HEAVY METALS
IN THE UPPER AND MIDLE ODRA RIVER SYSTEM
RECOMMENDATIONS FOR TRANSBOUNDRY RIVER CHEMICAL MONITORING

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The Odra River catchment area

136 528 km^2

84.9 % in Poland,

10.4 % in Germany,

4.7 % in the Czech Republic.

Study area - about 70 % of the total Odra catchment

the upper and middle Odra river section –

from Chałupki to the Nysa Klodzka river outlet.

Objectives

(1) To establish the spatial variability in concentrations of heavy metals (Cd, Zn, Pb, Cu, Ni, Cr, Mn, Fe, As) for PSM 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 PSM and sediments.

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

Sampling and Methods

In the Years 1997 - 2001 totally about 100 samples of each component in five sampling campaign: 11'97, 05'98, 11'98, 06'99, 05'2000

(1) water

(2) suspended matter – (filters of 0.45 μm diameter)

(3) bottom sediments - (the < 20 μm)

Analysis

- **Total amount of heavy metals concentration**
- **Mobile fraction - exchangeable and carbonatic bound metals**
- **Buffer capacity of sediments**
- **Acidic metal leachibility from sediments**

Data quality control

- **Analyses were subject to sampling and analytical quality program Robust Analysis of Variance, with ROB2 program**

  (1) Cd, Ni, Cr, Cu measurements indicates an excellent precision - percentage of the analytical and technical variances is < critical value of the total variances 4% and 20%, respectively,

  (2) Analytical variance for Pb (5%) slightly exceeds. For Mn and Zn analytical variance is 7 % and 9%, respectively.

  (3) Analytical variance for As and Fe - not enough satisfying.

  (4) Sampling variances for all samples in both cases for suspended matter and sediments are satisfying and not exceed 16% of total variances.

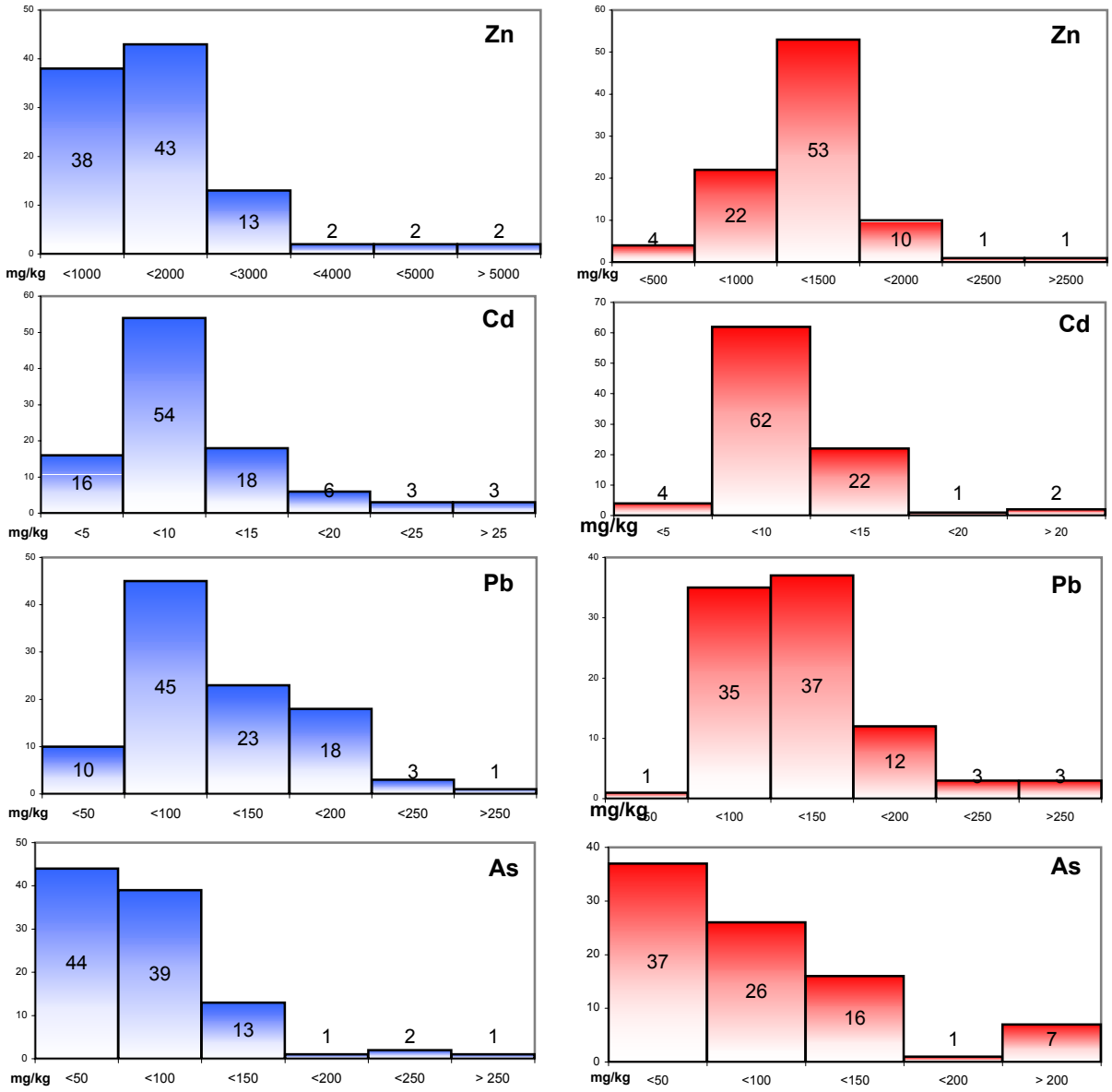
  (5) **Sediments - analytical precision is satisfying for Cu, Zn, and Mn and not enough satisfying. for Cd, Pb.**

