Distribution and Chemical Forms of Heavy Metals in the Flood 1997 Sediments of the Upper and Middle Odra River and its Tributaries, Poland

Verteilung und chemische Formen von Schwermetallen in den Flutsedimenten des Hochwassers 1997 der Oberen und Mittleren Oder und ihrer Nebenflüsse, Polen

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Keywords: Flood, Sediments, Heavy Metals, Mobility, Speciation

Summary: At the beginning of August 1997, 72 samples of flood sediments were taken along the Upper and Middle Odra river and its tributaries. The concentrations of Zn, Pb, Cu, Cd, Co, Ni, Cr, Mn, and Fe in the bulk samples and in the <20 µm fraction were determined by AAS method. The contents of metals vary in wide ranges and are significantly higher in the <20 µm fraction of sediments. The range concentrations vary as following: Zn 274...3 656 mg/kg, Pb 79...1 773 mg/kg, Cd 1.7...11.8 mg/kg, Cu 38...2 244 mg/kg, Cr 14...384 mg/kg, Co 4...73 mg/kg, Hg 0.2...3.9 mg/kg, Mn 214...6 972 mg/kg, and Fe 1.5...16.3 %. The highest amount of the metals was found in the Wrocław and Głogów regions. The mobile (exchangeable and carbonatic fractions) portions of metals reached up to 50 % of Zn, 40 % of Pb and Cu and 60 % of Mn.

Schlagwörter: Hochwasser, Sediment, Schwermetalle, Mobilität, Speziation

Zusammenfassung: Anfang August 1997 wurden entlang der Oberen und Mittleren Oder und ihrer Nebenflüsse 72 Proben von Hochwassersedimenten genommen. In den Gesamtproben sowie in der Korngrößenfraktion <20 µm wurden mit Hilfe der AAS die Konzentrationen von Zn, Pb, Cu, Cd, Co, Ni, Cr, Mn und Fe bestimmt. Der Metallgehalt variiert in starkem Maße und ist in der Fraktion <20 µm bedeutend höher als im Gesamtsediment. Die Gehalte schwanken wie folgt: Zn 274...3 656 mg/kg, Pb 79...1 773 mg/kg, Cd 1.7...11.8 mg/kg, Cu 38...2 244 mg/kg, Cr 14...384 mg/kg, Co 4...73 mg/kg, Hg 0.2...3.9 mg/kg, Mn 214...6 972 mg/kg und Fe 1.5...16.3 %. Der höchste Metallgehalt wurde in den Regionen Wrocław und Głogów festgestellt. Die leicht mobilisierbaren Anteile der Metalle (austauschbare und carbonatische Fraktionen) erreichten Werte bis zu 50% bei Zn, 40 % bei Pb und Cu sowie 60 % bei Mn.

1 Introduction

Heavy rains in southern part of Poland resulted in unusual increase of the water levels mainly in the Upper Odra and Vistula rivers catchment areas. Due to the rains, up to 50...60 mm/d, which occurred on 30 June – 1 July the retention of the soils has decreased significantly. After the rainy period at the beginning of July (5–9 July) the flood started.

The highest precipitation of 586 mm during this period was observed near Lysa Hora at the Odra river catchment area in Czech Republic. An area covered by those rains was about 12 000 km^2. A flood started at the Odra and Nysa Klodzka rivers area. In the centre of Klodzka Valley the flood waves from the Odra and Opawa rivers overlapped each other, resulted with unusual water level of 660 cm, and with flow of 2 010 m^3/s in Bohumin and the maximum water level reached 850 cm in Miedonia [1].

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With regard to the priority pollutants of N, TOC, Cu, Pb, Zn the load during a flood period was estimated to be approximately one third of an annual load, i.e. 1359 t, 9037 t, 23 t, 20.6 t, 168 t respectively [2].

First results of the metal contents in the Odra river flood sediments published by Helios Rybicka et al. [3] have shown wide ranges of Zn, Pb, Cu, and Cd in the bulk samples: 24...3 335 mg/kg, 22...463 mg/kg, 4...568 mg/kg and 0.2...8.9 mg/kg, respectively. According to the data obtained from the National Monitoring the range metal concentrations in the food sediments were rather low: 7.6...8.3 mg/kg of Pb, 1.6...6.3 mg/kg of Cr, 0.06...0.07 mg/kg of Hg, and 1.98...3.3 mg/kg of As [4]. Total concentration of metals in the flood sediments deposited on the meadow soils from the Odra Valley in Bytom Odrzański was found [5] as following: 116...834 mg/kg Zn, 152...184 mg/kg Cu, 143...183 mg/kg Pb, 36...50 mg/kg Ni, 39...82 mg/kg Cr, and 0.53...0.72 mg/kg Cd. Studies of the soils at Lower Silesia after the flood of 1997 carried out by Szerszeń et al. [6] have shown that the content of heavy metals in the Odra river flood deposits varies in wide ranges: 14...94 mg/kg Pb, 0.1...0.94 mg/kg Cd, 30...760 mg/kg Zn, 9...76 mg/kg Cu, 10...58 mg/kg Ni, and 9...255 mg/kg Cr.

