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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

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Abstract

The extensive investigations of total and mobile heavy metals concentrations in suspended matter (SPM) and bottom sediments of the upper and middle Odra river were carried out over the years 1997–2000. Significant levels of contamination were found. Median concentrations for Cd, Pb, Cu, Zn and As in the SPM and sediments were (mg/kg) 7.3 and 8.9, 97.2 and 119, 79.2 and 92.7, 1221 and 1158, and 52.9 and 67.9, respectively. The highest metal pollution of Odra river solids was found with cadmium, zinc, lead and arsenic. The frequency distribution of Cd, Zn, Pb and As in both type of samples, i.e. SPM and sediments, shows high similarity.

From all metals studied, 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 carbonatic fractions of Cd and Zn reached up to 50% of their total amount.

Besides the determination of total metal concentration, the "mobilisation test" of metals in river solids is recommend for monitoring purposes, allowing evaluation of the most mobile, and bioavailable metal fractions.

The results of four years of very wide studies of Odra river system suggest that for river monitoring purposes, the frequency and numbers of samples for chemical analysis of both water and solids - preferably suspended matter - could be reduced to twice a year, with few select sampling sites.

Keywords: Sediments, suspended matter, heavy metals, mobility, monitoring.

Introduction

The Odra River catchment area is 136,528 km^2 and 84.9% of it lies in Poland, 10.4% in Germany, 4.7% in the Czech Republic. The study area covered about 70% of the total Odra catchment – the upper and middle Odra river section – from Chałupki to the Nysa Klodzka river outlet. At the upper and middle Odra river catchment area, industrial – mainly coal and copper mining and processing activity, as well as agricultural, intensive crop production are the most important sources of contaminations.

The first studies of the Odra river carried out in 1989-1990 showed that the bottom sediments were contaminated mainly with Zn, Cu, Pb and Cd. The highest concentrations of all studied metals were found at the Lubin-Legnica Cu-mining and smelting region [1].

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The mean values of Zn and particularly of Pb and Cu were significantly higher if compared with results obtained within the framework of National Environmental Monitoring begining in 1990-1992 [2].

Investigations of the Odra river flood sediments (carried out immediately after the 1997 flood disaster) have shown high metal concentration, but lower compared with the Odra river bottom sediments examined earlier [3], [4]. However, high water flow caused a dilution effect of contaminations in the Odra river system. After re-deposition of the river bottom sediments being in anoxic conditions, the metals release processes appeared, since metals have been moved into more mobile forms [3], [5], [6], [7].

According to the EC Water Framework Directive the physico–chemical quality classification of a river system covers organic and inorganic contaminants as well as the main conventional measuring parameters such as nutrients, temperature, oxygen, and pH. The substance concentrations or other values, usually only in the river water, corresponding to class I are taken to characterise an anthropogenically unimpacted status. The respective most stringent of the “quality targets” for all protected assets considered is assigned to class II, and it enables the use of waters as well as protection of aquatic habitats [8].

Concerning the heavy metals situation, the quality of a river system should be described as follows:

(1) to determine the metal concentrations in the river water (see Part IV in this issue), suspended matter and sediments,

(2) to define a buffer capacity of river sediments, and acidic mobility of the metals,

(3) to estimate mobile, bioavailably portion of metals in the river solids.

In order to clarify the distribution of heavy metals and the extent of contamination in the river system, this higher sampling density and frequency follow-up investigation were carried out. The objectives of the study were:

(1) to establish the spatial variability in concentrations of heavy metals (Cd, Zn, Pb, Cu, Ni, Cr, Mn, Fe and As) for suspended matter and bottom sediments in the upper and middle Odra river system.

(2) To assess the level and extent of contamination by comparison with the river solids classification or geochemical background standards, and to identify any need for monitoring and/or remediation.

(3) To estimate the mobility and potential bioavailability of metals in the river suspended matter and sediments.

(4) To define kind and measuring frequency of the parameters for improvement of river chemical monitoring.

Sampling and Methods

In the years 1997-2001 intensive investigations of soluble and particulate metals in the Odra river system were carried out within the framework of the International Odra Project. Totally about 100 samples were collected from both, suspended matter and bottom sediments, from the upper and middle Odra river (516 km), in five sampling campaigns: November ’97, May ’98, November ’98, June ‘99 and May 2000.

The Odra river suspended matter samples have been separated from river water on the membrane filters with pores of 0.45 μm diameter, and its concentration was established. From the bottom sediment samples, the < 20 μm grain size fraction was wet separated, and its concentration calculated. The obtained samples underwent an analytical procedure described earlier [3], [9].

In order to assess the mobility and potential bioavailability of the metals in the suspended matter and sediment samples, the exchangeable and carbonatic bound metal fraction was estimated, using chemical extraction method proposed by Kersten and Förstner [10]. Additionally, the buffer capacity of selected sediment bulk samples, and acidic metal leachibility were studied by applying a procedure used earlier [11]. Metal concentrations were determined using ICP-MS and/or AAS methods.

Data Quality Control

Analyses were subject to a sampling and analytical quality program to describe random errors by Robust Analysis of Variance, with ROB2 program application [12]. During the sampling campaign in May 2000, the filed duplicates of 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.

In a case of suspended matter, results of Cd, Ni, Cr, Cu measurements indicates 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. For Mn and Zn analytical variance is 7% and 9%, respectively. The analytical variance accounted for As and Fe is not satisfying enough. Sampling variances for all samples in both cases for suspended matter and sediments are satisfying and do not exceed 16% of total variances. In a case of sediments analytical precision 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 satisfying enough.

In order to estimate accuracy and bias of the analytical method, reagent blanks and certified reference materials (Lake Sediment LSKD-4, River Sediment 1645, Sediment CRM 7002) were used to assure criteria related to quality of the analytical results. Unambiguous and unbiased use of the ICP-MS technique was confirmed in cases of suspended matter by TXRF, and for sediments with AAS measurements.

Heavy Metal Situation in the Odra River Solids

About 100 samples each of suspended matter (SPM) and bottom sediments in the upper and middle Odra river were collected in five sampling campaigns: November ’97, May ’98, November ’98, June ‘99, and May 2000. Table 1 shows the statistical parameters of metal contents obtained for all of the SPM and sediment samples, SPM concentration, and content of the < 20 μm sediment size fraction.

For comparison of the metal levels of the Odra River sediments with metal content from other flooded regions selected data are shown in Table 2.

The impact of the '97 flood on the Odra River catchment area has been significant; metal contents in flood sediments from Lower Silesia were much higher than in the Tisza River sediments (Table 2). Our results have shown the metals enrichment in the Odra River bottom sediments studied after the flood (see Table 1). This could be as the result of different analitycal procedure applied, e.g. sediment grain size fraction, methods of metal extraction.

Suspended Particulate Matter

SPM concentrations vary; the lowest of 1 mg/dm^3 and the highest of 116 mg/dm^3 were found in the samples from Opole taken in May '98 and November '98, respectively. The concentration of studied metals in the all SPM samples, varied in wide ranges (mg/kg): 8.0 - 302 of As, 1.8 – 39.8 of Cd, 42.4 - 351 of Cr, 6.2 - 493 of Cu, 22.1 - 1287 of Ni, 24.4 - 401 of Pb, 351- 31369 of Zn, 1152 - 11010 of Mn, and 2.08 - 12.13% of Fe (Tab. 1). In the SPM samples taken in November '97, the concentration of Cd, Cr, Cu and Pb was higher (mean values - 18.41, 175, 173, 185, respectively) than in the samples from later sampling periods. The highest concentrations of Ni (1287), Zn (31369) and As (302) were stated in the samples from May '98 [13].