Reagent blanks and certified reference materials

- **(Lake Sediment LSKD-4, River Sediment 1645, Sediment CRM 7002) were used to assure quality criteria. ICP-MS was confirmed for PSM by TXRF, and for sediments with AAS measurements.**

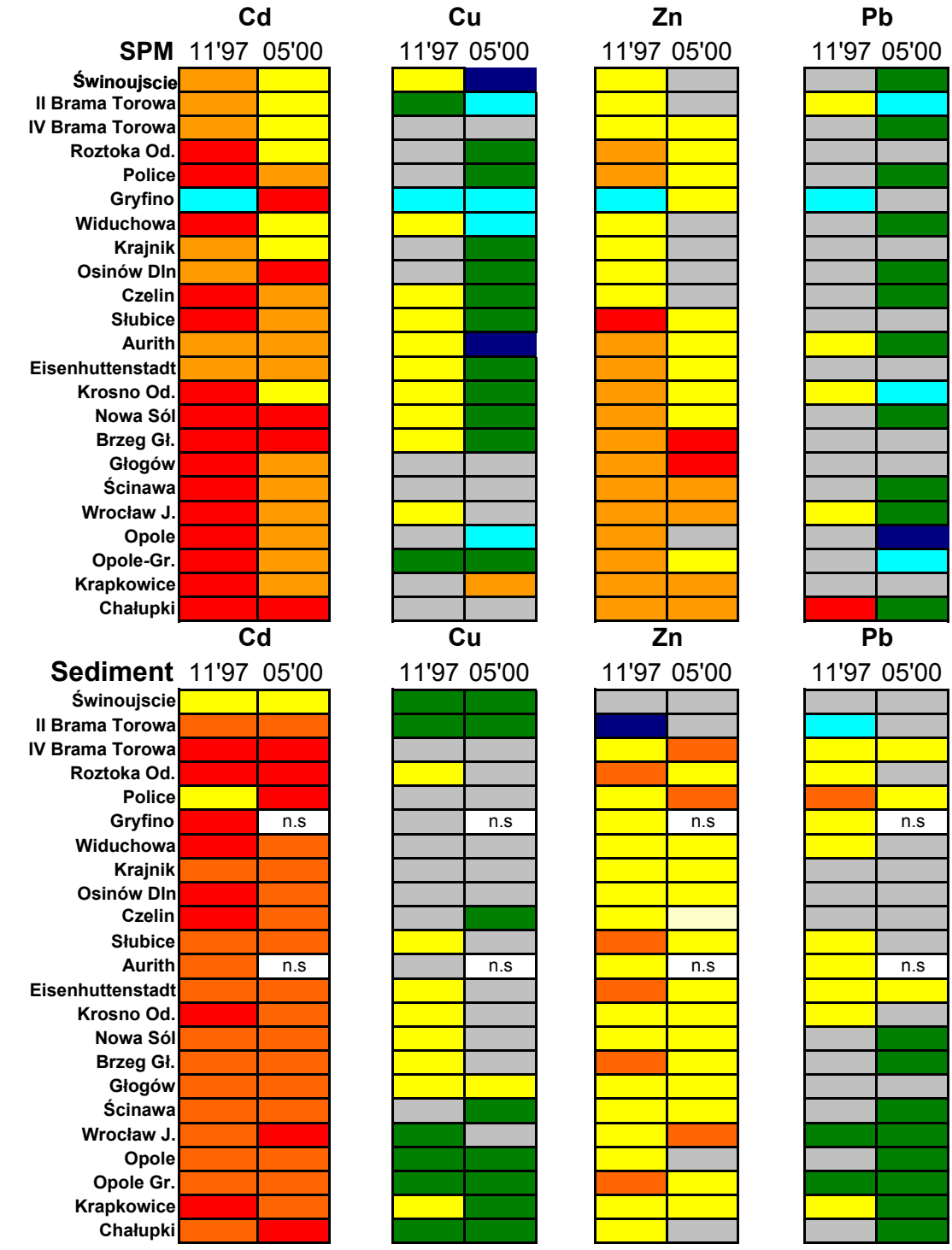
		As	Cd	Cu	Ni	Pb	Zn
					mg/kg		
SPM n= 101	**SPM Conc. mg/l**						
min	**1,2**	**8,0**	**1,8**	**6,2**	**22,1**	**24,4**	**351**
max	**116**	**302**	**39,8**	**493**	**1287**	**401**	**31369**
arithm.mean	**28,9**	**63,8**	**9,3**	**98,4**	**133**	**110**	**1867**
geom.mean	**23,0**	**50,5**	**8,0**	**77,9**	**88,9**	**98,0**	**1321**
median	**26,5**	**52,9**	**7,3**	**79,2**	**81,6**	**97,2**	**1221**
SD	**18,9**	**47,4**	**6,2**	**76,3**	**165**	**55,9**	**3430**
Sediments n= 90	**fr.<20 μm %**						
min	**2,2**	**5,0**	**3,0**	**31,3**	**37,0**	**19,2**	**333**
max	**63,8**	**516**	**21,7**	**298**	**108**	**343**	**2591**
arithm.mean	**28,6**	**92,1**	**9,4**	**110,0**	**51,6**	**123**	**1158**
geom.mean	**24,0**	**52,2**	**8,9**	**97,9**	**50,8**	**114**	**1098**
median	**28,4**	**67,9**	**8,9**	**92,7**	**49,9**	**119**	**1158**
SD	**14,3**	**113**	**2,98**	**55,1**	**10,0**	**49,6**	**359**

