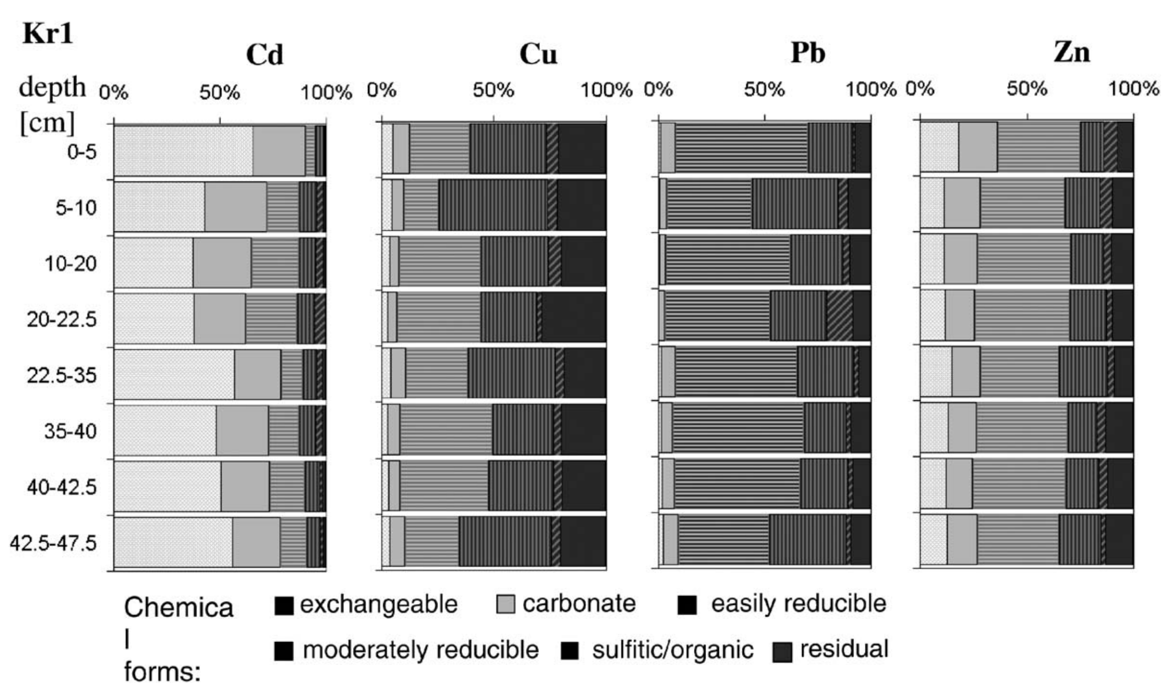

Fig. 6. Metal chemical forms and their changes in the Odra River sediment core (Kr1) from Krapkowice.