Various metal concentrations obtained by the authors mentioned above result from different sampling and chemical digestion methods. Also the grain size effect of flood sediments should be taken into account, thus in order to ensure comparability of essential different types of sediments, the metals content should be analysed in the <20 μm size fraction of sediments [7–9].

To obtain information on the heavy metal distribution in the flood sediments at the Upper and Middle Odra river catchment area and, to assess the metal mobility effects, 72 samples of flood sediments were taken. The metal contents were measured in the <20 μm size fraction of flood sediments and compared with their concentration in the bulk samples. The results from the sequential extraction procedure were taken to assess the mobilisation of metals.

2 Sampling and Methods

Flood sediments were collected along the Odra river, soon after flood disaster (August 1997), when the sediments deposited on the ground were still wet. The 72 samples were collected along the Odra river at the distance from Olza town (close to the border with Czech Republic) to Slubice. Sampling sites were chosen at a distance of 1 m from river bed broadened by the flood. Sediment samples as a rule, were taken from the surface of the alluvial layer (part enriched in fine-grained fraction), and placed to the plastic boxes of 500 cm^3 volume. Colours of the sediments varied from light brown by red-brown to black. The black sediment samples with a strong odour, contained organic matter and hydrogen sulfide, had greasy bloom on a surface.

Separation of grain size fraction <20 μm. Before grain size fraction separation, all the samples were thoroughly homogenised, mixed with distilled water and left for 24 h. Then, each sediment sample was stirred for 5 min and sieved wet by the plastic sieve of 20 μm and was dried under UR Lamps; the percentage of the grain size fractions below 20 μm was calculated. Sampling localities and the proportions of the <20 μm size fraction are presented in Figures 1–4.

Analytical procedure. For the heavy metals extraction from both bulk and the <20 μm size fraction of flood sediments the aqua regia (modified DIN 38414 method) was used as following: to 0.5 g of each flood sample weighed to the plastic containers added subsequently 6 cm^3 HCl and 2 cm^3 HNO_3. Then the samples were aged for 3 h and put to the microwave oven. Sediment samples were treated using modified SW 3051 EPA procedure characterised by: pressure – 70 psi; ramp – 15 min; hold – 5 min; power 100 %. After the treatment procedure was completed the samples were placed to the volumetric flasks and filled to the volume 50 cm^3 with 0.01 M HNO_3. To study the metals mobilisation in the flood sediments a sequential chemical extraction method has been used [10]. Heavy metals concentration was determined using AAS method.

3 Results and Discussion

3.1 Flood Sediments Contamination

The most important statistical parameters shows Table 1. The content of the <20 μm size fraction of the Odra River flood sediments varies in a wide ranges 2.3...77 % (Table 1). In the Odra river tributaries the highest amount 73.86 % of this fine fraction was found in the Obrzyca river and the lowest 1.09 % in the Olobok river flood sediments (Fig. 1). It depends on the locality, flow rate during the flood, rapidity of the flood return wave, thus also on the sedimentation rate of the particulate matter.

Distribution of Pb, Zn, Cd, and Cu in the flood sediments along the Odra river course are presented in Figures 1–4. In the <20 μm size fraction of the Odra river sediments the concentration of Zn varies from 274 to 3 656 mg/kg, of Pb from 79 to 1 773 mg/kg, of Cd from 1.7 to 10.6 mg/kg, of Cu from 38 to 2 244 mg/kg, of Cr from 26 to 136 mg/kg, of Ni from 30 to 69, of Co from 8.2 to 41.4, of Hg from 0.2 to 3.7 mg/kg, of Mn from 556 to 5 737 mg/kg, and of Fe from 2.08 to 5.65 %.

The geometric mean values in the flood sediment bulk samples were as following: Zn 403 mg/kg, Pb 78 mg/kg, Cd 2.7 mg/kg, Cu 47 mg/kg, Cr 18.9 mg/kg, Ni 25.8 mg/kg, Co 10.1 mg/kg, Mn 465 mg/kg, and Fe 15 557 mg/kg (Table 1).

Table 1: Statistical parameters of heavy metal concentrations in flood sediments of the Odra river and its tributaries.