Bottom Sediments

The amount of sediment grain size fraction < 20 μm ranged from 2.2 to 63.8 %. The mean values among

Table 1. Statistical parameters of heavy metals concentrations in the suspended particulate matter (SPM) and bottom sediments of the upper and middle Odra river; SPM concentrations and content of the <20 μm sediment fraction.

		As	Cd	Cr	Cu	Ni	Pb	Zn	Mn	Fe
		mg/kg								
SPM n= 101	SPM Conc. mg/l									
min	1.2	8	1.8	42.4	6.2	22.1	24.4	351	1152	20806
max	116	302	39.8	351	493	1287	401	31369	11010	121316
arithm.mean	28.9	63.8	9.3	131	98.4	133	110	1867	4168	50679
geom.mean	23	50.5	8	120	77.9	88.9	98	1321	3637	47929
median	26.5	52.9	7.3	125	79.2	81.6	97.2	1221	4051	48822
SD	18.9	47.4	6.2	57.4	76.3	165	55.9	3430	2060	17309
Sediments n= 90	fr.<20 μm %									
min	2.2	5	3	19.3	31.3	37	19.2	333	546	13872
max	63.8	516	21.7	208	298	108	343	2591	7022	79464
arithm.mean	28.6	92.1	9.4	72.9	110	51.6	123	1158	2670	41103
geom.mean	24	52.2	8.9	61	97.9	50.8	114	1098	2038	39958
median	28.4	67.9	8.9	69.6	92.7	49.9	119	1158	1938	41154
SD	14.3	113	2.98	42.4	55.1	10	49.6	359	1895	9205

Table 2. Total metal concentration in sediments from the flood areas (mg/kg).

Type and origination of sediments	Cd	Cu	Zn	Pb
	mg/kg			
Tisza River - reference grab sample[1]	0.22	25	79	32
Tisza River - Kötelek grab sample[1]	2.18	88	281	44
Flood sediments from Wrocław[2]	0.14-9.31	6-102	23-16232	9-953
Flood sediments from Lower Silesia after flood'97[3]	0.1-1.1	7-76	30-760	14-94

[1]after Black M.C et al., [25], [2]after WIOS [26], [3]after Szerszeń et al., [27].

sampling periods, 11’97, 05’98, 11’98, 06’99 and 05’00, varied as follows: 30.5, 28.2, 39.9, 23.8, 20.9, respectively.

In the Odra river (< 20 μm) sediment samples the mean metal concentrations were as high as (mg/kg): 92.1 of As, 9.4 of Cd, 72.9 of Cr, 110 of Cu, 51.6 of Ni, 123 of Pb, 1158 of Zn, 2670 of Mn and 4.11 % of Fe (Tab. 1). In the samples from May 2000 the highest concentration – 21.7 mg/kg of Cd and 190 mg/kg of As was found. Generally the sediment samples taken in the spring exhibited the highest contamination degree.

Quality Assessment of the Odra River Suspended Matter and Sediments

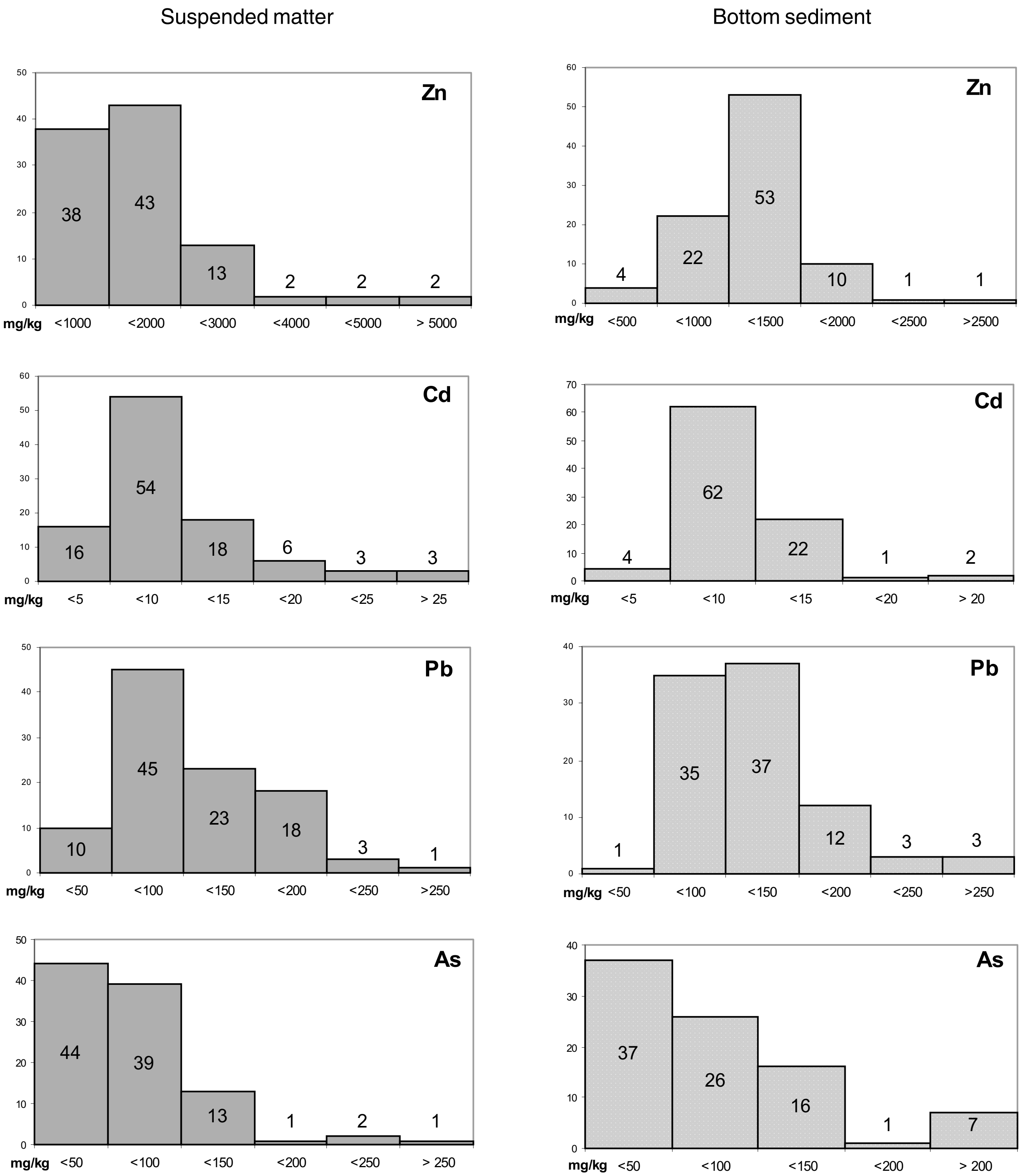
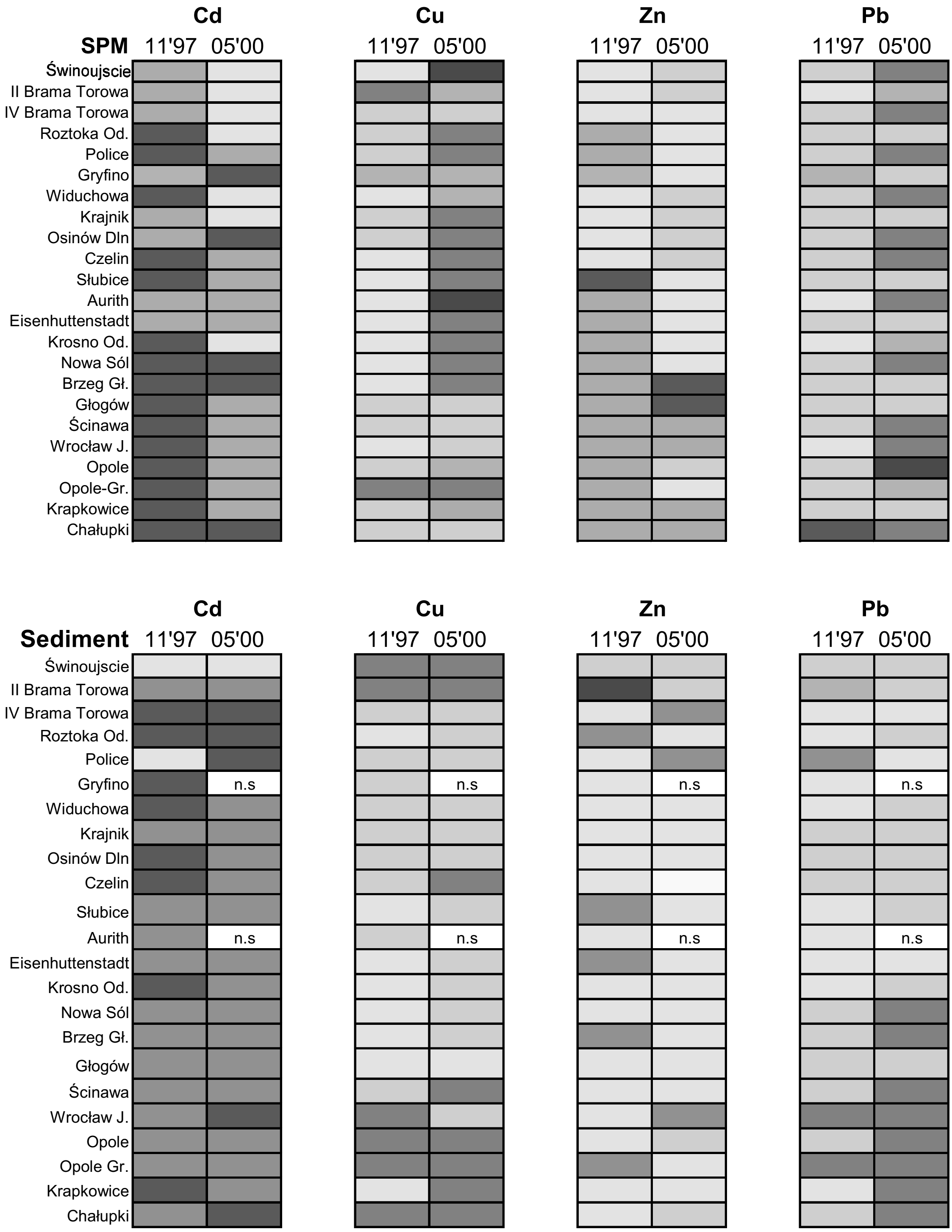