Tab. 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.



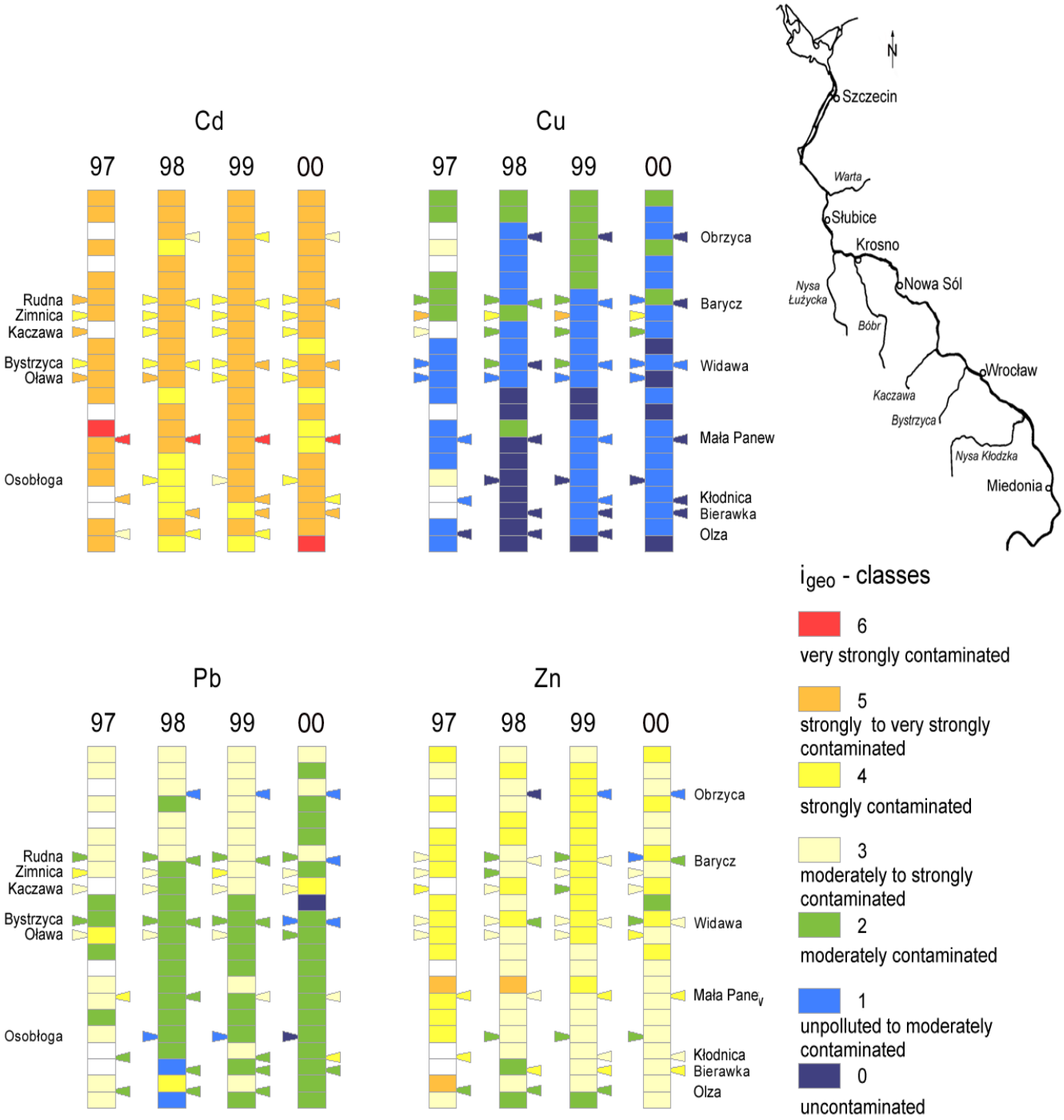
Frequency distribution of Zn, Cd, Pb and As occurring in suspended matter and sediments samples of the upper and middle Odra River.