Statistische Parameter der Schwermetallkonzentrationen in Hochwassersedimenten der Oder und ihrer Nebenflüsse.

		Fraction <20 μm content, %	Zn	Pb	Cu	Fe	Mn	Cr	Cd	Co	Hg*	Ni
							mg/kg					
Odra river bulk samples	maximum	–	3 335	463	568	52 904	2 539	90.3	8.9	26.5	n.m.	51.8
	minimum	–	24	22	4	2 308	133	<5	<1.0	<4.8	n.m.	<5.9
	arithmetic mean	–	640	100	85	19 650	568	33.5	3.4	13.5	n.m.	29.0
	geometric mean	–	403	78	47	15 557	465	18.9	2.7	10.1	n.m.	25.8
	median	–	508	79	50	18 500	514	24.4	2.9	13.5	n.m.	28.7
	standard deviation	–	645	86	112	12 616	432	26.6	2.2	6.9	n.m.	12.3
Odra river <20 μm fraction	maximum	77.15	3 656	1 773	2 244	56 509	5 737	136	10.6	41.4	3.71	68.9
	minimum	2.31	274	79	38	20 802	556	26	1.7	8.2	0.20	30.4
	arithmetic mean	31.82	1 292	237	202	39 326	1 451	74	5.4	24.1	1.31	44.6
	geometric mean	22.43	1 096	172	112	38 429	1 124	68	5.0	22.3	0.97	43.8
	median	32.49	1 078	142	96	40 374	938	67	5.0	24.6	1.10	43.2
	standard deviation	21.72	795	307	405	7 903	1 421	29	1.9	8.8	0.96	8.7
Odra river tributaries <20 μm fraction	maximum	73.86	3 215	434	1 292	163 058	6 872	384	11.8	72.9	3.92	230.6
	minimum	1.09	108	26	18	15 952	214	14	<1.0	<4.8	0.12	19.6
	arithmetic mean	23.62	741	119	126	45 742	1 517	78	4.3	27.3	0.61	44.7
	geometric mean	17.43	595	100	79	41 710	1 205	59	3.7	23.4	0.45	40.2
	median	20.42	554	103	74	40 656	1 003	52.3	4.0	26.5	0.49	40.6
	standard deviation	16.57	569	81	198	24 531	1 308	73	2.3	13.9	0.66	31.1

* results based on researches of Prof. M. Protasowicki

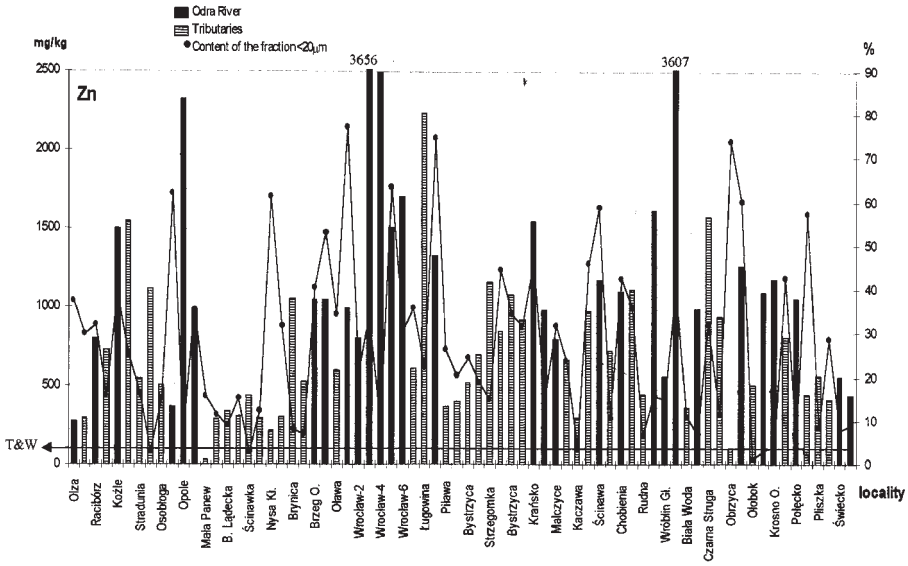

Fig. 1: Content of the <20 µm size fraction and Zn concentration in the <20 µm size fraction of flood sediments of the Odra river and its tributaries. (T&W – Turekian and Wedepohl [14] geochemical background value of Zn).

Gehalt der <20-µm-Fraktion und Zn-Konzentration in der <20-µm-Fraktion von Flutsedimenten der Oder und ihrer Nebenflüsse. (T&W – geochemischer Hintergrundwert von Zn nach Turekian und Wedepohl [14]).