Fig. 1. Frequency distribution of Zn, Cd, Pb and As occurring in suspended matter and sediments samples of the upper and middle Odra River.



LAWA classes

	[mg/kg]	Cu	Cd	Zn	Pb
IV	Very strongly contaminated	640	9,6	3200	800
III-IV	Strongly to very strongly contaminated	320-640	4,8-9,6	1600-3200	400-800
III	Strongly contaminated	160-320	2,4-4,8	800-1600	200-400
II-III	Moderately to strongly contaminated	80-160	2,4-1,2	400-800	100-200
II	Moderately contaminated	40-80	1,2-0,6	200-400	50-100
I-II	Unpolluted to moderately contaminated	20-40	0,6-0,3	100-200	25-50
I	Uncontaminated	<20	<0,3	<100	<25

Fig. 2. The heavy metals situation in the Odra River suspended matter and bottom sediments from November 1997 and May 2000, expressed in LAWA classes.

The wide concentration ranges of selected metals found in the sediment and SPM samples for the five sampling surveys are shown in Figure 1. The frequency distribution of Cd, Zn, Pb and As in both type of samples, i.e. SPM and sediments, shows high similarity.

The results of metal concentrations determined in the suspended matter and in the fine grained (pelitic) fraction of the sediments (< 20 µm) derived from suspended load could be expressed either in terms of LAWA classification [14], or according to the I_{geo} classes [15].

Figure 2 shows the LAWA classifying metals contamination of the SPM and sediments in the upper and middle Odra river, for the two sampling campaigns. The obtained results showed that the strong to very strong contamination (classes III/IV and IV) of the suspended matter and sediments with Cd was typical for almost all samples along the Odra river over two sampling periods. Only sporadically was class III stated, thus slight improvement of Cd contamination 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 '97. However, after three years the situation has improved and in 2000, class II (moderate contamination with Cu, Zn, and in the upper river section with Pb) was dominated [16].

The mean contents of Ni and Cr for the SPM are about two times higher, but for the sediments very similar, if compared with their background values. While the contents of As in less than 20% of studied sediment and SPM samples, were higher than the tentative threshold value (TTV) of 100 mg/kg for stream sediments, proposed by Aston and Thornton [17], the mean concentration neither in the SPM (63.8 mg/kg) nor in sediment samples (92 mg/kg) were higher than TTV value.

Results of metal contents determined in the grain size fraction < 20 µm of the Odra river sediments were also used for the calculations of the I_{geo} – the Index of geoaccumulation, the classification proposed by Müller [15]. The background concentrations (mg/kg) of the heavy metals considered in this study (determined by Turekian and Wedephol [18]) were: 95 Zn, 20 Pb, 45 Cu, 0.3 Cd, 90 Cr, 68 Ni, 850 Mn.

