Polish Journal of Environmental Studies Vol. 14, No. 3 (2005), 305-317

Original Research

Fractionation of Some Heavy Metals in Bottom Sediments from the Middle Odra River (Germany/Poland)

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Received: 10 February, 2004
Accepted: 28 September, 2004

Abstract

Fractionation of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn has been performed in bottom sediment samples collected along a 75 km section of the middle Odra River by a modified method of 5-step sequential extraction according to Tessier. The results have shown the presence of Cu, Ni, Zn and Mn already in exchange fraction (I); the mean percent content of metals in mobile phases (exchange and carbonate) reached 35% (Cu), while the maximum values reached 59% (Ni). From among the metals studied, Zn, Mn, Fe, Cr and Ni were dominant in the species bound to hydrated iron and manganese oxides, so the metals contained in the bottom sediments were not permanently immobilized.

Good correlation was found between the concentrations of Zn, Mn and Cd in the mobile phases (I+II) and their total concentrations. Similarly, the concentrations of all metals determined in the reducible fraction and in the fraction bound to organic matter (except for Cd and Cr) were well correlated to their total content.

Keywords: heavy metals, bottom sediments, fractionation, bioavailability, the Odra River

Introduction

The Odra River, situated in the geographical centre of Europe, has gained increasing political and economic significance. The river has been an important channel for transportation and, as many industrial centres have developed in the direct vicinity of the river, its state has been of great concern in the aspect of environmental protection. The first measures aimed at protection of the Odra have been taken in the southern and northern sections, and concentrated on protection of the areas that are preserved in the rivers drainage area [1].

The Odra belongs to the six greatest river systems in Europe. It receives both purified and non-purified pollution, very often from uncontrolled sources or as a result of temporary failures. The great amounts of pollutants have had a particularly disastrous effect on the legally protected fragments of the Odra River catchment area and prevent its recreational use.

The purity of the Odra in its middle and lower courses depends significantly on the influx of wastes from cities and industrial centres in Upper and Lower Silesia, in the Czech Republic and on the German side in the bordering section of the river. The status of its water also depends on the state of wastewater management in the area of the whole catchments of the river, and on the state of the wa-

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ter in the tributary rivers: Barycz, Bóbr, Nysa Łużycka and Warta [2].

The study of emissions of heavy metals to the Odra River carried out in 1993-1997 proved the dominant effect of point sources of pollution, mainly municipal waste purification plants. They contributed 34% of Cu and 73% of Cd of the total amount of these metals in the river. Apart from the point sources, urban areas were also responsible for the introduction of 16% Cd and 31% of Cu and Pb [3]. In Western Europe over 70% of the load of heavy metals comes from large area sources [4]. In comparison with the heavy metal content in the other river systems, the load of the Odra River is estimated as not high, which is a consequence of a high retention of metals in the river system [3]. Recently, a decrease in the heavy metal load in the Odra River has been observed, especially pronounced over the last decade (e.g. 85% decreases in the content of Zn) [5].

Heavy metals can occur in different species or complexes in the river bottom sediments. In unpolluted sediments they are mainly bound to silicates and primary minerals. Such species are relatively immobile and usually not available for living organisms. In polluted sediments heavy metals are more mobile and bound to different phases of the sediment. The biogeochemical and ecotoxicological significance of heavy metals in bottom sediments is usually determined on the basis of the presence of particular species bound to specific phases of the bottom sediment, which determines their reactivity, and not on the basis of the coefficient of metal accumulation in the sediment [6]. The total content of a given metal is not informative as it does not describe the amount of the metal available for living organisms and thus may overestimate the real threat. The most important from the ecological point of view is to know which part of the total concentration of a given metal is available to living organisms as it determines the real toxic effect of this metal [7]. This need demanded development of new analytical methods of bottom sediment study based on fractionation.

The aim of our study was to determine the contribution of particular fractions (species) of selected heavy metals in their total content in the samples from the Odra River bottom sediments collected at 7 cross section profiles, by the modified method of a 5-step sequential extraction according to Tessier et al. [8].

The Area of Study

The study was performed on samples collected along a 75 km section of the middle Odra River, between the estuary the Nysa Łużycka River (544 km) and that of the Warta River (619 km). Seven cross-sections were demarcated as shown in Fig. 1, and from each of them 3 samples of bottom sediments were collected: one from the German bank, labelled A; one from the centre of the riverbed, labelled B; and one from the Polish bank, labelled C.

The locations of the cross-sections was as follows:

1 - about 2 km below the Nysa Łużycka River estuary;

2 - above the estuary of the Odra-Sprewa channel, at this cross-section only one sample was collected near the German bank, labelled 2A;

3 - below the estuary of the Odra-Sprewa channel, immediately below the city of Eissenhuttenstadt (steelworks);

4 - below the estuary of the backwater channel passing through Cybinka (steelworks);

5 - below the cities Słubice-Frankfurt n/O;

6 - above the Warta River estuary;

7 - below the Warta River estuary, below the city of Kostrzyn n/O.

The field work was performed in June 2002.

The Methods

Sample Collection and Preparation

The samples to be studied were collected by boat using a tubular scoop-type Czapla. The top layer of the bottom sediments from the river (10 cm thick) was collected, as this layer takes part in the processes of matter exchange in rivers. The bottom sediment samples were collected into tight plastic containers of 1l capacity and transported to the lab taking care that they would not become polluted on the way. In the lab the samples were frozen and stored in a freezer at about –20^{0}C [9,10]. After defrosting they were dried at 105^{0}C for 24 h [11], then homogenized in an agate mortar and sifted (with nylon sieves) to separate the mesh size fraction < 0.8 mm. This fraction makes about 85% of all grains in the bottom sediments studied and thus we assumed that the content of heavy metals in this fraction will be representative and will provide reliable information on the real environmental risk.