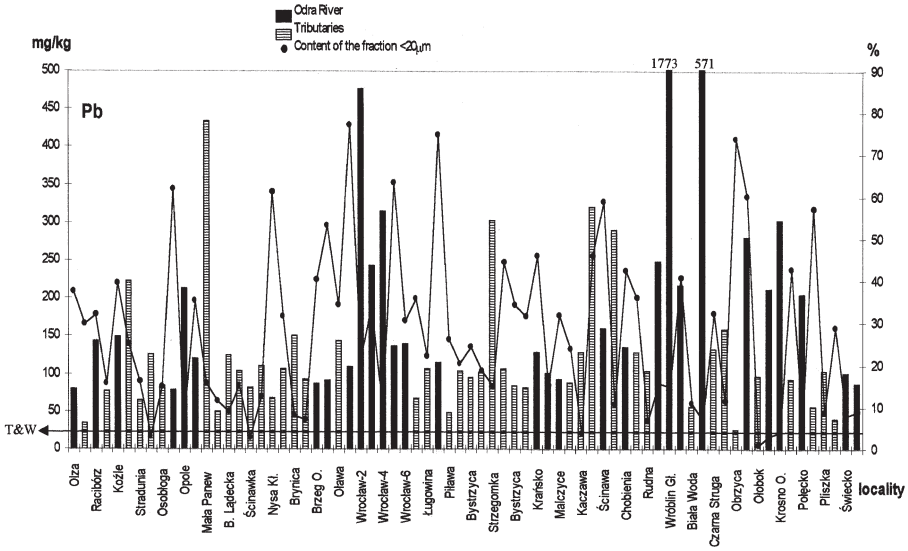

Fig. 2: Content of the <20 µm size fraction and Pb concentration in the <20 µm size fraction of flood sediments of the Odra river and its tributaries. (T&W – Turekian and Wedepohl [14] geochemical background value of Pb).

Gehalt der <20-µm-Fraktion und Pb-Konzentration in der <20-µm-Fraktion von Flutsedimenten der Oder und ihrer Nebenflüsse. (T&W – geochemischer Hintergrundwert von Pb nach Turekian und Wedepohl [14]).

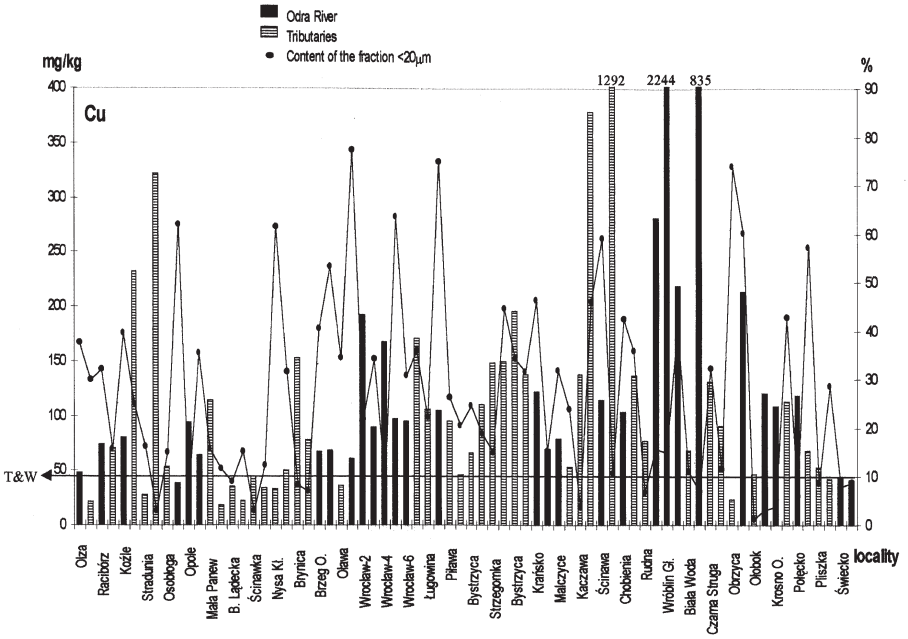

Fig. 3: Content of the <20 µm size fraction and Cu concentration in the <20 µm size fraction of flood sediments of the Odra river and its tributaries. (T&W – Turekian and Wedepohl [14] geochemical background value of Cu).

Gehalt der <20-µm-Fraktion und Cu-Konzentration in der <20-µm-Fraktion von Flutsedimenten der Oder und ihrer Nebenflüsse. (T&W – geochemischer Hintergrundwert von Cu nach Turekian und Wedepohl [14]).