Figure 3 presents the heavy metal situation in the upper

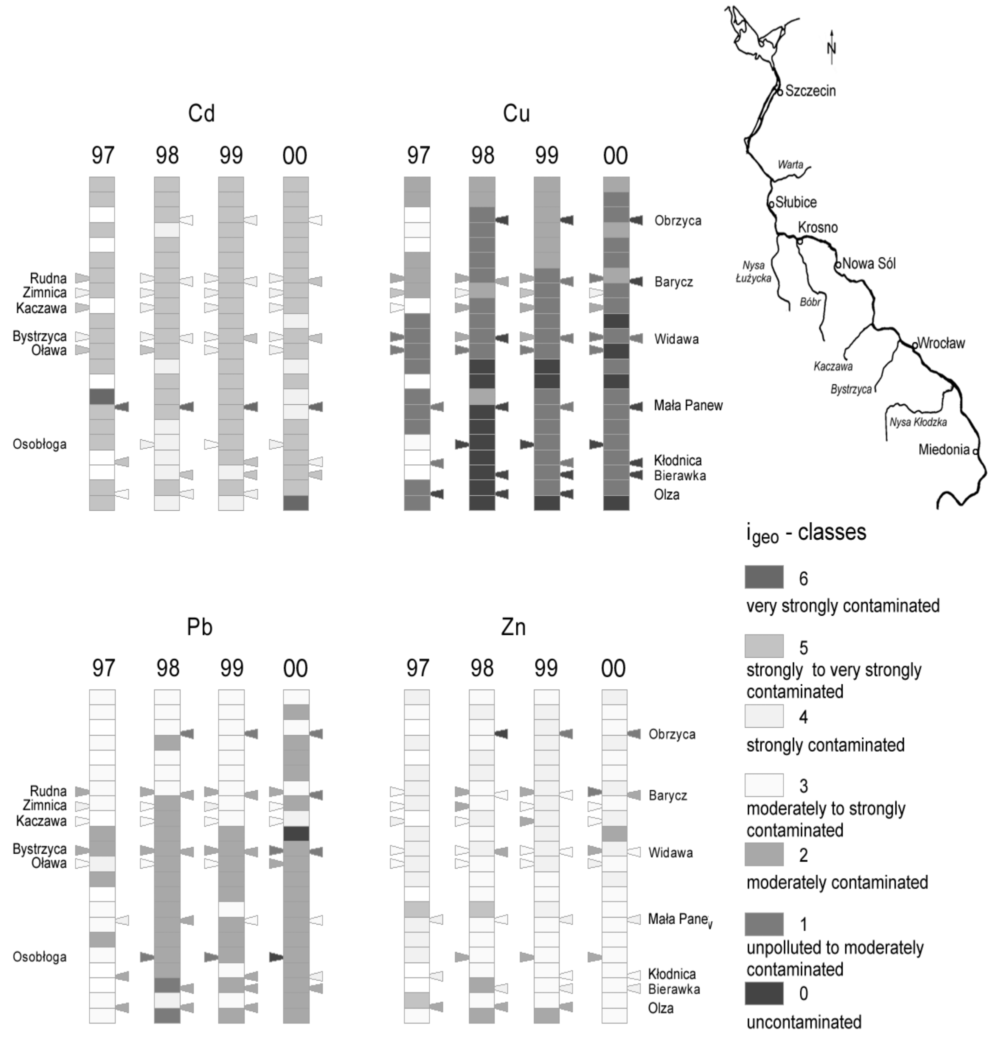


Fig. 3. The heavy metals situation in the Odra River bottom sediments for four sampling campaigns from years 1997 - 2000, expressed in I geo classes.

and middle Odra river sediments for Cd, Cu, Pb and Zn, respectively, expressed in I_{geo} classes, for the four sampling campaigns carried out over three years. As expected, the highest contamination was found with cadmium. The distribution of Cd contamination over the time period of four years shows a similar pattern; class 5 dominated and sporadically class 4 appeared, i.e. the sediments were strongly to very strongly contaminated.

Concerning other metals, Odra river sediments are unpolluted to moderately contaminated with Cu (dominate class 1), moderately to strongly contaminated with Pb (classes 2 and 3), and strongly to very strongly polluted with Zn (classes 3 and 4).

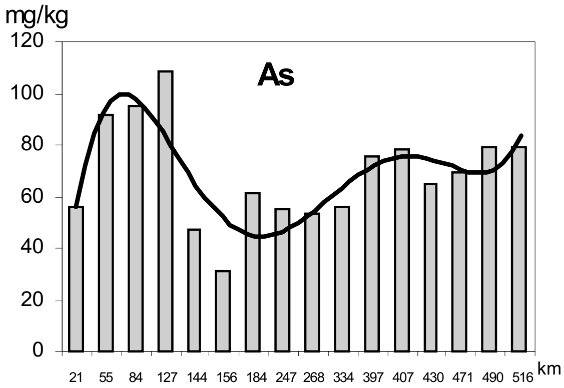
It is unquestionable that the heavy metal situation in the sediments of the Odra river system between 1998 and 2000 has improved considerably, especially for Pb and Cu. For all metals studied in the Odra river suspended matter and sediment samples, substantial reduction by Cd contamination, neither at the period after the '97 flood (Fig. 2 and 3) nor if compared with earlier results for sediments from'97, has been observed [4].

The pattern of spatial variation of the metals in the river solids indicates that a variety of sources might be responsible for the contamination. Intensive past and current mining and smelting activities are probably the most significant.

Results and Discussion - Recommendations for Transboundary River Monitoring

Analysis of The results Obtained

From the obtained results no considerable differences of heavy metal contents were observed among the samples for the same river compartment from the same locality within the five sampling periods. Thus, selection of both river compartment and sampling strategy after its optimisation will be proposed (see frame).



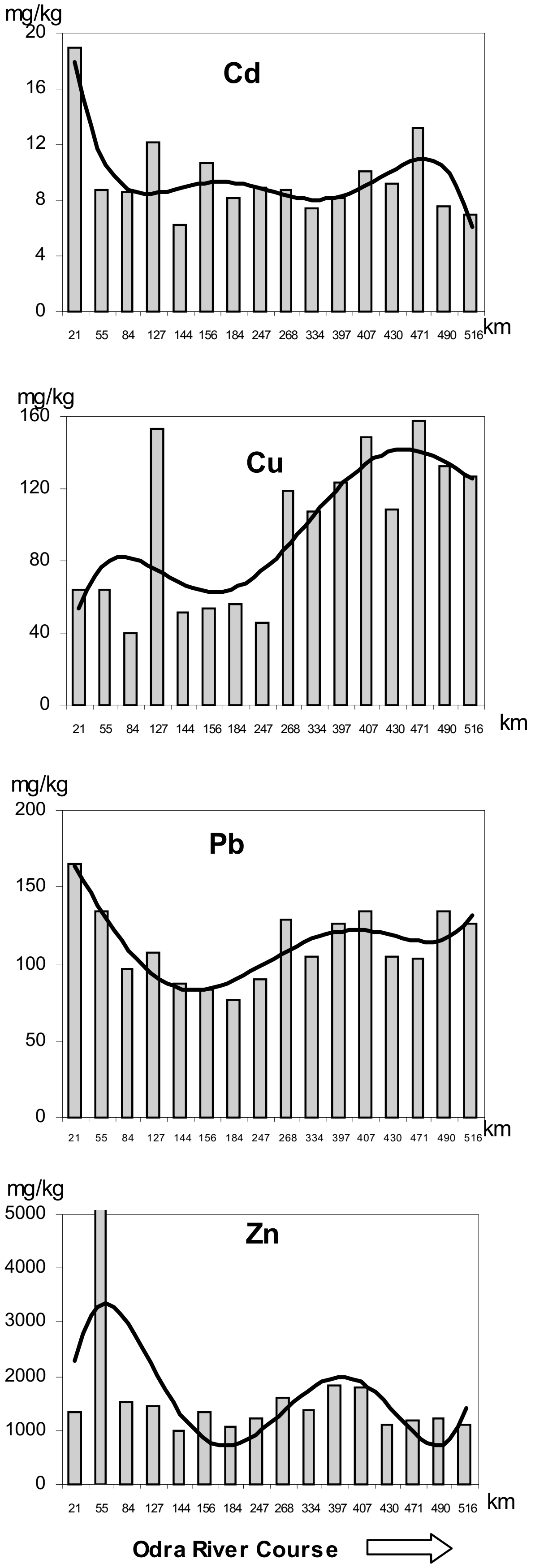


Fig. 4. Distribution of As, Cd, Pb, Cu and Zn (arithmetical mean values of metal concentration in the suspended matter samples from five sampling campaigns) with their "trend" lines along the upper and middle Odra river course.