Sieving and mixing in order to obtain a representative sample for bioavailability analysis may lead us to precise but inaccurate results [10].

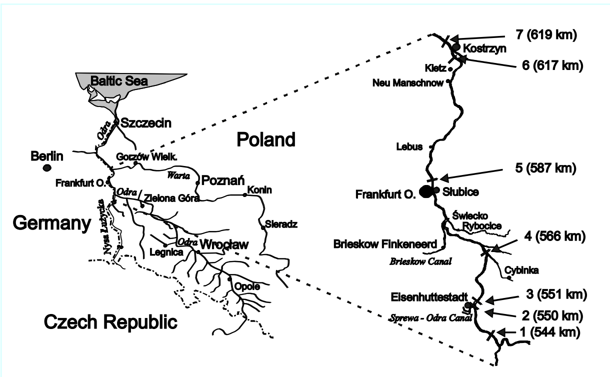


Fig. 1. The study area.

Table 1. The modified scheme of sequential extraction according to Tessier, used in our study [11].

15 ml 1 M CH_3COONH_4, pH 7 shaking time 1h room temp.	Step 1	Fraction I Exchangeable fraction
30 ml 1M CH_3COONa acidified CH_3COOH to pH 5 shaking time 5 h (experimentally stated) room temp.	Step 2	Fraction II Metals bound with carbonates
30 ml 0.04M $NH_2OH.HCl$ in 25 %(v/v) CH_3COOH shaking time 5 h temp. 95°C	Step 3	Fraction III Metals bound with hydrated iron and manganese oxides
7.5 ml 0.02M HNO_3 + 7.5 ml 30 % H_2O, pH 2 shaking time 2 h temp. 85° 7.5 ml 30 % H_2O, pH 2 shaking time 3 h temp. 85°C 15 ml 3.2M CH_3COONH_4 in 20 %(v/v) HNO_3 shaking time 0.5 h room temp.	Step 4	Fraction IV Metals bound with organic matter
4.5 ml 10M HNO_3 + 3x3 ml H_2O_2 time 1 h + 15 ml H_2O time 0.5 h boiling temp.	Step 5	Fraction V Mineral fraction

Analytical Procedure

Total content of heavy metals was determined after sample digestion with concentrated HNO_3 and 30% H_2O_2. Samples of bottom sediments were subjected to sequential extraction according to the scheme presented in Table 1. The content of metals in fraction V was calculated by subtracting the contents of metals in fractions I-IV from the total content of metals in the sample determined by the way presented at stage 5 of the procedure [11].

The total content of heavy metals and the content of metals in the solutions obtained after each step of the sequential extraction was determined by flame absorption spectrometry (AAS) on a Perkin-Elmer spectrometer AAnalyst 300. Cadmium was determined by the graphite furnace technique.

Standard Reference Material LKSD-2 (Canadian Lake Sediment) was analyzed routinely as a laboratory reference material for heavy metals. Recoveries of heavy metals were: Hg-97%, Cu-88%, Pb-86%, Ni-82%, Cr-79%, Mn-85%, Zn-88%, and Fe-79%.

In order to assess the repeatability of results provided by the method of sequential extraction, the experiment was conducted in parallel for 5 samples. In the extracts the concentrations of the following metals were determined: Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn. The arithmetic mean values, standard deviations and relative standard deviations were calculated. The results are collected in Table 2. As follows from relatively low values of standard deviations and relative standard deviations, the method is characterized by good repeatability. Most important is that most of the values of standard and relative standard deviation do not exceed 10%. The errors that could appear in the process of analysis can be due to inhomogeneity of the material studied and the complex extraction procedure.

Results

The total contents of particular heavy metals determined in the samples of bottom sediments collected from the Nysa Łużycka River estuary (Fig. 1, cross-section profile 1) to the Warta River estuary (Fig. 1, profile 7) are shown in Table 3. Results of determinations of the total concentrations of some heavy metals in bottom sediments of the Middle Odra River are presented and discussed in a separate paper [12].

The percent contribution of particular fractions of heavy metals separated by sequential analysis is given in Fig. 2. Analysis of the plots permits estimation of the migration possibilities of individual metals and hence their potential bioavailability to living organisms.

Cadmium. In the bottom sediments from the middle Odra River section Cd does not occur in the exchange fraction, but is released during the second step of extraction (fraction II) in the amount of 20-40% of total content. Similar amounts of Cd (13-40%) are bound with organic compounds (fraction IV). The content of Cd bound to the oxides Fe-Mn (III) and in the residual fraction (V) varies from 0.6 to 20% and from 19 to 45%, respectively. Rela-

Table 2. Assessment of method repeatability.