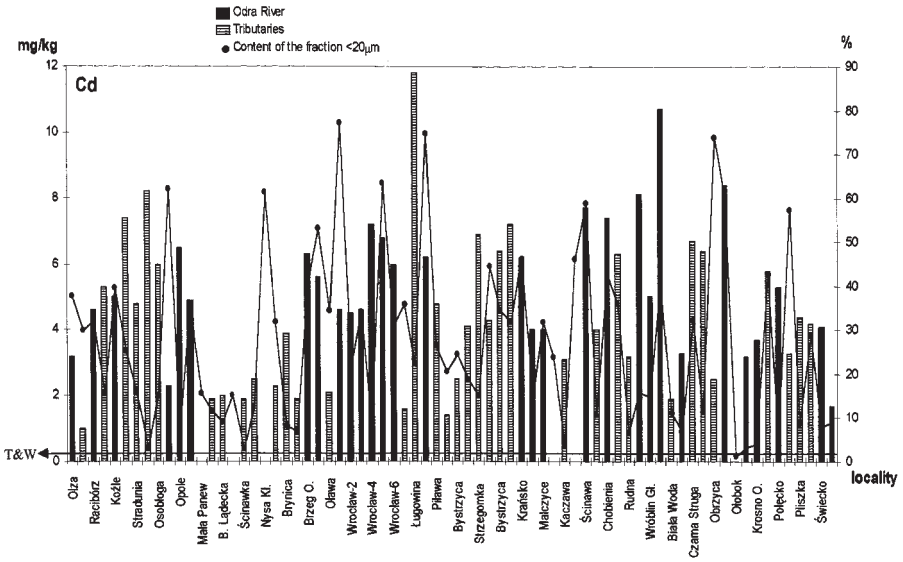

Fig. 4: Content of the <20 µm size fraction and Cd concentration in the <20 µm size fraction of flood sediments of the Odra river and its tributaries. (T&W – Turekian and Wedepohl [14] geochemical background value of Cd).

Gehalt der <20-µm-Fraktion und Cd-Konzentration in der <20-µm-Fraktion von Flutsedimenten der Oder und ihrer Nebenflüsse. (T&W – geochemischer Hintergrundwert von Cd nach Turekian und Wedepohl [14]).

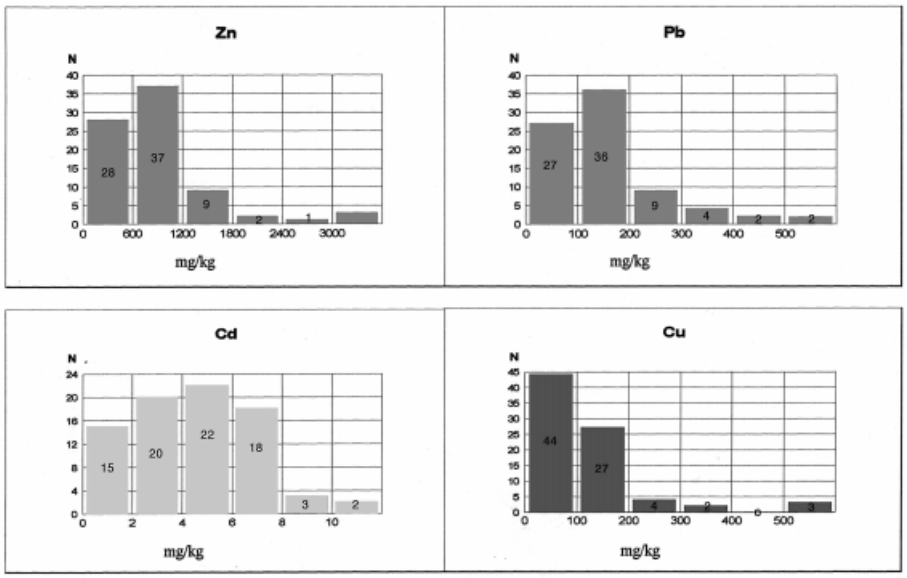

Fig. 5: Frequency distribution of Zn, Pb, Cu, and Cd of flood sediments (<20 µm size fraction) of the Odra river and its tributaries.

Häufigkeitsverteilung von Zn, Pb, Cu und Cd in den Flutsedimenten (<20-µm-Fraktion) der Oder und ihrer Nebenflüsse.

In both types of samples the highest concentration of Zn and Cd was found in the sediment sample from Bytom Odrzanski, whereas of Pb, Cu, Hg, and Fe in the sediment sample from Wróblin Glogowski; both samples are located near the Lubin-Glogów copper mining and smelting area at Lower Silesia. It seems that substantial amount of Zn and Cd can migrate to the further distances from the source than Cu, Hg, and Pb. The lowest contents of all metals were found in the sediment samples of the middle (Bedów – Slubice) and upper sections (Olza – Racibórz) of the Odra river.