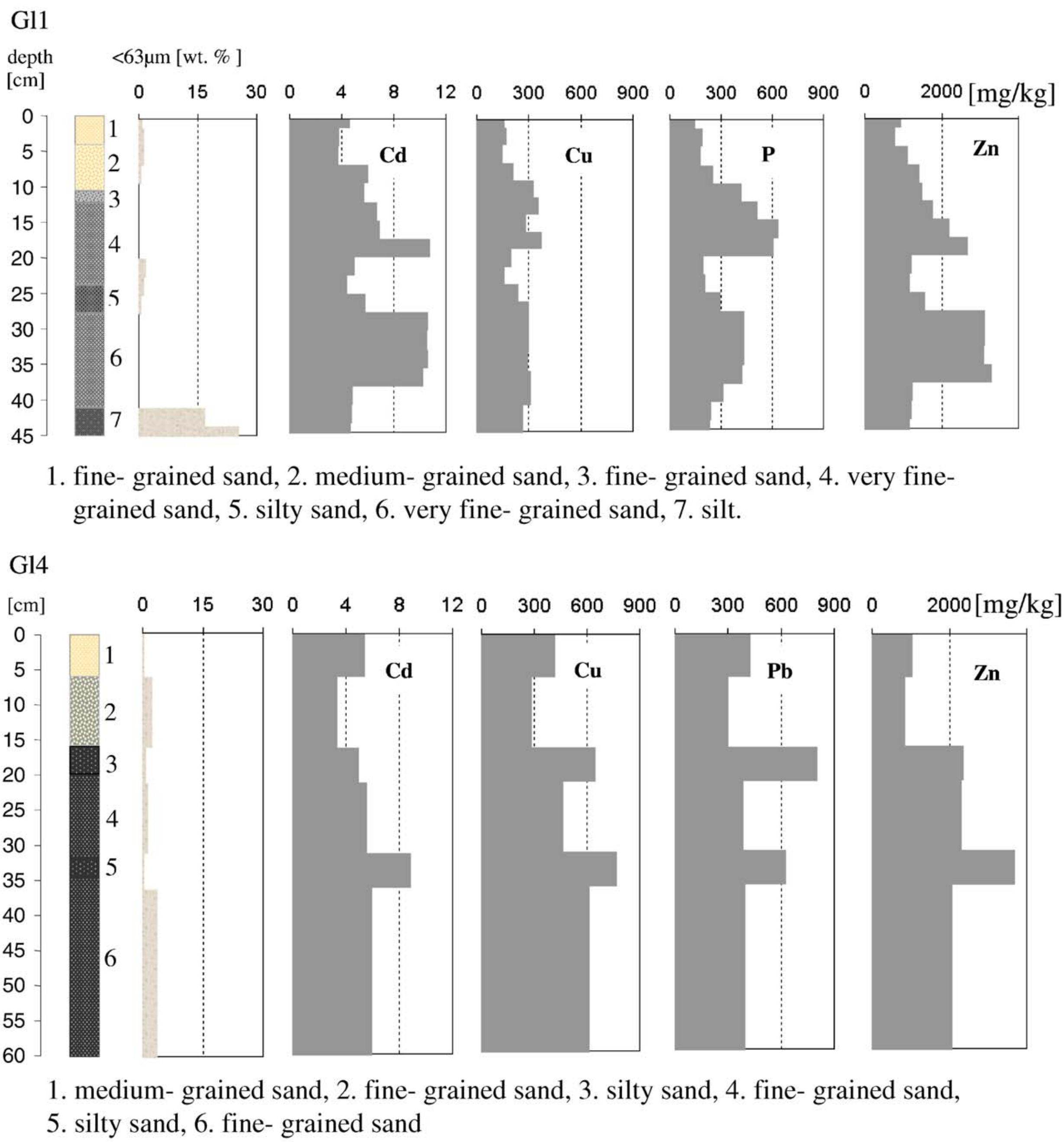

Fig. 7. Vertical distribution of the $<63\,\mu m$ sediment fraction and Cd, Cu, Pb and Zn contents in the Odra River sediment cores from Glogów.

that the strong to very strong contamination (classes III/IV and IV) with Cd was typical for almost all samples along the Odra River, over five sampling periods. Only sporadically was class III stated, thus slight improvement of Cd content in the SPM from May 2000 could be observed. With Pb, Zn and Cu the situation was at no time as critical as with Cd. Strong and moderate contamination for Pb and Cu (II–III, III classes), and very strong and strong for Zn (III–IV, III classes) was typical for sediments taken in '97. However, after 3 years the situation has improved, and in 2000, class II – moderate contamination with Cu, Zn, and in the upper river section with Pb dominated. The mean contents of Ni and Cr in SPM were about two times higher if compared with their background values, but on similar level in the sediments. While the contents of As, in less than 20% of studied sediment and SPM samples, were higher than the tentative threshold value (TTV) of