Optimisation Procedure of the Results:

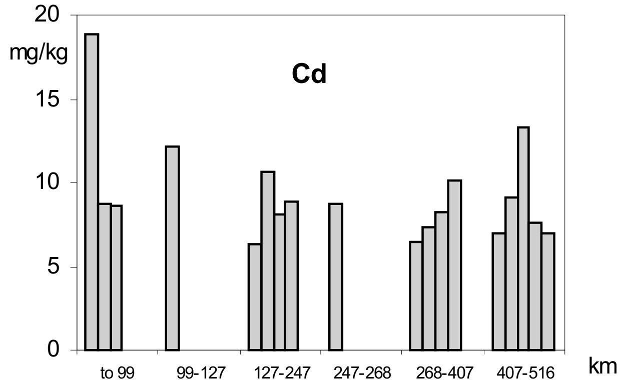
1. Demonstration of the metal “trend” lines for every sampling campaign on the basis of each metal distribution in the solids samples, over the five sampling campaigns.
2. Calculation of metal arithmetical mean values from five sampling campaigns.
3. Selection of the sample groups, based on the results of arithmetical means for each metal, from five sampling campaigns.
4. Calculation of metal arithmetical mean values from selected sample sets in the particular groups, which allow only one sampling point for each of the selected Odra river sections (six sampling points at most).

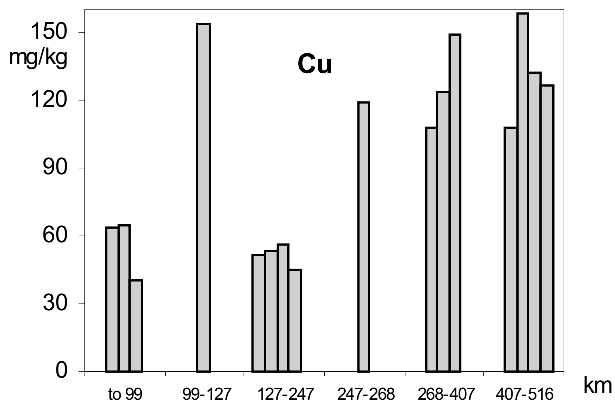
Selection of the River Compartment for Monitoring Purposes

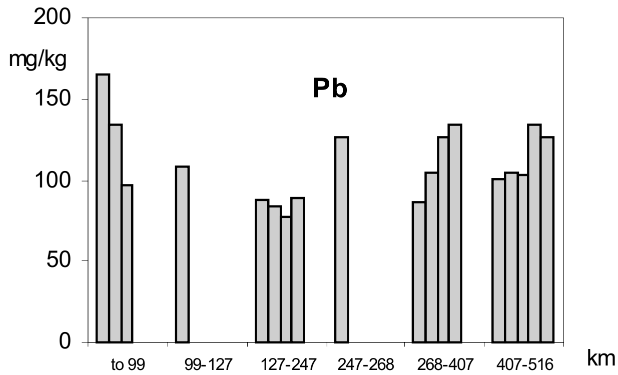
Metals concentrations in Odra water were relatively low and allowed it to be classified as class I. Generally, metal concentrations in water are lower than the limited value for drinking water in Poland. In spite of the metal level in the river water (see part IV in this issue), very limited site numbers for water monitoring should be selected, and the samples investigated no more often than twice a year (spring and autumn).

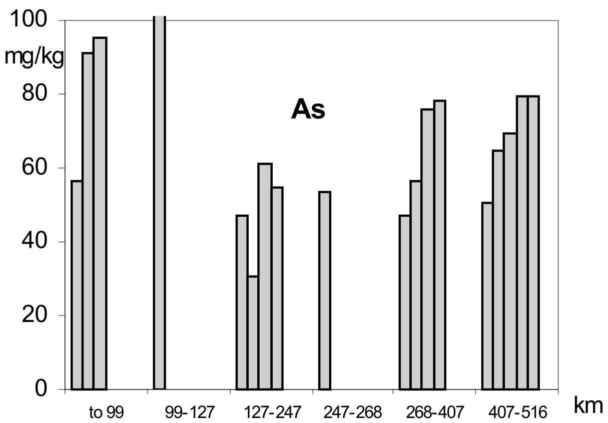
Interesting results were obtained for suspended matter. Figure 4 shows the “trend” lines of As, Cd, Pb, Cu and Zn distribution based on the arithmetical mean values of each metal in SPM from five sampling campaigns.

On the base of the above demonstrated metals “trend” lines, the samples were grouped, using the results of arithmetical mean values of metals from five sampling campaigns. The results are shown in Fig. 5 (each bar corresponds with arithmetical mean value of metals from five sampling campaigns). Calculation of metal arithmetical mean values from selected sample sets in particular









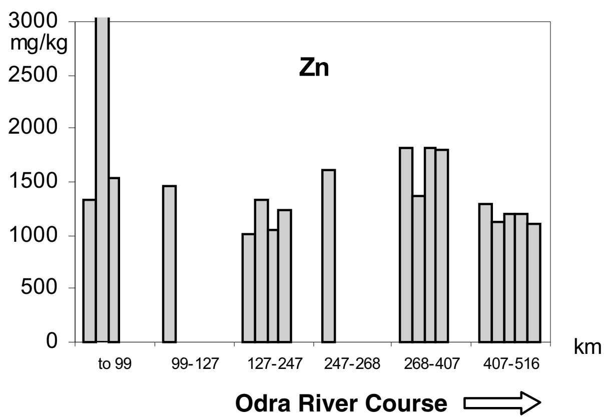


Fig. 5. Mean concentrations of As, Cd, Pb, Cu and Zn for suspended matter samples grouped in six sets along the upper and middle Odra river course (each bar corresponds with arithmetical mean value of metals from five sampling campaigns).

groups allowed proposing only one sampling point for each of the six selected Odra river sections (Fig. 6).

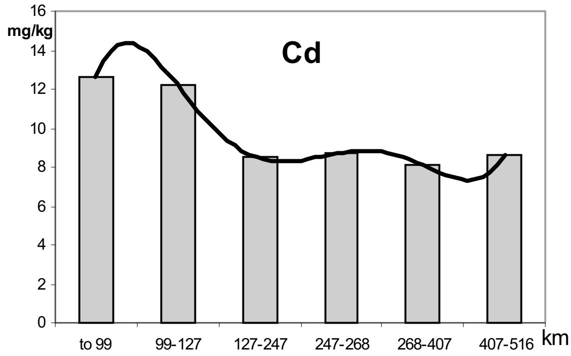
Concerning sediment quality of the Odra river, concentrations of Zn, Pb and in particular of Cd were high. For individual metals, no substantial differences among sediment sampling sites over the five sampling campaigns were observed. The metal distribution "trend" lines for the sediments from five samplings are similar (Fig. 7). Because of the more complicated (if compared with SPM) sampling and analytical procedures used for the bottom sediment investigations, we will not recommend for monitoring purposes to study the heavy metal contents in river sediments.