The wide range of Zn, Pb, Cu, and Cd concentrations found in a survey of the <20 µm flood sediments size fraction of the Odra river and its tributaries is shown in Figure 5. The compared selected results (Fig. 6) show that the metals content in the <20 µm size fraction of the Odra river flood sediments is significantly higher than in the bulk samples [9].

Metal concentrations in the Odra river tributaries vary in very wide ranges (Table 1, Fig. 1–5). The highest amounts were found: in the Mala Panew river 3 215 mg/kg Zn and 434 mg/kg Pb, in the Zimnica river 1 292 mg/kg Cu and 384 mg/kg Cr, in the Kaczawa river 3.9 mg/kg Hg, in the Lugowina river (Wroclaw) 11.8 mg/kg Cd and 16.3 % Fe, in the Slaska Ochla river 6 872 mg/kg Mn, and in the Prudnik river 72.9 mg/kg Co.

The results of the recent studies have shown that in general, both the flood bulk sediment samples and their <20 µm grain size fraction contain lower metal concentration – the first one significantly lower – if compared with the Odra river bottom sediments (Fig. 6) examined earlier [11]. However, it should be remembered that the high water flow could result in the dilution processes. The smallest difference between metal contents in both kinds of sediments was observed for samples collected in Wroclaw, Racibórz and Opole, at the places where the flood caused the highest damages.

3.2 Mobilisation of Heavy Metals

Ecotoxicological effects can be caused by a release of the examined heavy metals from the flood sediments, since they were exposed to the oxidation processes and in some regions to the acidic leaching. Most of the Odra river bottom sedi-

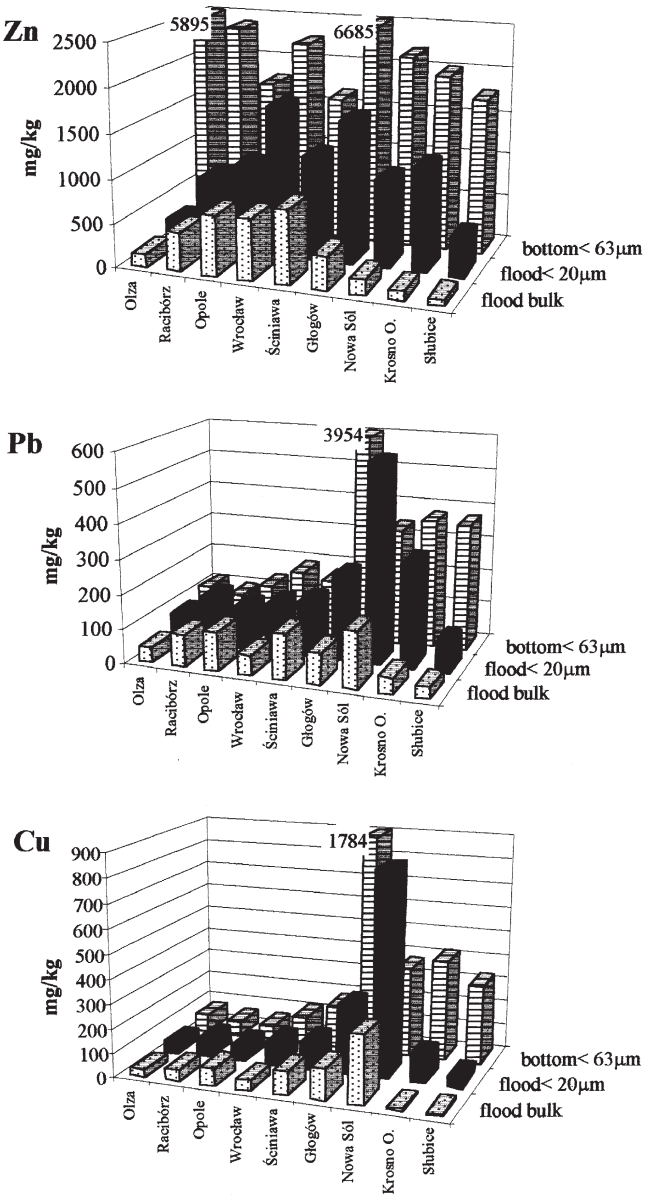

Fig. 6: Concentration of Zn, Pb and Cu in the <20 µm size fraction and bulk samples of flood sediments and in the <63 µm fraction of bottom sediments of the Odra river.