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



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

ODRA RIVER SEDIMENTS (<20µm)



Optimisation procedure for four years 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.**

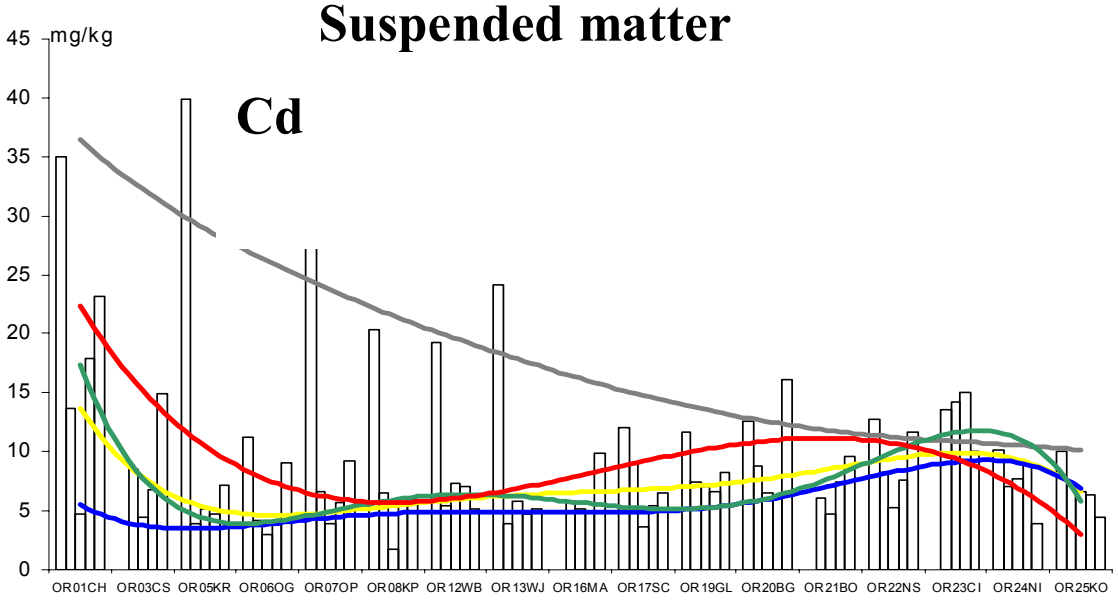
2. **Calculation of metal arithmetical mean values from five sampling campaigns.**

3. **Selection of the samples groups, based on the results of arithmetical means for each metal, from five sampling campaigns.**

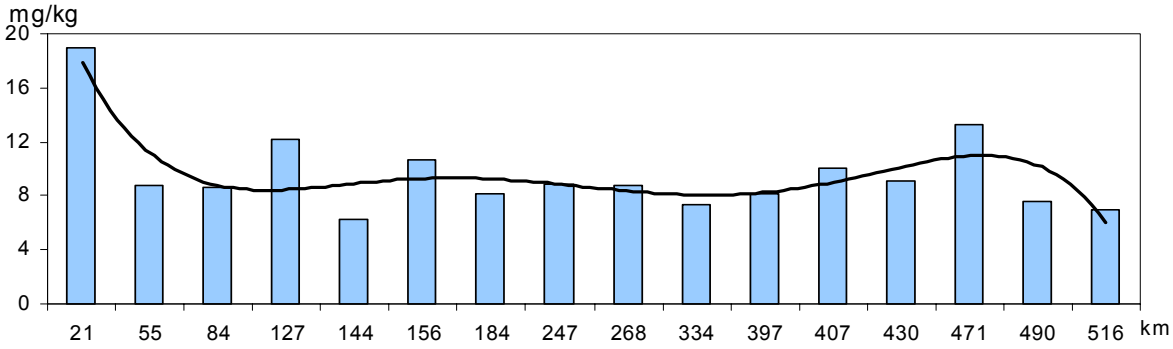
4. **Calculation of metal arithmetical mean values from selected sample sets in the particular groups, which allow to proposed only one sampling point for each of the selected Odra river sections (at the most six sampling points).**