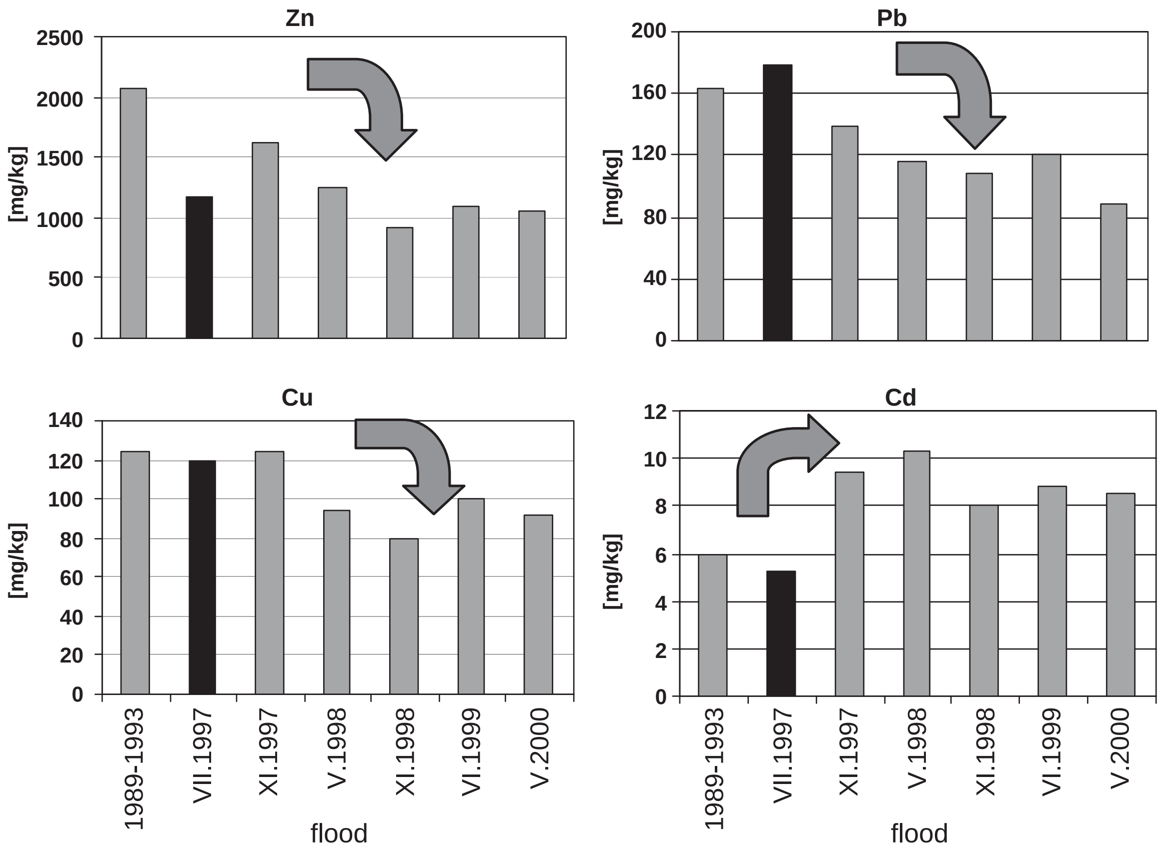

Fig. 8. Changes of the metal mean contents in the Odra River bottom sediments before and after the '97 flood.

$100\,mg\,kg^{-1}$ for stream sediments (Aston & Thornton, 1977), the mean contents neither in the SPM ($63.8\,mg\,kg^{-1}$) nor in sediments ($92\,mg\,kg^{-1}$) were higher than TTV.

Generally, in the Odra River the metal contamination decreased, especially for Zn, Pb and Cu; thus an improvement was observed for these metals, compared with the results from different sampling periods. As the reasons for these findings, the dilution processes after the '97 flood should not be excluded. Among all metals studied in the Odra River sediments, no substantial reduction with Cd contamination was observed, neither in the period after '97 flood, nor if compared with the earlier results obtained before '97 (Fig. 8).

In the river system, water and suspended matter are responsible for metal transport. It is evident from our calculations that Cu, As, Cr, Ni and Zn were mainly transported by river water, while Cd, Pb and Fe by river suspended matter (Fig. 9).

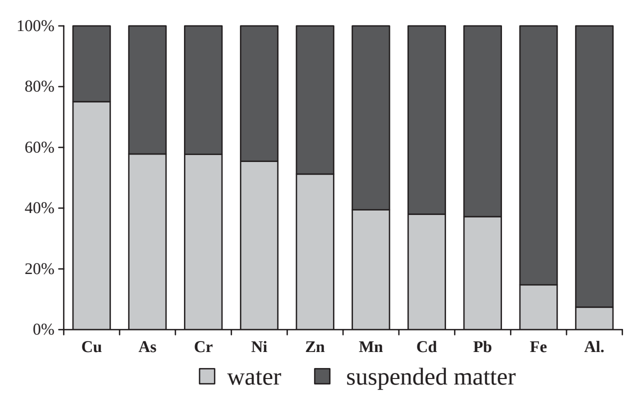

Fig. 9. Relative portions of trace metals transported by the Odra river water and suspended particulate matter.