Konzentration von Zn, Pb und Cu in der <20-µm-Fraktion, den Gesamtproben der Flutsedimente und in der Fraktion <63 µm der Flußsedimente der Oder.

ments are in the anoxic conditions (average Eh –330 mV). The earlier studies [10, 12] have shown that if the anoxic sediments are exposed to air the metal speciations will move to the more mobile forms.

Because of the selectivity of reagents used in a sequential chemical extraction procedure, the results give metal distribution among main substrates of the sediments. However, when compared with the results obtained by direct methods e.g. SEM method, the sequential extraction gives a knowledge of the chemical and/or mineralogical forms of metals and thus of their relative bioavailability [13].

In the Odra river, no significant difference between binding forms of metals has been observed in the flood sediment samples taken from different sampling sites, as well as between bulk and fine fraction of the same sediment samples. Partitioning data (Fig. 7) confirmed rather a low metal mobility in the Odra river flood sediments; the mean proportion of Pb (about 1.8 %), Zn (about 4 %), and Cu (about 8 %) extracted in step I is generally low. From the examined metals higher exchangeable proportions only for Mn (11...28 %) were found. Much higher proportions of Zn (23...40 %), Pb (13...65 %), Mn (20...38 %) and Cu (up to 29 %) were extracted in step II suggesting their presence in the carbonate or others specifically adsorbed phases. Relatively high portions mainly of Cu (32...60 %), but also of Pb (up to 40 %) appear in the iron oxides fraction (step IV) and of Zn (36...50 %) in the Fe-Mn oxides fractions (steps III and IV). The organic/sulfidic fraction (step V) contains about 4...35 % of Cu, 6...16 % of Pb, 1...12 % of Zn.

From the leaching tests we have learned that the Odra river sediments contain up to 534 mg/kg SO_4^{2-}, one of the dominating oxidant for the degradation of organic matter, thus the last findings supporting the presence of metal sulfides in the flood sediments, although they have been exposed some time to the oxidation conditions.

The immobile portion (step VI) of Cu, Pb, and Zn in some flood sediment samples can reach 63 %, 61 %, and 31 % respectively, however in Figure 7 can be observed that, the lowest total heavy metal concentration the highest their portion in the residual fraction.

4 Final Remarks

Results of the present studies have shown that in general, both the flood sediment bulk samples and their <20 µm size fraction contain high metal concentrations, but lower compared with the Odra river bottom sediments examined earlier. However, it should be mentioned that the high water flow can have a diluting effect on the river system. The smallest difference between metal content in both kinds of flood sediment samples is observed for samples collected in Wrocław, Racibórz and Opole, at the places where the flood caused the highest damages.

After redeposition of the Odra river bottom sediments being in anoxic conditions, flood sediments because of the oxidation processes have released some portion of metals since they have moved to the more mobile forms [12, 13]. Our results have shown that the most mobile ion exchangeable metal portion is lower compared with the same, obtained for the bottom sediments examined earlier (Fig. 8). Thus, it seems that a part of the most bioavailable metal amount has been already released from the flood sediments.

It seems that the obtained results of the sequential extraction procedure confirmed the earlier findings. Because the flood sediments were exposed to atmospheric conditions the anoxic – sulfidic form of Cu, Zn, and Pb were still present in the flood sediments only in very low portions (Fig. 7), supporting the partly oxidation of the sulfides and moving to the more mobile forms. Thus rather high portions of metals were observed in the Mn-Fe-oxides forms.