Suspended matter

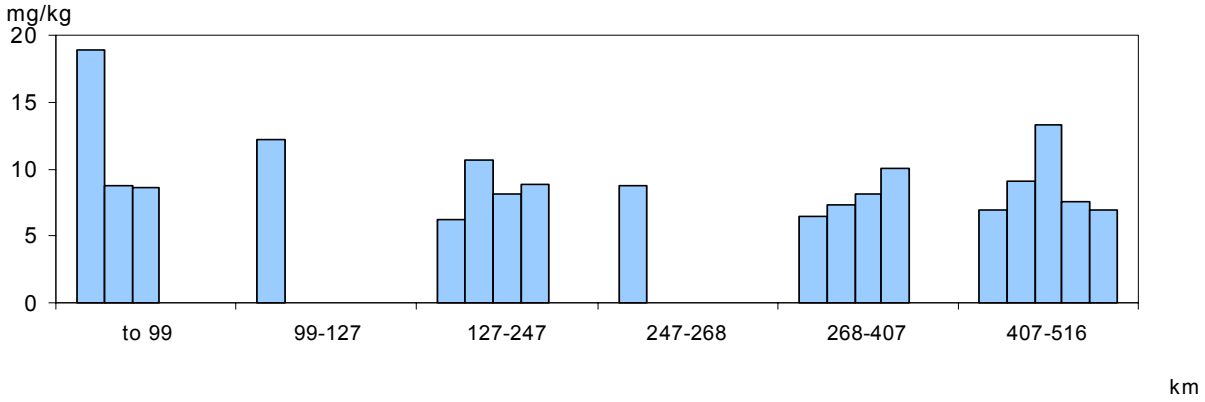
I



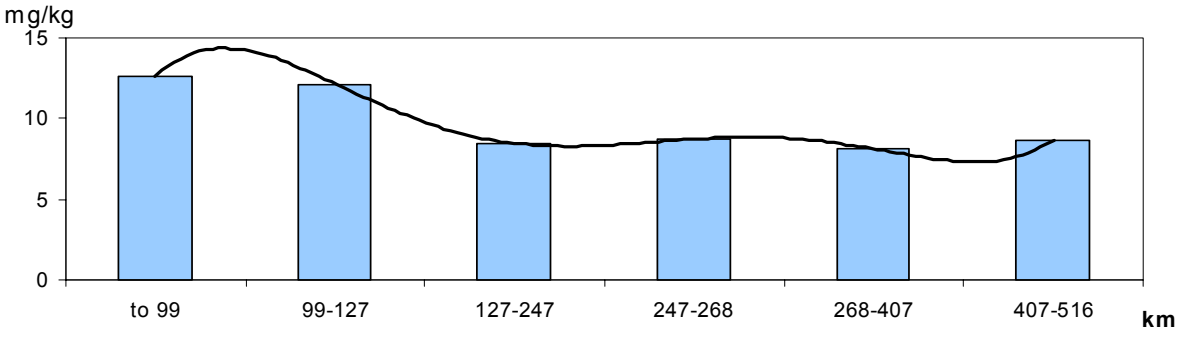
II

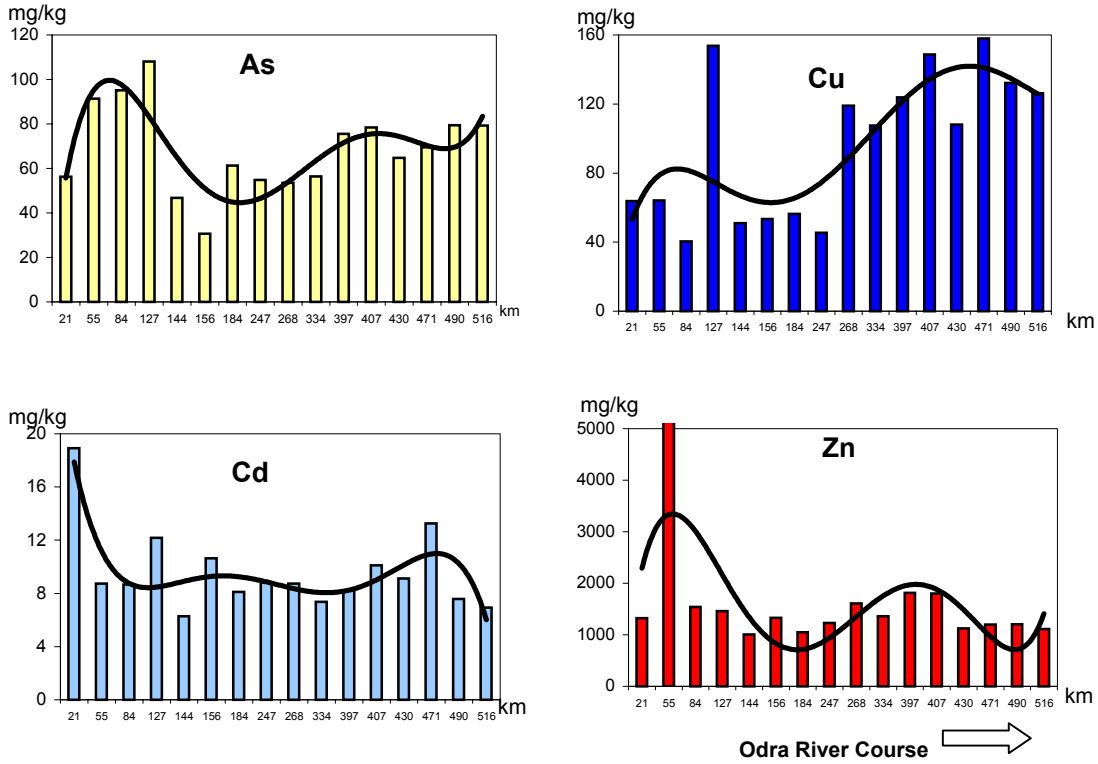


III