Fraction	Metal	Statistical parameter		
		$\bar{x}$	S_x	*RSD* [%]
I	Cu	1.72	0.08	4.86
	Fe	20.0	1.2	6.12
	Mn	67.8	6.0	8.81
	Ni	1.20	0.10	8.33
	Zn	12.0	0.2	1.40
II	Cd	3.28	0.19	5.86
	Cu	2.74	0.05	2.00
	Cr	1.58	0.08	5.30
	Fe	226	9	3.96
	Mn	101	5	5.14
	Ni	3.12	0.19	6.17
	Pb	6.20	0.37	5.93
	Zn	88.2	3.6	4.04
III	Cd	1.72	0.08	4.86
	Cu	7.08	0.49	6.95
	Cr	12.80	0.84	6.54
	Fe	6200	141	2.28
	Mn	206	15	7.36
	Ni	5.12	0.32	6.24
	Pb	38.6	2.1	5.37
	Zn	184	11	6.20
IV	Cd	1.76	0.05	3.11
	Cu	26.0	1.6	6.08
	Cr	1.14	0.05	4.80
	Fe	888	28	3.12
	Mn	53.0	3.2	5.97
	Ni	4.12	0.26	6.28
	Pb	4.54	0.11	2.51
	Zn	24.2	1.3	5.39
V	Cd	1.02	0.04	4.38
	Cu	4.28	0.25	5.82
	Cr	4.44	0.13	3.02
	Fe	4020	84	2.08
	Mn	4.54	0.18	4.00
	Ni	1.04	0.05	5.27
	Pb	19.0	1.2	6.45
	Zn	11.2	0.8	7.47

$\bar{x}$ - mean value; S_x - standard deviation; *RSD* - relative standard deviation

tively large amounts of Cd, from 19 to 45%, occur in the mineral fraction. No significant variation in the amounts of Cd over the profile is noted.

Chromium does not occur in faction I, and its content in the fraction bound to carbonates (II) varies in the profile and along the river. The scatter of results is particularly pronounced on the Polish bank, along which Cr content varies from 0 to 53%, in the central part of the riverbed and on the German bank the content of Cr in fraction II reaches 27%. In much greater amounts Cr occurs in the reducible fraction (III), where its content varies from 24 to 82%. The content of Cr bound to organic matter (IV) varies from 2 to 36%. In the mineral fraction Cr has been found mainly in the samples on the German bank in the content from 11 to 57%.

Copper. In the bottom sediments of the middle Odra River, Cu appears in the exchange fraction (I), in the contents varying in the profiles. On the German bank it does not exceed 10%, on the Polish bank it reaches 12%, while in the samples collected in the central part of the riverbed it varies from 9-18%. The greatest amount of Cu is bound to the fractions of carbonates (II), oxides (III) and organic matter (IV), and varies in the profiles. The distribution of Cu in fraction II is the most uniform in the central part of the riverbed (28-36%), less uniform on the Polish bank (14-37%) and varied on the German bank (6-34%). The distribution of Cu in fraction III on the German bank varies from 10 to 20%, is more uniform in the central part of the riverbed (18-28%) and still more uniform on the Polish bank (21-30%). The content of Cu in the organic matter is variable on the banks (7-46%) and more uniform in the central part of the riverbed (16-29%).

Iron. In fraction I Fe practically does not occur (max. 0.4%), in fraction II it occurs on the two banks in the amounts of 2-3%, and in the greatest amounts it occurs in fraction III, on the German bank (43-61%), on the Polish bank (40-74%) and in the central part of the riverbed (36-57%). In the organic matter (IV) Fe occurs in small amounts up to 7%. High content of Fe is found in the mineral fraction (22-63%), the highest in the samples from the central part of the riverbed.

Manganese is found mainly in the fraction of oxides Fe-Mn (III), its content in the profile varies and is the highest and the most uniform in the central part of the riverbed 84-85%, while on the German bank it varies from 38 to 69%, on the Polish from 37 to 85%. Much lower content of Mn is found in the carbonate fraction (II), on the banks it varies from 14 to 31% and in the central part of the riverbed from 7 to 9%. In relatively large amounts, Mn occurs in the exchange fraction (I), in the bottom sediments on the German bank its content varies from 4 to 25%, on the Polish bank from 7 to 18%. The percent of Mn bound to organic matter (IV) and mineral fraction (V) is 0-3% and 2-14%, respectively, while its mean content in the organic fraction in the samples from the central part of the riverbed is 1%.

Nickel. In the exchange fraction (I) Ni is found in the lower part of the Odra River section studied (below the backwater channel, Fig. 1), in the amount varying from 3 to 12% over the profile, only exceptionally on the Polish bank does it occur in the amount of 23%. The amount of Ni bound in the carbonate fraction (II) varies along the course of the river and in the profile, from 8% on the German bank to 53% on the Polish one. In all samples the greatest amount of Ni occurs in the fraction of oxides Fe-Mn (III), from 36 to 58%. To the fraction of organic matter (IV) Ni is bound mainly in the upper part of the river section studied (25-45%), while in the lower it's only 0-23%. The contribution of Ni in the mineral fraction is low and in the samples from the central part of the riverbed and from the Polish bank it is undetectable.