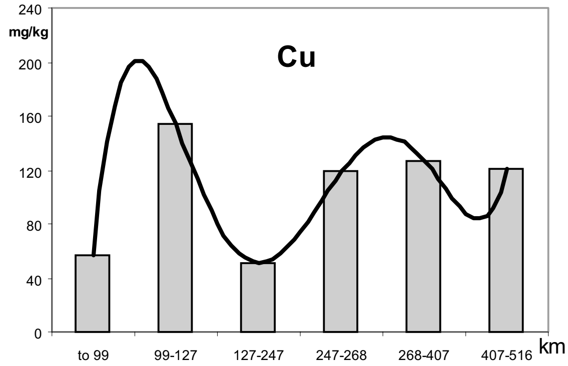
Metals mobility in the Odra River Solids

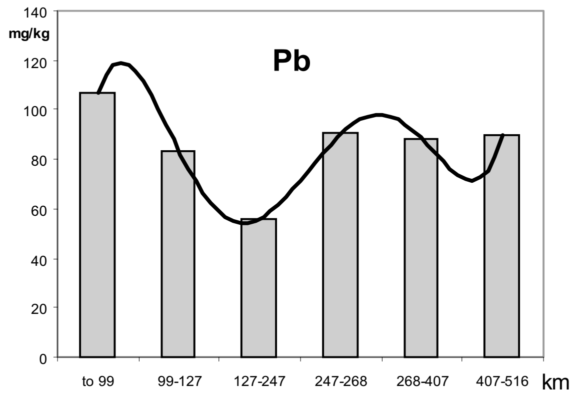
With respect to metal mobility, pH is the dominant factor. Generally the lowering of pH by one unit increases metal solubility by a factor of 10 [19, 20, 11].

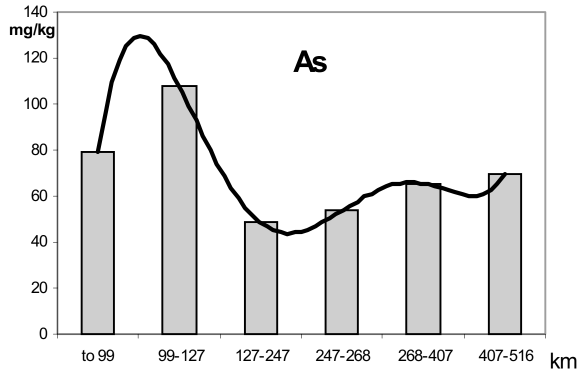
The study carried out earlier has shown that the Odra river sediments exhibit intermediate and poor buffering capacity [7], [11], [21]. Metals released into solution at increasing acidity of sediment suspension depend on their composition, thus on buffer capacity, and on the type of metal and its total amount. Figure 8 shows how the mobile portions of Cd, Cu, Zn and Pb increase with decreasing pH

Odra km	Mean concentration mg/kg				
	As	Cd	Pb	Cu	Zn
up to 99	79	13	106	57	2825
99-127	108	12	83	154	1462
127-247	48	8	56	52	1155
247-268	54	9	90	119	1609
268-407	65	8	88	127	1696
407-516	69	9	90	121	1182









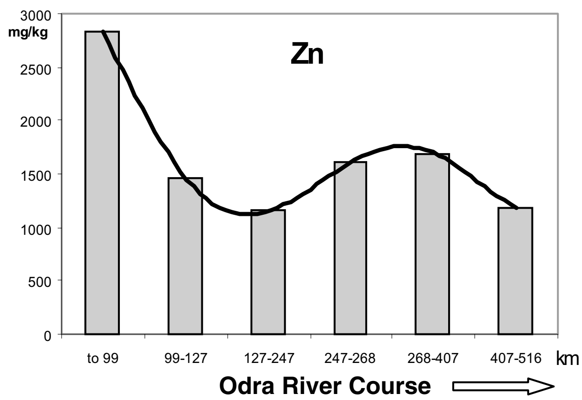


Fig. 6. Mean concentrations of As, Cd, Pb, Cu and Zn for suspended matter samples for each of the six sample groups in the upper and middle Odra river course.

of the sediment suspensions. For Zn and Cd, there seemed to be a threshold pH value of about 4 below, which was a significant increase (up to 50% in their mobilisation portion). At pH 4, Cu and Pb show very low mobilisation; about 20% of Cu and Pb were mobilised at pH 3 and 2, respectively.

To estimate the mobility and potential bioavailability of metals in the river solids, the exchangeable (pH 7) and

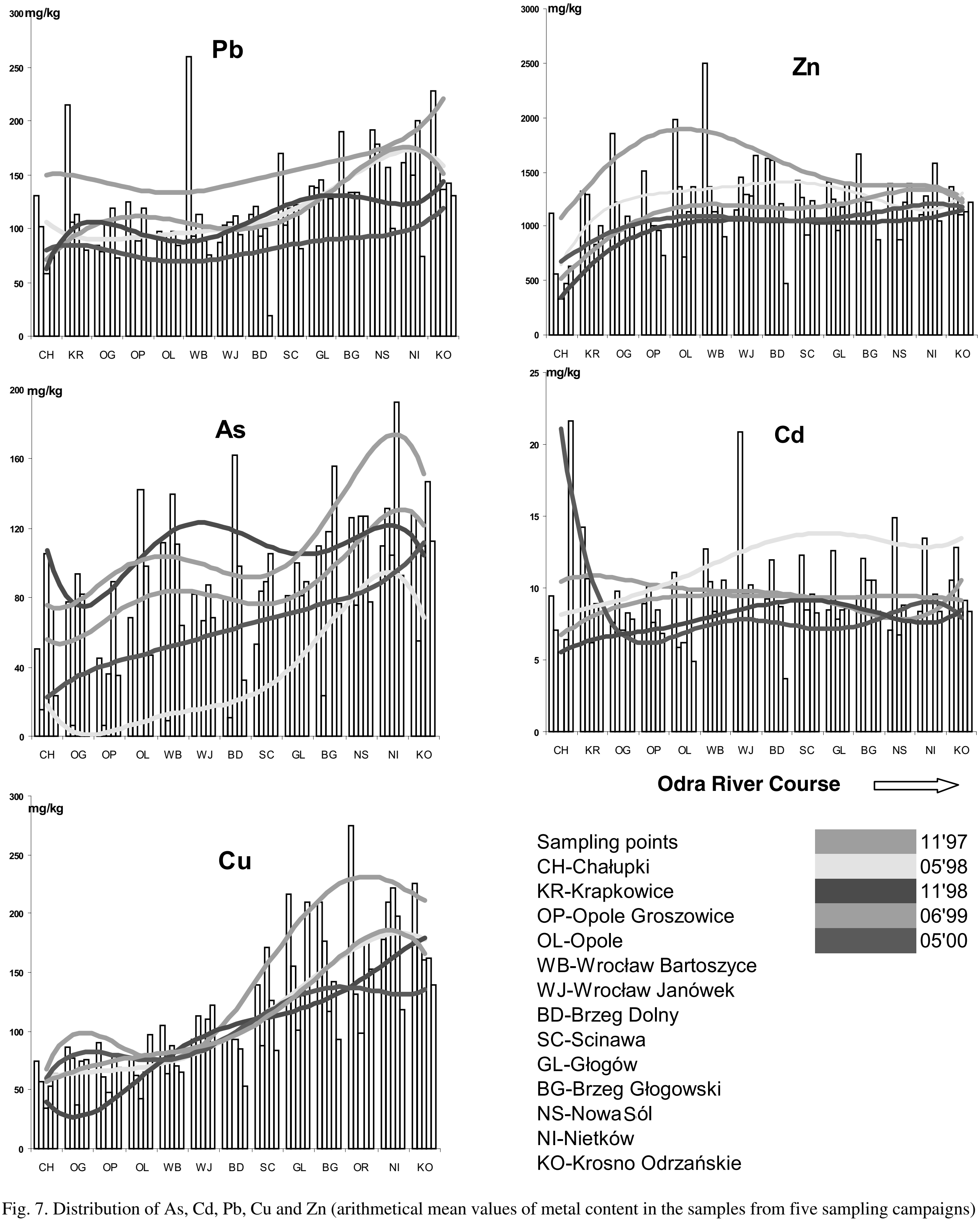


Fig. 7. Distribution of As, Cd, Pb, Cu and Zn (arithmetical mean values of metal content in the samples from five sampling campaigns) with their “trend” lines for the bottom sediment, along the upper and middle Odra river.