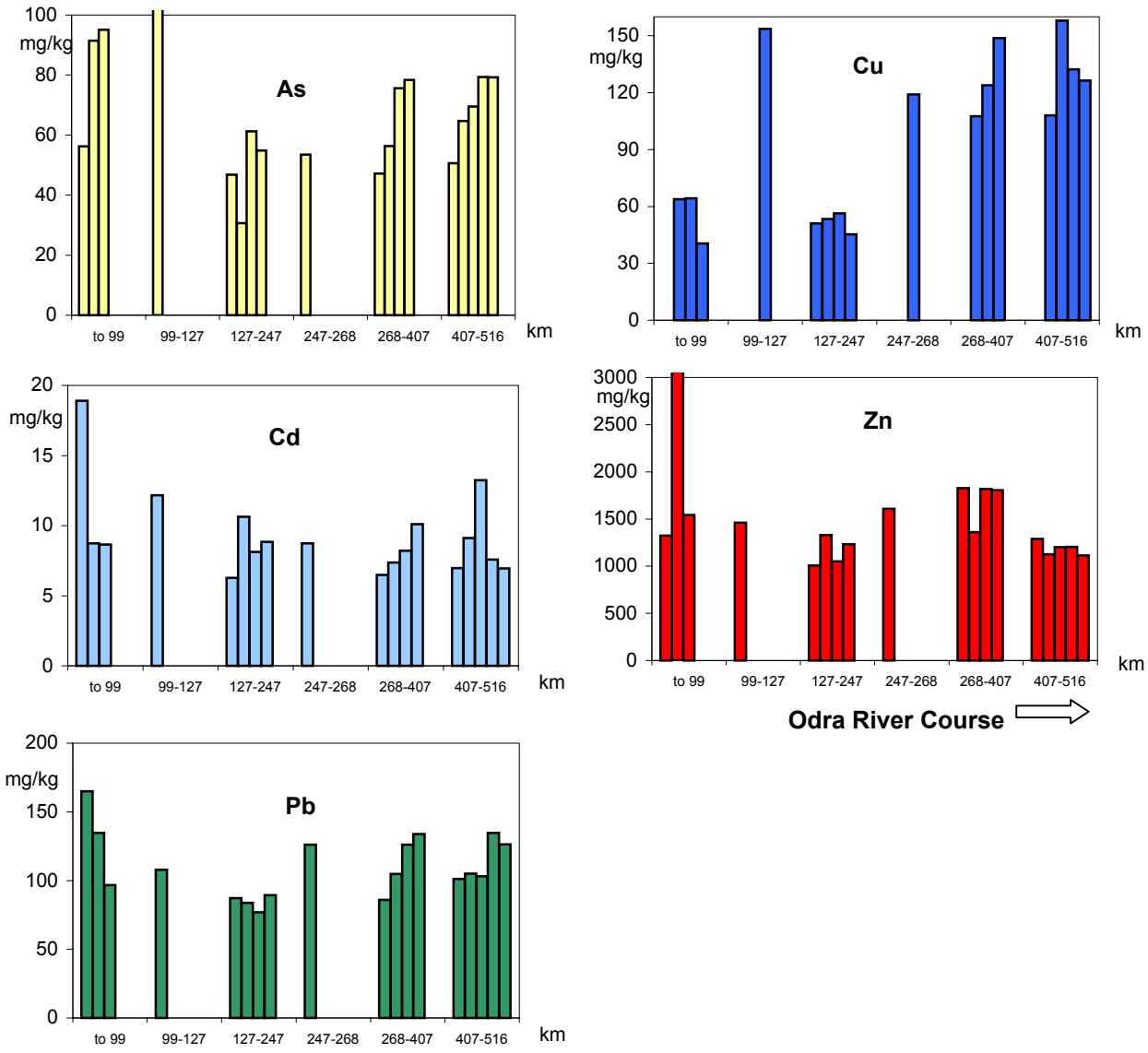


IV

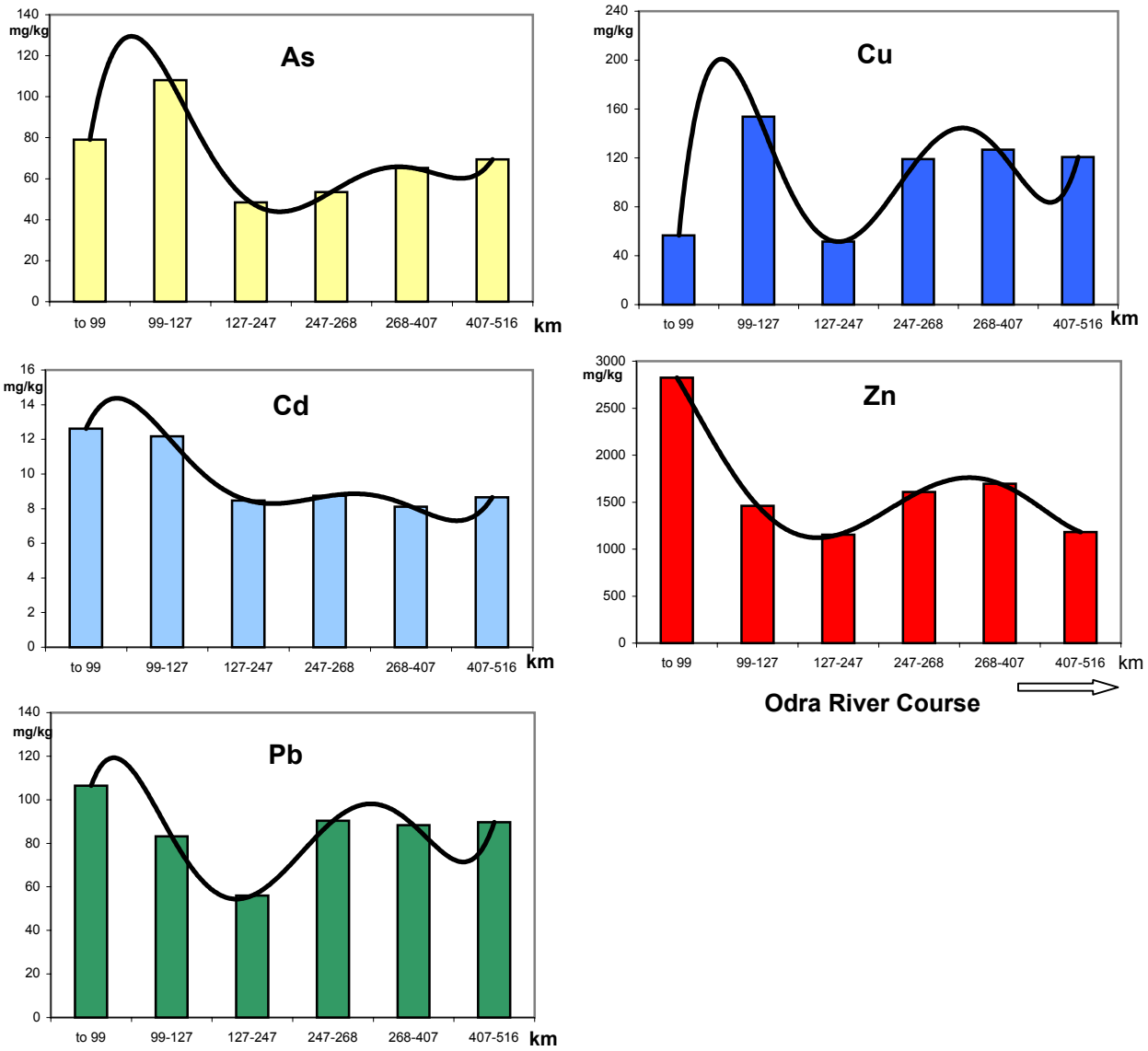




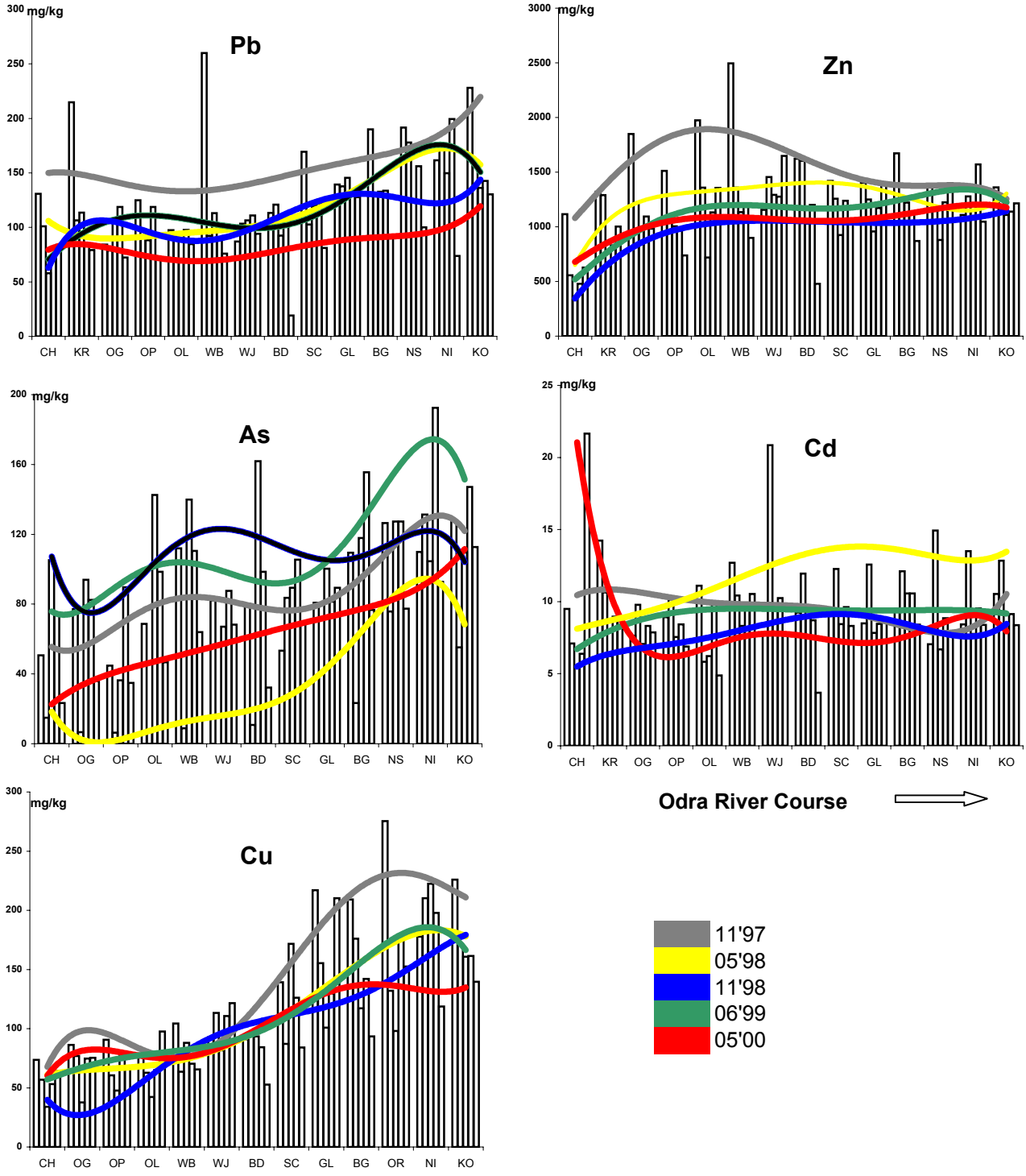
Distribution of As, Cd, Pb, Cu and Zn (arithmetical mean values of metal concentration in the suspended matter samples from five sampling campaigns) with their "trend" lines along the upper and middle Odra river course.