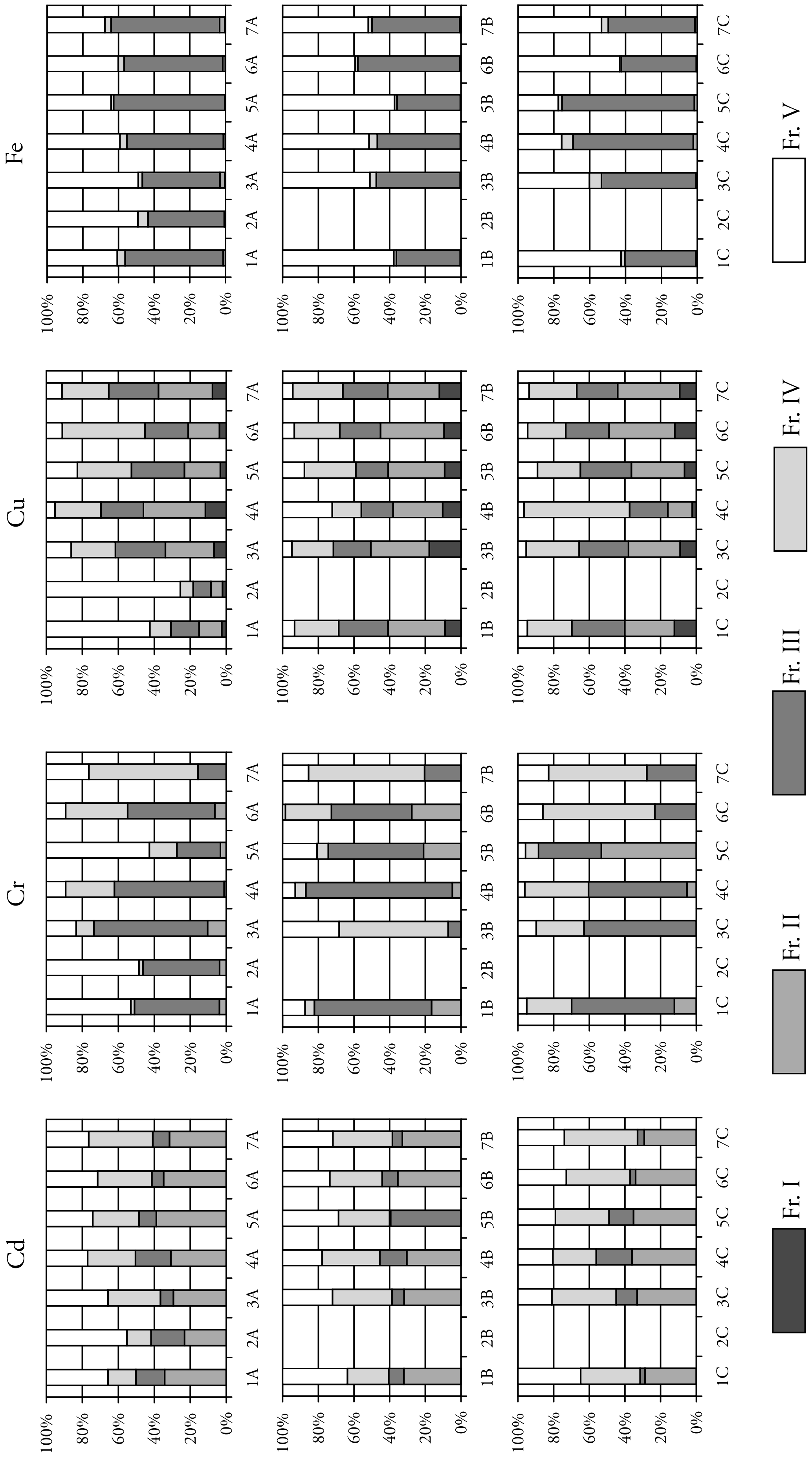
Lead does not occur in the exchange fraction (I), its content in the fraction bound to carbonates (II) varies

Table 3. Total concentration of heavy metals [mg/kg dried mass] along the riverbed and in transversal profile of the middle Odra River section studied.