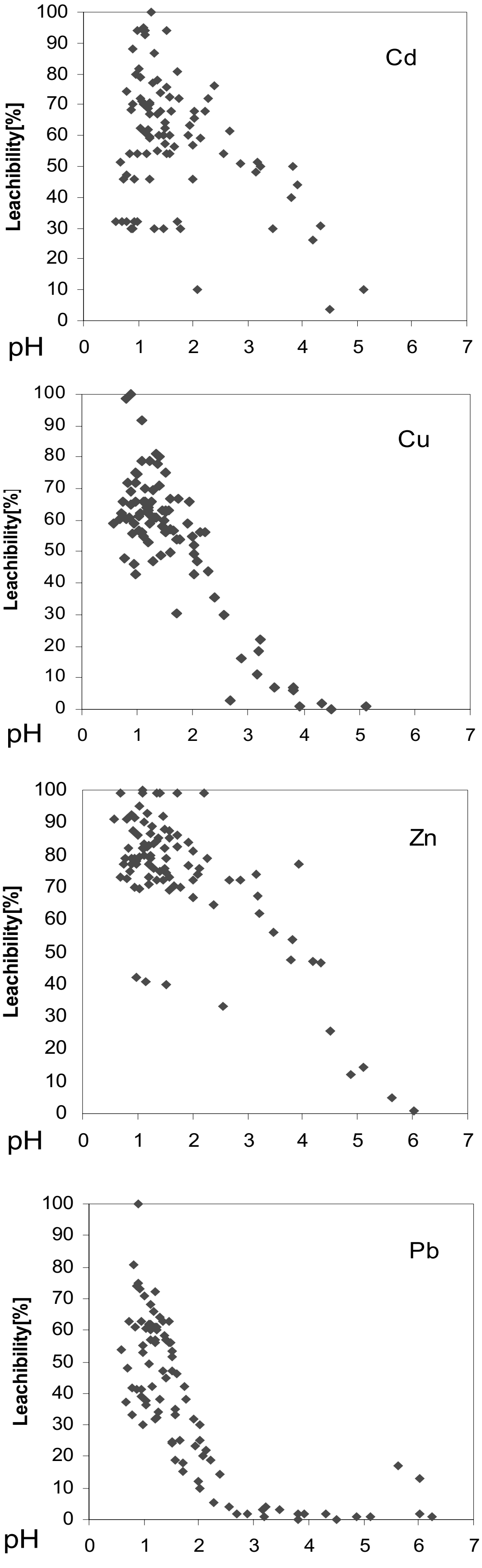


Fig. 8. Variation of acidic metal leachibility from river sediments with their suspension pH showing relatively low mobility of Pb and Cu above pH 4.

bound with carbonates (pH 5) metals, for the selected samples of river SPM and sediments, were estimated using sequential solubilization of metals as fraction procedure [10, 22, 23]. Following the discussion on speciation analysis and/or fractionation of elements carried out by Tempelton et al, [24]. These two extraction steps allowed us to evaluate a role of very important subtracts i.e., clay minerals and carbonates in the accumulation procedure of trace metals in the river system.

Figure 9 shows the sum of exchangeable and bound with carbonates portion of Cd, Zn, Pb Cu and As, in the selected suspended matter and bottom sediment samples. The highest mobile portions were stated for Mn, Cd, Zn and As in sediment but especially in suspended matter samples, up to about 75, 70, 80 and 50%, respectively. Generally the mobile amount of Zn, Cu, Cd, Mn and Pb depends on their total amount in the solids (Fig. 10), regardless of the sample nature (suspended matter, bottom sediment, river bed-rock).

From both experiments, which were carried out determining the mobile metal amount in the river solids, the last one (extraction of the exchangeable metals and bound with carbonates) seems to be more suitable for monitoring purposes. If so, the two extraction steps can be replaced with one, using buffering solution (Na-acetat + acetic acid) at pH 4. This test is relatively simple, definite, and allows omission of significant differences between strong and poor buffer capacity of sediments, and thus their very variable metal release (which arises if acidic leaching is used).

Conclusions

1. The detected levels of metal contamination, mainly Zn, Cu, Pb and Cd, in most suspended matter and sediment samples of the Odra river were found to exceed the geochemical background or threshold values. The highest metal pollution of the Odra river system was found with cadmium, zinc, lead and arsenic. The results showed that the dilution, re–suspension, and re–deposition processes of the extremely high Odra river water events in July 1997 caused an additional increase of metal concentrations in the suspended matter and bottom sediments immediately after flood.

2. Metals variability in the Odra river sediments was less significant if compared with suspended matter, thus the last component will be recommended for chemical monitoring. Additional arguments for selection of suspended matter are: easy sampling procedure, better homogenity of the material, less time for sample preparation and chemical digestion, and simpler matrix composition for the ICP–MS method.

3. From all elements studied, cadmium, zinc and arsenic appear to be of particular concern because of the high level that appears to be bioavailable and their high mobility. However, taking into account applied metal mobility procedures, (*) buffer capacity of sediments – acidic metal leaching, and (**) extraction of exchangeable and carbonatic bound metals from river solids, the more

favourable seems to be the last one, replaced with one extraction step.

4. The results further show that in the contaminated sediments the great preponderance of heavy metals is held in form, where it is mainly associated as ion exchangeable and with carbonates, i.e. in more mobile forms. In suspended matter carbonates play an important role in the accumulation processes of metals.

5. Besides the determination of total metal concentration, this well defined "mobilisation test" of metals in river solids, is recommend for monitoring purposes, allowing to evaluate the most mobile portion of metals, which can be