The chemical forms for selected samples of river SPM and sediments were estimated using the sequential extraction procedure. The changes of the Cd and Pb chemical forms in the suspended matter samples along the Odra River course are shown in Fig. 10. Along the Odra River course essential differences among chemical forms are observed for Pb, when compared with Cd. There are four river sections where 80–90% of the total Pb amount was found in the residual fraction of sediment. The mobility of Pb is low, in most samples the relative portion of the carbonate fraction is below 10%. Generally, the highest mobile portions were stated

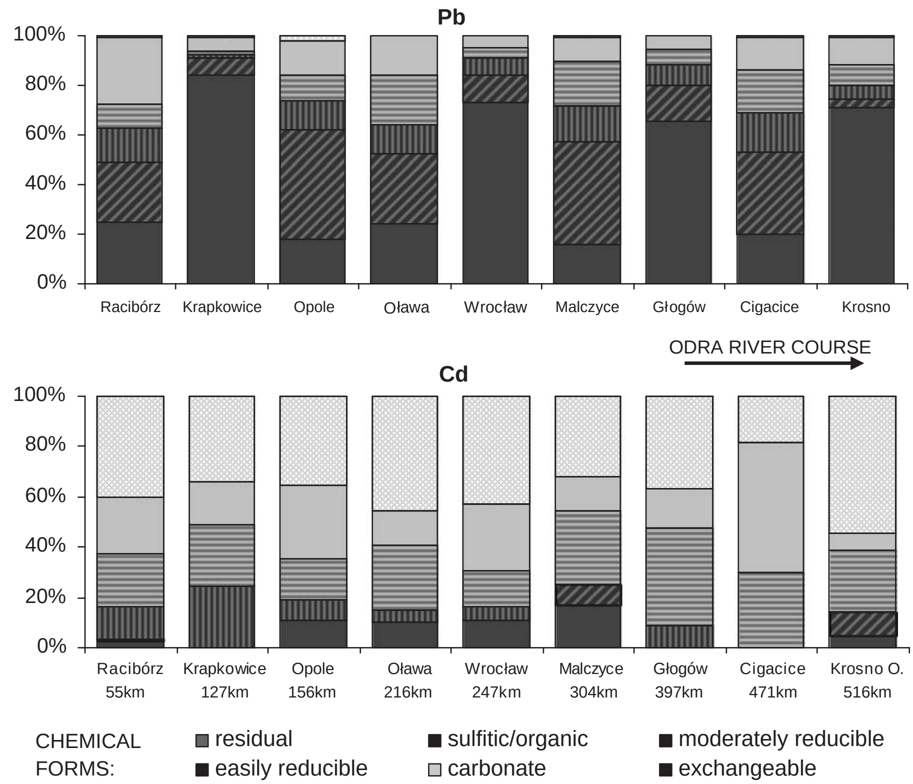

Fig. 10. Changes of metal chemical forms in the suspended matter sampled along the Odra river course.

for Mn, Cd, Zn and As in the Odra River solids, up to about 75%, 70%, 80% and 50%, respectively. Our earlier studies (Report IOP, 2002) have shown that the mobile portions of Zn, Cu, Cd, Mn and Pb depend on their total amount in the solids; regardless of the sample nature, i.e. suspended matter, bottom sediments and river bedrock. It seems that the considerable mobile portions of Zn, Cu, Cd, Mn and Pb depend also on the amount and kind of organic-biological material present in the Odra River SPM.

From the study of the Odra River sediments cores it is evident that metals can migrate into deeper layer. In the core (Kr0), taken from overbank sediments in Krapkowice, the highest amount of Pb, Cd and Zn was stated at a depth below 110 cm, thus, a migration of heavy metals into ground water can be possible. Cadmium seems to be of particular concern because of high level in all river compartments, along the whole river course.

Conclusions

1. Water samples were strongly contaminated with Cd, Cu and Zn, and the highest contents were observed particularly in the middle Odra section, at the Lubin–Glogów Cu-mining and processing region.
2. Suspended matter and sediments of the Odra River are strongly contaminated with Zn but mainly with Cd. Their spatial distribution over the time period of 4 years showed a similar pattern: classes IV and III–IV were dominating. For other metals in the Odra River, elevated regional concentration of solids was found for Hg, Cu and Pb.
3. Metal pollution has decreased, especially for Zn, Pb and Cu, if compared with the results from different sampling periods. Among all metals studied in the Odra River sediments, no substantial reduction with Cd contamination was observed, neither in the period after the '97 flood, nor if compared with the earlier results obtained before '97.
4. No essential differences of the metal contents were observed among the samples for the same river compartment, from the same locality, taken within the five sampling periods. Thus, both selection of the river compartment and optimisation of the sampling strategy could be proposed.
5. From all metals studied, Cd, Zn and As appear to be of particular concern because of their high levels and high mobility. The exchangeable and carbonate forms of Cd and Zn in river PSM and sediments reached for each up to 50% of their total amount.
6. The pattern of spatial and vertical variation of the metals in the river sediments indicates that the variety of sources might be responsible for the contamination; very intensive, historical and current mining and smelting activities probably are the most important ones.