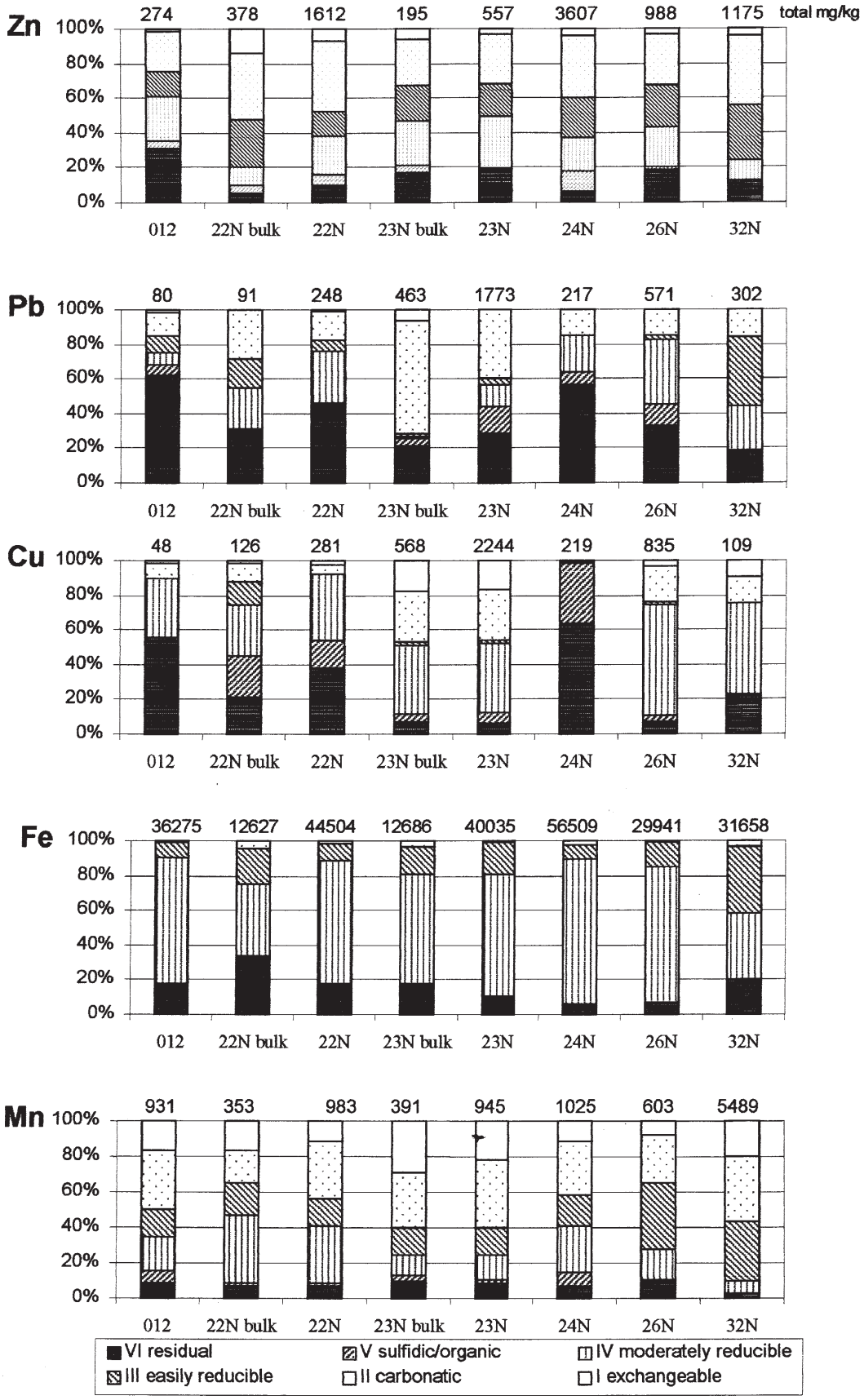

Fig. 7: Speciation of heavy metals in the <20 µm size fraction of the Odra river flood sediments.
Speziation der Schwermetalle in der <20-µm-Fraktion der Flutsedimente der Oder.

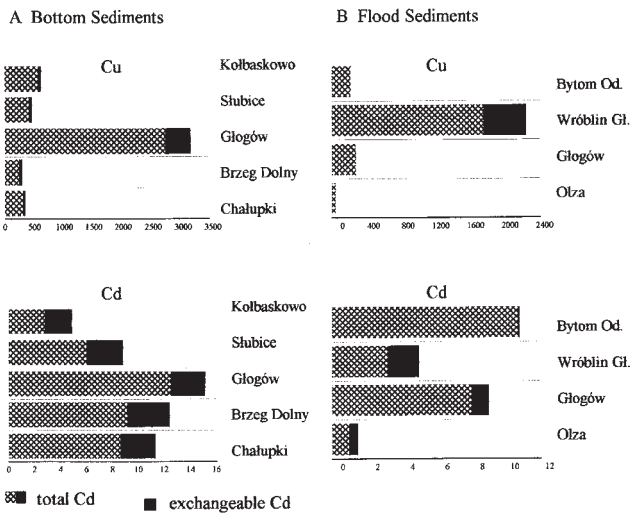

Fig. 8: Total and bioavailable concentration of Cu and Cd in the selected samples of the Odra river flood and bottom sediments. (Sample sites: 012 Olza, 22N Glogów, 23 Wróblin Glogowski, 24 Bytom Odrzanski, 26 Nowa Sól, 32N Krosno Odrzanskie).

Gesamt- und bioverfügbare Konzentrationen von Cu und Cd in ausgesuchten Proben von Flut- und Bodensedimenten der Oder. (Probenahmeorte: 012 Olza, 22N Glogów, 23 Wróblin Glogowski, 24 Bytom Odrzanski, 26 Nowa Sól, 32N Krosno Odrzanskie).

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