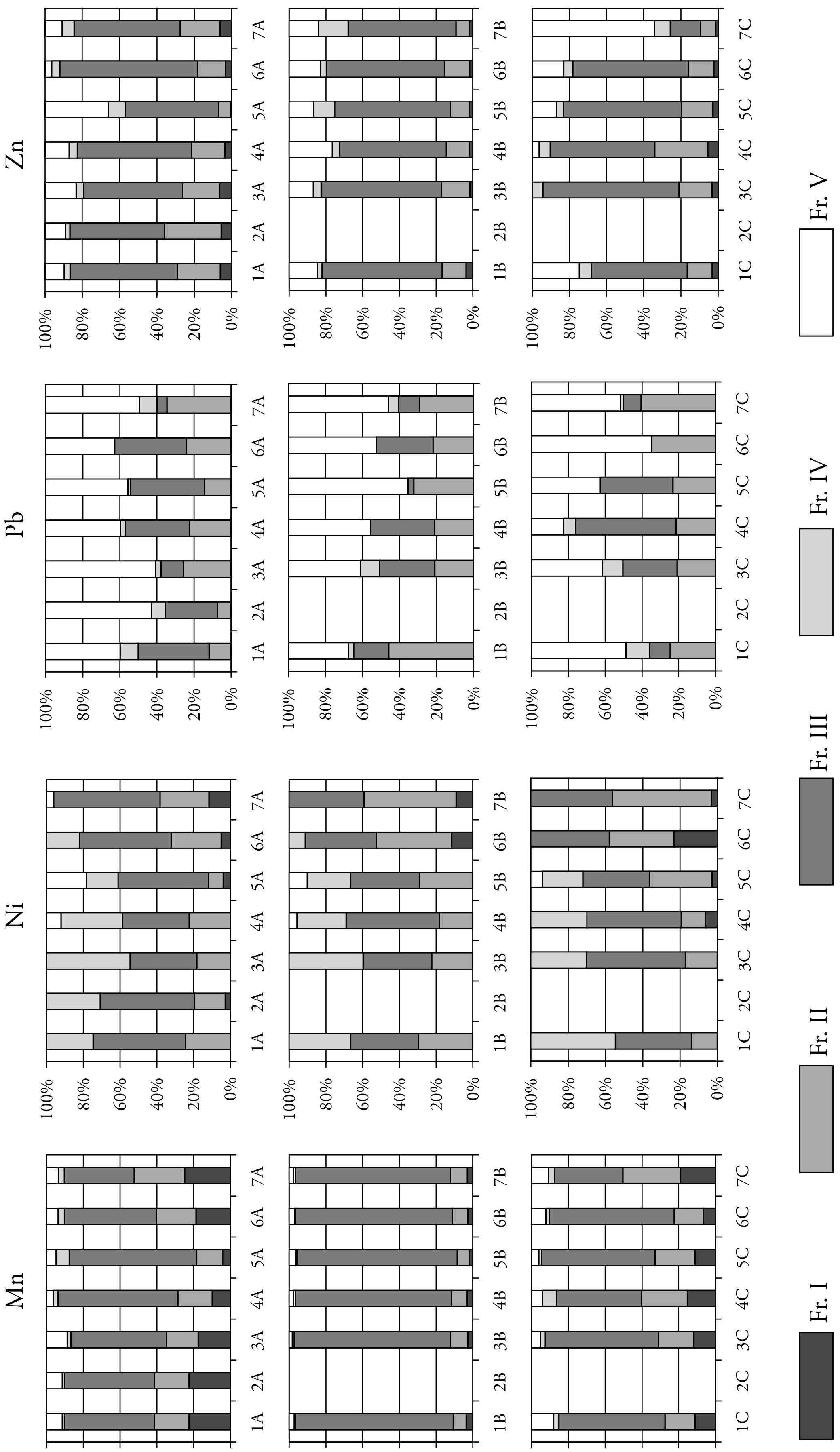
Samples collecting places	German shore A	Race B	Polish shore C	German shore A	Race B	Polish shore C
	Cd			Pb		
1	4.74	4.48	3.69	91.1	60.3	28.8
2	7.87	samples weren't collected		163.3	samples weren't collected	
3	3.36	3.36	3.27	33.5	38.4	31.0
4	3.44	3.34	4.18	30.8	31.8	83.3
5	3.86	2.93	3.90	42.8	23.9	38.5
6	4.35	4.63	3.73	42.8	33.6	21.2
7	3.88	4.33	4.37	27.3	30.0	28.7
	Cr			Zn		
1	47.5	2.4	3.0	323	59	47
2	44.2	samples weren't collected		471	samples weren't collected	
3	3.4	2.0	3.0	70	56	62
4	4.3	1.6	20.6	92	71	225
5	13.5	2.3	7.5	71	69	58
6	12.6	2.3	2.0	303	72	56
7	4.1	2.6	2.0	62	47	28
	Cu			Mn		
1	51.7	11.5	14.2	418	284	48
2	88.3	samples weren't collected		711	samples weren't collected	
3	14.8	13.4	15.2	96	263	100
4	16.2	14.8	64.5	138	257	324
5	25.1	13.3	16.4	1,242	248	110
6	30.6	13.9	12.5	205	222	109
7	16.2	13.5	11.7	79	284	51
	Ni			Fe		
1	19.2	13.6	13.3	14,916	1,999	1,994
2	31.0	samples weren't collected		17,399	samples weren't collected	
3	17.6	19.0	14.1	2,969	1,876	2,867
4	11.5	8.2	14.0	2,564	1,985	8,958
5	18.0	12.0	7.6	37,973	2,136	3,451
6	14.1	11.7	5.1	5,558	1,841	1,996
7	9.6	12.1	10.5	2,163	1,675	1,494

from 7 to 46%, depending on the site of sample collection. Similarly, in the oxide fraction (III), the content of Pb varies from 10 to 54%. The contribution of Pb in the organic matter fraction (IV) is low, reaching 12% in maximum, and in 1/3 of the samples no Pb has been detected in this fraction. In the mineral fraction Pb occurs in large amounts, its contribution varies from 17 to 65%.

Zinc. The dominant content of Zn is bound to the fraction of oxides Fe-Mn (III). The content of Zn in this fraction in the samples collected from the central part of the


Cd
Cr
Cu
Fe
1A 2A 3A 4A 5A 6A 7A
1B 2B 3B 4B 5B 6B 7B
1C 2C 3C 4C 5C 6C 7C
100% 80% 60% 40% 20% 0%
Fr. I
Fr. II
Fr. III
Fr. IV
Fr. V

Fi□


Mn
Ni
Pb
Zn
100%
80%
60%
40%
20%
0%
1A 2A 3A 4A 5A 6A 7A
1B 2B 3B 4B 5B 6B 7B
1C 2C 3C 4C 5C 6C 7C
Fr. I
Fr. II
Fr. III
Fr. IV
Fr. V

Fi

riverbed does not show much variation and changes from 58 to 66%. The samples collected on both banks are characterized by greater variation – from 50 to74%, an exception is one sample containing 16% Zn in this fraction. The content of Zn in the carbonate fraction (II) varies along the course of the river and in the profile. On the German bank the content of Zn bound in this fraction varies from 15 to 30% (except one sample in which it is 6%), on the Polish bank it varies from 8 to18% (except one sample in which it is 29%). In the samples collected from the central part of the riverbed the content of Zn in fraction II varies from 11 to 15% (except one sample in which it is 7%). The organic matter fraction (IV) binds a small amount of Zn from 2 to 9% in the whole profile, except two samples collected in the central part of the riverbed, in which the contribution of Zn in this fraction is 11 and 16%. Zinc is also present in the exchange fraction (I), in the samples from the central part of the riverbed in about 2%, on the German bank – up to 6% and on the Polish bank up to 5%.