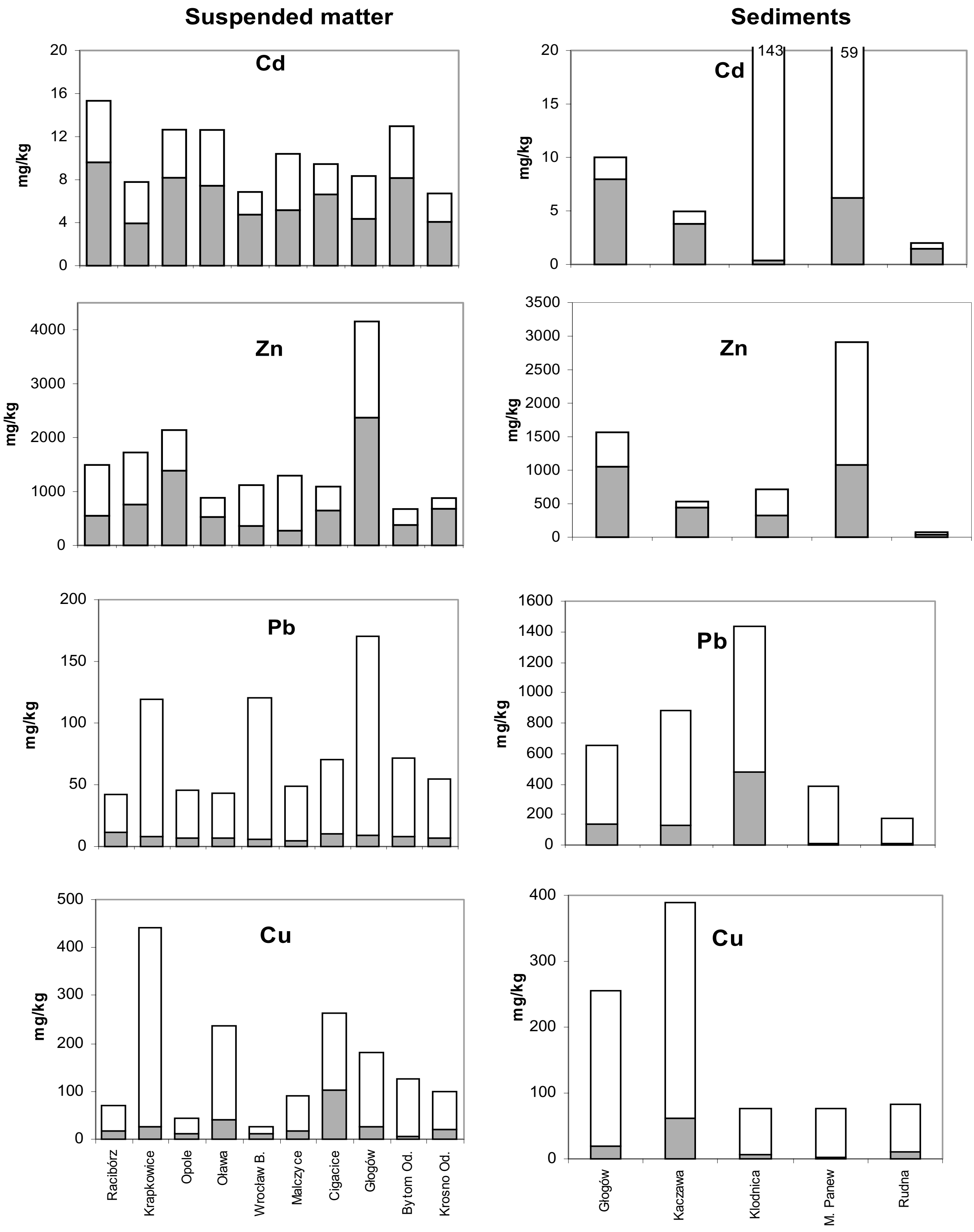


Fig. 9. Total and mobile content of metals in the selected suspended matter and sediment samples of the Odra river.

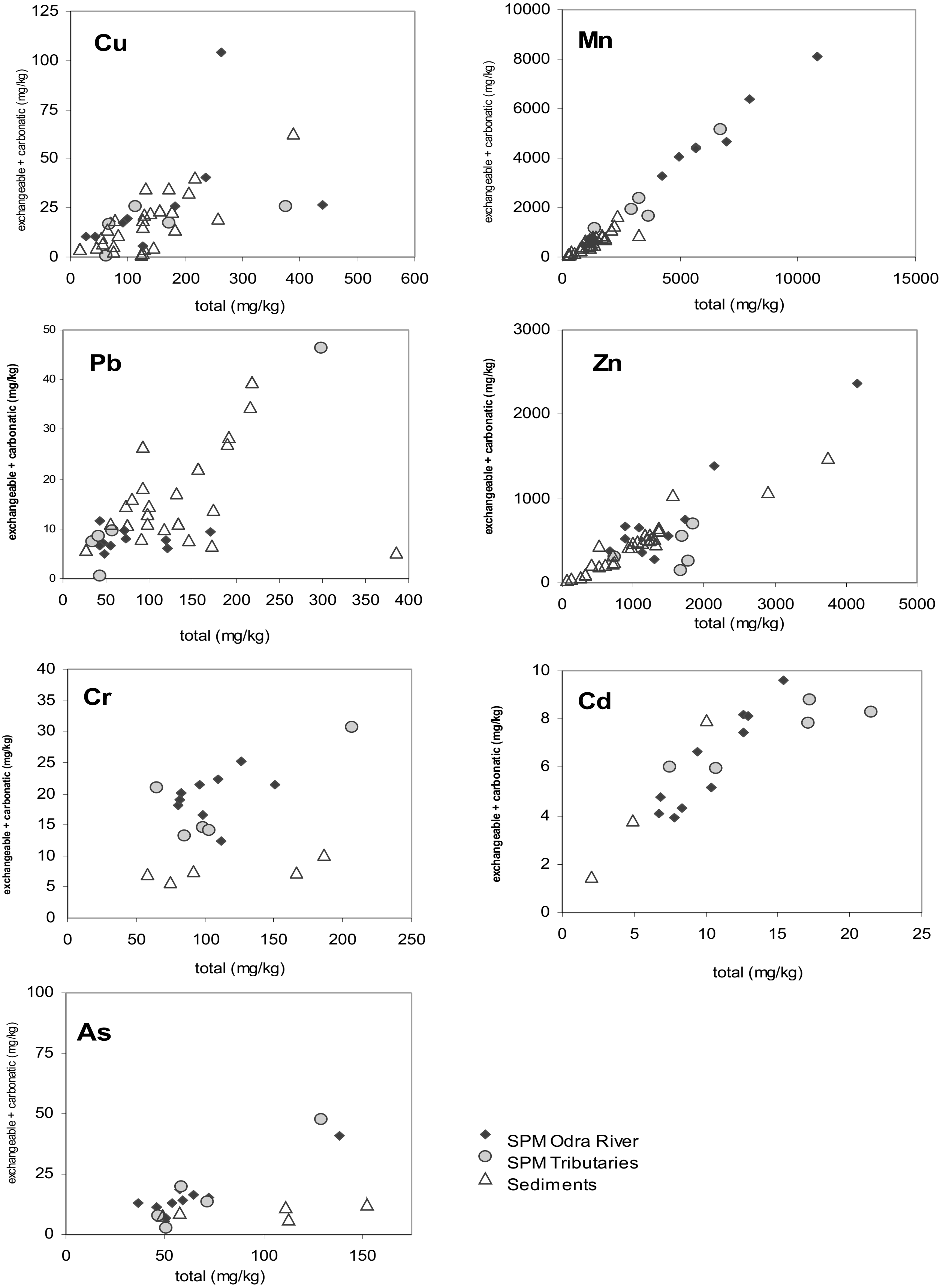


Fig. 10. Variation of mobile metal contents of the suspended matter and bottom sediments selected samples of the Odra river and its tributaries showing good correlation of Pb , Zn, Cd and Mn with their total amount in the suspended matter (SPM) and bottom sediments.

easily released as soluble and bioavailable fractions. This mobile portion of metals is crucial for river quality assessment and remediation method selection, if required.

6. As wide studies of the Odra river system suggest, for river monitoring purposes the frequency and number of samples for chemical analysis of both water and solids - preferably suspended matter - could be reduced to twice a year using a few carefully selected sampling sites.

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