Acknowledgements

These studies were carried out within the research activities of the Department of Environmental Protection Faculty of Geology, Geophysics and Environmental Protection at the University of Sciences and Technology in Krakow (project no: 11.11.140.053).

References

Adamiec, E., & Helios Rybicka, E. (2002a). Distribution of pollutants in the Odra river system. Part IV. Heavy metal distribution in water of the upper and middle Odra river, 1998–2000. *Polish Journal of Environmental Studies*, *11*(6), 669–673.

Adamiec, E., & Helios Rybicka, E. (2002b). 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), 675–688.

Aleksander-Kwaterczak, U. (2004). *Rozmieszczenie metali ciężkich w pionowych profilach osadów wybranych rzek Polski* (*Heavy metals distribution in the sediment cores from the selected rivers in Poland*). Ph.D. Thesis, The Main Library of the AGH University of Science and Technology, AGH in Krakow, p. 126.

Aleksander-Kwaterczak, U., & Helios Rybicka, E. (2004a). Mobility of heavy metals in the Mala Panew River sediment depth profiles and their migration in to groundwater system. In W. Geller, et al. (Eds.), *Proceedings of the international conference, 11th Magdeburg on waters in central and eastern Europe: Assessment, protection, management*. UFZ-Bericht, No. 18/2004, pp. 199–200.

Aleksander-Kwaterczak, U., & Helios Rybicka, E. (2004b). Rozmieszczenie metali ciężkich w pionowych profilach osadów rzecznych Małej Panwi. (Heavy metals distribution in the river sediment depth profile of the Mala Panew River (southern Poland)). *Geologia*, *30*(2), 153–164.

Aston, S. R., & Thornton, I. (1977). Regional geochemical data in relation to seasonal variations in water quality. *Science of the Total Environment*, *7*, 247–260.

Bojakowska, I., & Sokołowska, G. (1993). Zmiany zawartości Cd, Cr, Pb, Zn w aluwiach wybranych rzek Polski. Monitoring geochemiczny osadów wodnych Polski 1990–1992 (Changes of Cd, Cr, Pb and Zn concentration in alluvia of the selected rivers in Poland. Geochemical monitoring of aquatic sediments of Poland). *Przeglad Geologiczny*, *3*, 155–162.

Ciszewski, D. (2003). Heavy metals in vertical profiles of the Middle Odra River overbank sediments: Evidence for pollution changes. *Water, Air and Soil Pollution*, *143*, 81–98.

Förstner, U., Ahlf, W., Calmano, W., & Kersten, M. (1990). Sediment criteria development – contributions from environmental geochemistry to water quality management. In D. Helling, P. Rothe, U. Förstner, & P. Stoffers (Eds.), *Sediments and environmental geochemistry, selected aspects and case histories* (pp. 31–338). Berlin: Springer.

Helios Rybicka, E. (1996). Environmental impact of mining and smelting industries in Poland. *Environmental Geochemistry and Health Geological Society Special Publications*, *113*, 183–193.

Helios Rybicka, E., & Strzebonska, M. (1999). Distribution and chemical forms of heavy metals in the flood 1997 sediments of the upper and middle Odra river and its tributaries, Poland. *Acta Hydrochimica et Hydrobiologia*, *27*, 331–337.

Helios Rybicka, E., & Knöchel, A. (2000). Crucial load in the river Odra – impacts of floods on the situation of hazardous substances. *BMBF symposium, Elbeforschung, Gewässer Landschaften*, *21*, 79–99.

Irmer, U. (1997). Bewertung der Ergebnisse aus der Elbeschadstoff-Forschung. *IKSE – Workshop*, Geesthacht, pp. 36–40.

Martin, J. M., & Meybeck, M. (1979). Elemental mass balance of material carried by major world rivers. *Marine Chemistry*, *7*, 173–206.

Ramsay, M. H. (1993). Sampling and analytical quality control (SAX) for improved error estimation in the measurement of Pb in the environment using robust analysis of variance. *Applied Geochemistry*, *2*, 149–153.

Report IOP. (2002). *Die Belastung der Oder, Ergebnisse des Internationalen Oderprojekts (IOP)*. ISBN-No. 3-924330-54-9.

Turekian, K. K., & Wedephol, K. H. (1961). Distribution of the elements in some major units of the earth's crust. *Geological Society of America Bulletin*, *72*, 175–184.