Discussion

Analysis of the contents of particular metals in individual fractions determined by the method of sequential extraction has shown a high percent contribution of Cu, Ni (in particular in the samples collected near Kostrzyn), and Zn in the exchangeableable fraction. In the conditions of high total concentration of Zn (Table 3). Its easy leaching can result in a dangerous increase in the content of this metal in bulk water. In the conditions of changing salinity of the Odra River water along the German riverbank, the leaching of Mn is increased and a considerable amount of this metal can be released.

A comparison of the percent contributions of heavy metals in particular fractions of bottom sediments from the Odra River and other rivers is shown in Table 4. In the bottom sediments from the upper Odra River, the contents of Mn and Zn are quite similar, whereas the proportions of Cu and Pb in the exchangeable fraction are small. Also small is the content of Cu, Pb and Ni in the main rivers of Latvia; however, their bottom sediments contain relatively high contributions of toxic Cd. The content of Cd in the rivers analyzed is in general high, in particular in the bottom sediments of the La Palais River. The bottom sediments from the Kangjiaxi River contain small contents of Pb, but also a much lower proportion of Cu and Zn, when compared to those in the Odra River samples. The exchangeable fraction in the bottom sediments of the Kromme Rijn River contains only Mn and insignificant amounts of exchangeable Ni.

The metals bound in fraction II (carbonates) can penetrate the bulk water easily as a result of a pH decrease in rivers. Relative to the bottom sediments of the middle Odra River studied in this work, those of the upper Odra River contain much more Zn released in the second step of extraction, similarly as those of the Taiwan rivers. Lower than in the Odra River are the amounts of easily accessible Zn in the bottom sediments of the Guadalquiver River. Relatively small amounts of Zn in this fraction (comparing to the Odra River sediments) have been reported from the bottom sediments of the Kromme Rijn River. The content of Cu in our samples is comparable to those in the bottom sediments of the Latvia rivers, but much higher than that in the Guadalquiver River (Spain), in whose sediments it occurs in amounts of above 5%. The bottom sediments of the Kromme Rijn River have been found not to have Cu in the fraction bound to carbonates. Much smaller amounts of Pb washed out at the second stage have the bottom sediments from the Guadalquiver River, the Latvian rivers and the Kromme Rijn River. The content of Ni in this fraction in the bottom sediments of the Latvian rivers, the Kromme Rijn River and Guadalquiver River are lower than in the sediments of the Odra River studied. The content of Cd in the sediments of the Guadalquiver River is comparable to that of the Odra River, it is much lower in the Latvian rivers and it has not been detected in the sediments of the Kromme Rijn River in this fraction. The contents of Cd, Cu, Zn and Pb in the carbonate fraction in the bottom sediments of the Kangjiaxi River in China are also lower than in the sediments of the Odra River studied.

In the samples of bottom sediments collected along the studied section of the Odra River, the contribution of metals bound to hydrated Fe-Mn oxides (III) dominates. This fraction contains the greatest amount of these metals in the bottom sediments of the middle and upper Odra River, Guadalquiver River, the Kangjiaxi River (except Cu) and La Palais River (except Cd). Only the content of Pb in the bottom sediments of the Guadalquiver and La Palais rivers are comparable with those in the bottom sediments in the Odra River section studied. The latter contained first of all much more Cr, Ni and Zn in the fraction of Fe-Mn oxides. Much smaller proportions of Pb, Ni and Cu occur in the sediments of the Latvian rivers. The sediments of the Kromme Rijn River contain only insignificant amounts of Fe, and Zn and Cd in much lower concentrations than in the Odra River sediments studied in this work, while Ni, Cu and Pb have not been detected in this fraction in the Kromme Rijn River sediments. In the bottom sediments of the rivers in Taiwan, the fraction of hydrated Fe-Mn oxides also contains significant amounts of heavy metals.

The organic matter fraction (IV) contains mostly Cu (in the sample collected below Eissenhuttenstadt - 59%), Ni, Cd and Cr. Much smaller amounts of metals bound to organic matter or sulphides were found in the bottom sediments of the upper and middle Odra River, while the results obtained for the Latvian rivers are comparable with those reported in this work. The content of Cu in the bottom sediments of the Guadalquiver River is similar to that determined for the Odra River section we studied, but the contents of the other metals analyzed were much lower. In the bottom sediments of the main five rivers in Taiwan, the proportions of metals bound to organic matter

Table 4. Proportions of heavy metals in particular fractions of bottom sediments of the Odra River and selected other rivers, (sequential extraction according to Tessier [8]).

Rivers		Metals in the exchangeable fraction	Metals bound with carbonates	Metals bound with Fe- Mn oxides	Metals bound with organic matter	Residual fraction	References
Middle Odra River (section studied)	Cd	n.d.[5]	23-39	max 20	13-40	13-41	
	Cr	n.d.	1-53	24-82	2-36	max 57	
	Cu	2-18	6-37	10-30	7-59	3-74	
	Fe	max 0.4	max 3	36-74	max 7	22-63	
	Mn	2-25	7-31	37-87	max 8	2-14	
	Ni	3-23[1]	8-53	36-58	max 46	4-10(22)[2]	
	Pb	n.d.	7-46	max 54	max 13	17-65	
	Zn	max 6	6-30	16-74	2-16	max 34(66)[3]	
Upper Odra River	Cu	max 2	max 18	max 46	max 7		[13][a]
	Fe	max 1	n.d.	max 60	n.d.	no data	
	Mn	max 20	max 40	max 25	n.d.		
	Pb	max 2	max 20	max 63	max 9		
	Zn	max 8	max 43	max 41	max 5		
Guadalquiver[4] River (Spain)	Cd	5	35	25	3	30	[14][d]
	Cr	n.d.	3	15	15	65	
	Cu	max 5	5	5	30	55	
	Fe	n.d.	3	2	5	90	
	Mn	5	30	40	max 5	20	
	Ni	3	20	20	5	50	
	Pb	1	20	40	20	20	
	Zn	2	20	30	3	40	
Kromme Rijn[4] River (Netherlands)	Cd	n.d.	n.d.	max 10	90	n.d.	[15][d]
	Cu	n.d.	n.d.	n.d.	85	15	
	Fe	n.d.	15	2	30	50	
	Mn	10	30	20	40	n.d.	
	Ni	2	15	n.d.	30	50	
	Pb	n.d.	12	n.d.	45	40	
	Zn	n.d.	5	20	65	10	
Rivers of Latvia	Cd	5	18	22	28	27	[16][b]
	Cu	1	21	6	28	44	
	Ni	1	12	11	30	46	
	Pb	1	15	17	23	44	
Kangjaxi River (China)	Cd	3-15	11-16	21-52	10-36	11-33	[17][d]
	Cu	max 1.5	3-7	0.5-32	34-90	6-34	
	Fe	n.d.	n.d.	13-24	3-21	60-73	
	Mn	max 2.8	7-10	65-79	5-8	8-16	
	Pb	max 0.5	4-16	65-79	9-26	7-42	
	Zn	max 0.8	6-13	29-54	9-38	11-30	

Table 4 continues on next page...

Rivers of Taiwan	Cr	5.7	n.d.	9	66	19	[18][d]
	Cu	3.9	n.d.	7	16	73	
	Ni	5.5	23	32	40	n.d.	
	Pb	3.6	11	27	58	n.d.	
	Zn	4.5	33	33	30	n.d.	
Le Palais[4] River (France)	Cd	60	8	25	n.d.	8	[19][c]
	Cu	18	30	23	17	5	
	Pb	10	20	55	5	10	
	Zn	15	13	42	5	25	

[1]in 1/2 of the samples – n.d.
[2]in 2/3 of the samples – n.d., in one sample 22%
[3]in one sample 66%
[4]approximated values
[5]below the limit of determination of the method

[a] fraction of 0.020 mm
[b] fraction of 0.063 mm
[c] fraction of 0.315 mm
[d] not fractionated

was rather high relative to the values determined for the Odra. The bottom sediments of the Kromme Rijn River in the fraction bound to organic matter contained Ni in a proportion similar to that obtained by us for the Odra River section studied. However, the proportions of Cu and Cd were much greater, on average close to 90%, showing particular affinity to organic matter, which was not evidenced in our results (the sediments in the Odra River are mostly sandy), where the proportions of Cu in the fractions bound with carbonates, bound with oxides and bound with organic matter are almost the same. A high proportion of Cu bound to organic matter also has been noted in the bottom sediments of the Kangjiaxi River in China, where the contribution of Cu in this fraction dominates. The proportion of Cd in this fraction in the bottom sediments of this river is similar to that determined from our results.

The most mobile heavy metal species occur in fractions I and II, so in the sum of exchangeable fraction and that bound with carbonates. Some authors study the content of metals in these fractions in order to determine the greatest mobility of metals in bottom sediments [20, 21]. Analysis of the proportions of metals in these fractions provides information on the scale of a potential risk of environment pollution by heavy metals accumulated in the river bottom sediments.

In the sequential extraction scheme proposed by the European Union's Standards, Measurements and Testing program (SM&T, formerly BCR) [6, 22] fraction I, defined as acid soluble metals, includes exchangeable ions and carbonates [21, 23]. This definition permits comparative analysis of the proportions of metals in the most mobile fractions with those obtained by the Tessier method and by the procedure proposed by BCR. A comparison of the quality of bottom sediments from the Odra River section studied in this work and from the rivers Meža (Slovenia) [21] and Odiel (Spain) [23] (analyzed according to the BCR procedure) are shown in Table 5. The content of Zn, Pb and Cd in fractions I and II in the Odra River samples are comparable with those in the samples from the Meža River. The Odra bottom sediments are potentially more dangerous than those from the Odiel because of the greater content of Cu, Pb, Ni and Cr. The content of Zn is comparable to the bottom sediments from these

Table 5. Proportions of heavy metals in the most mobile fractions of the bottom sediments of selected rivers.

	Odra River (section studied)	Meža River (Slovenia)	Odiel River (Spain)
Cd	23-39	2-40	15-70
Cr	1-53		up to 2
Cu	9-50		5-17
Ni	12-59		2-20
Pb	7-46	12-32	up to 9
Zn	7-36	10-40	5-48
Procedure	Tessier modification [11]	BCR modification [21]	BCR modification [23]
Fractions	exchangeable + carbonate	soluble	acid soluble

Table 6. Proportions of metals in nonresidual fractions in the bottom sediments of the middle Odra River section studied.

Metal	Proportions of metal							
	Sum of fractions I-II		Fraction III		Fraction IV		Sum of fractions I- IV	
	Medium	Max	Medium	Max	Medium	Max	Medium	Max
Cd	33	39	10	20	30	41	72	81
Cr	14	53	55	82	17	36	86	100
Cu	35	50	23	30	26	59	85	95
Fe	1	3	50	74	3	7	55	78
Mn	28	52	64	87	3	8	94	98
Ni	30	59	44	58	23	46	97	100
Pb	25	46	25	55	4	13	55	83
Zn	19	36	58	74	6	16	83	100

two rivers (in the samples from the Odiel River mostly up to about 40%). Taking into regard the content of Cd, the Odra bottom sediments are less potentially harmful than those from the Odiel, although content of this metal is still high.

Table 6 presents percent contributions of metals (mean and maximum values) in the most mobile fractions (I + II), in fractions III, IV and in total in non-residual fractions (I – IV). In the bottom sediments from the Odra River section studied, the mean proportions of metals in the most mobile fractions reaches 35% (Cu), while the maximum contribution reaches 59% (Ni). In the bottom sediments and suspended matter of the upper and middle Odra [20], the proportions of the metals in these fractions are higher: Cd up to 70%, Mn up to 75% and Zn up to 80%, while the contents of Zn, Cu, Cd, Mn and Pb in the most mobile fractions depend on their total content, irrespective of the type of sample (suspended matter, bottom sediment, river bedrock).

In bottom sediments of the examined part of the river (Table 7) high correlation coefficients indicate very good correlation of Zn, Mn and Cd (to a lower degree Cu) in the most mobile fractions (I+II) with their total content, the concentrations of all metals in the reducible fraction are very well correlated with their total contents, and the concentrations of the majority of metals (except Cd and Cr) in the organic matter fraction are also well correlated with their total content. Similar correlations have been reported for the rivers in Taiwan [18], the Kangjiaxi River in China [17] and the Cauvery River in India [25].

In general, in the bottom sediments of the Odra River section we studied the proportion of the potentially reactive metals, contained in non-residual fractions, is greater than that in the residual one, ranging on average from 55% (Fe) to 97% (Ni), whereas the proportions of Cr, Ni and Zn in the bioavailable fractions can reach 100% (Table 6). Similarly, the proportions of potentially highly reactivity metals from the bottom sediments of the

Table 7. Correlation coefficients characterizing the correlation between the concentrations of different metals in particular fractions and their total concentrations ($t = 2.110$; $n = 19$)[1].

Metal	Fractions I + II		Fraction III		Fraction IV	
	R	t_R	R	t_R	R	t_R
Cd	**0.80**	5.468	**0.76**	4.814	0.06	0.244
Cr	0.44	2.023	**0.99**	25.990	0.30	1.279
Cu	**0.73**	4.398	**0.84**	6.317	**0.56**	2.790
Fe	**0.52**	2.533	**0.99**	28.737	**0.73**	4.395
Mn	**0.84**	6.280	**0.96**	14.349	**0.91**	9.318
Ni	0.30	1.315	**0.95**	12.386	**0.79**	5.388
Pb	0.39	1.721	**0.89**	7.959	**0.88**	7.471
Zn	**0.97**	15.490	**0.98**	19.484	**0.79**	5.334

[1] t - tabular critical value of t parameter (Student's distribution), t_R - calculated value of t parameter; correlation is significant, if $t_R \geq t$ [24]

Kromme Rijn River [15] are: Mn and Cd -100% each, Zn (on average up to 90%) and Cu (on average up to 85%), but they are related mainly to organic matter and theoretically expected to be less mobile. In the bottom sediments of the Guadalquiver River [14] a considerable proportions of metals were bound in the non-residual fractions, mainly in the fraction of Fe-Mn oxides (similarly as in the Odra River samples studied), although the actual values were lower. In the bottom sediments of the Latvian rivers, the metal found in the greatest proportion in the potentially reactive fractions was Cd. The bottom sediments in the Kangjiaxi River (China) are characterised by lower content of heavy metals in non-residual fractions, ranging from 60 to 88%, while the bottom sediments from the Elba River (Czech Republic) have a similar (over 70%) content of metals in the potentially reactive fractions [26].

Conclusions

In the bottom sediments of the middle Odra River, in the section from the Nysa Luzycka River estuary to the Warta River estuary, the majority of the heavy metals determined occur in the mobile species, mainly Cu, Ni, Cd, Zn and Pb. Poor buffering capacity of the bottom sediments from the Odra River [27] means that the metals can easily get into the bulk water, in particular this refers to Cd, Pb, Ni and Zn, whose significant amounts are bound to carbonates. A distressing phenomenon is the presence of Cu, Ni and Zn in the exchangeable fraction.

Apart from Cu, Pb and Cd, the heavy metals determined occur in the dominant contribution in the fraction of hydrated iron-manganese oxides. The contribution of Ni, Mn, Cr and Cu in the potentially bioavailable fractions reaches 85-97%, so the metals are not permanently immobilized in the bottom sediments.

There are some differences in the distribution of particular metals in individual fractions in the cross-section profiles. In the samples collected in the central part of the riverbed, the percent contribution of Cu in non-residual fractions, while Cr and Zn in the iron-manganese oxides fraction is more uniform than in the sediments from near banks. The bottom sediments from the central part of the riverbed have a greater content of Fe in the fraction of Fe-Mn oxides than those collected near the banks. The Mn and, to a lesser degree, Zn occurring in the sediments collected near the two banks have increased mobility thanks to their greater contribution in the exchange and carbonate fraction.

The concentrations of the metals studied in potentially reactive species are well correlated with the total concentration of these metals, the exception are Cr and Cd species bound with organic matter. From among the metals in the most mobile fractions (I + II) only the concentrations of Zn, Mn and Cd correspond well with their total content.

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