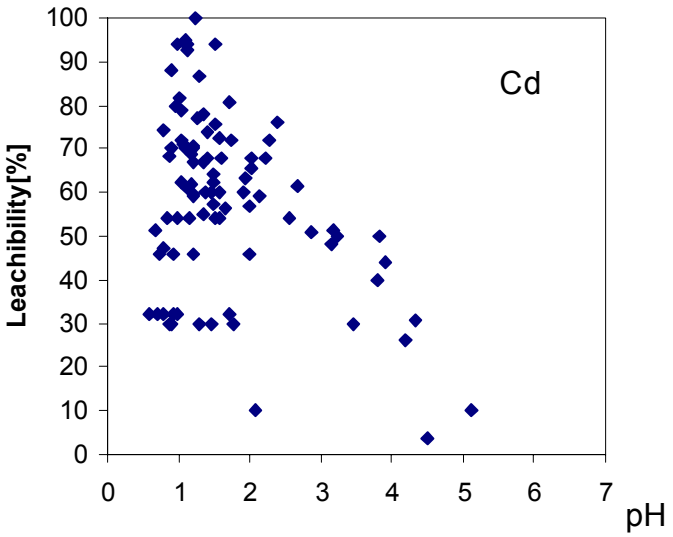
Mean concentration of As, Cd, Pb, Cu and Zn for suspended matter samples grouped in six sets along the upper and middle Odra river course (each bar correspond with arithmetical mean value of metals from five sampling campaigns).

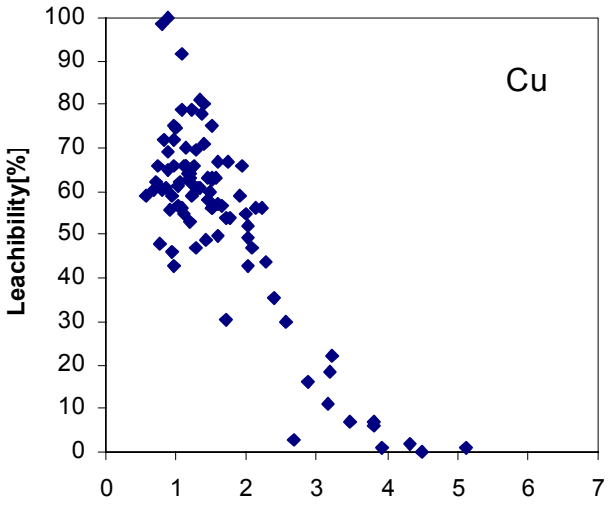


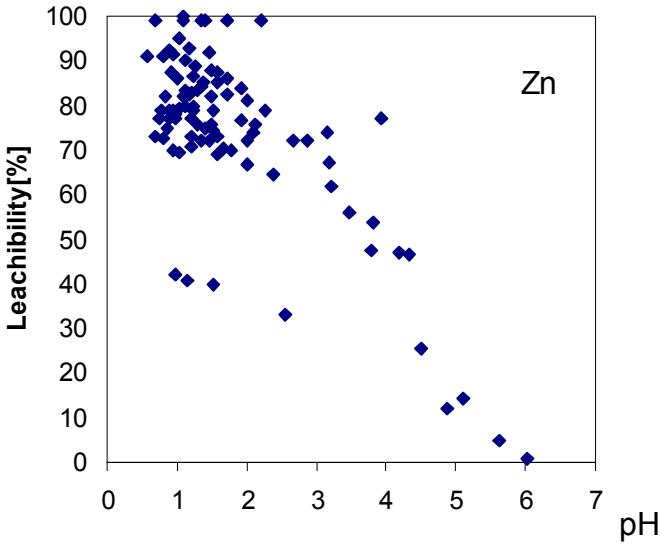
Mean concentration of As, Cd, Pb, Cu and Zn for suspended matter samples of each from the six samples group in the upper and middle Odra river course.

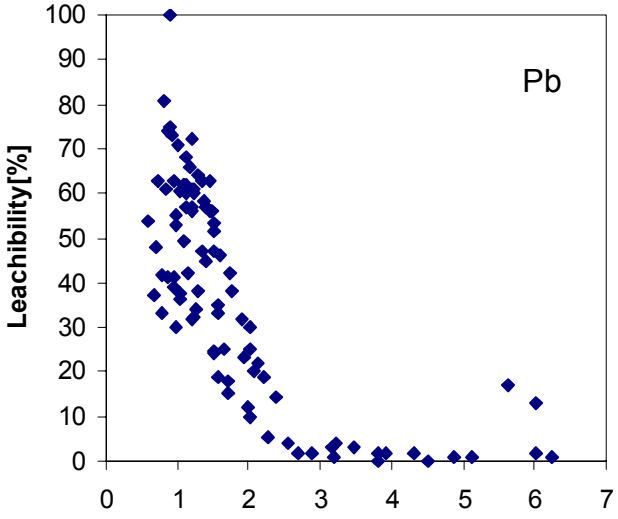


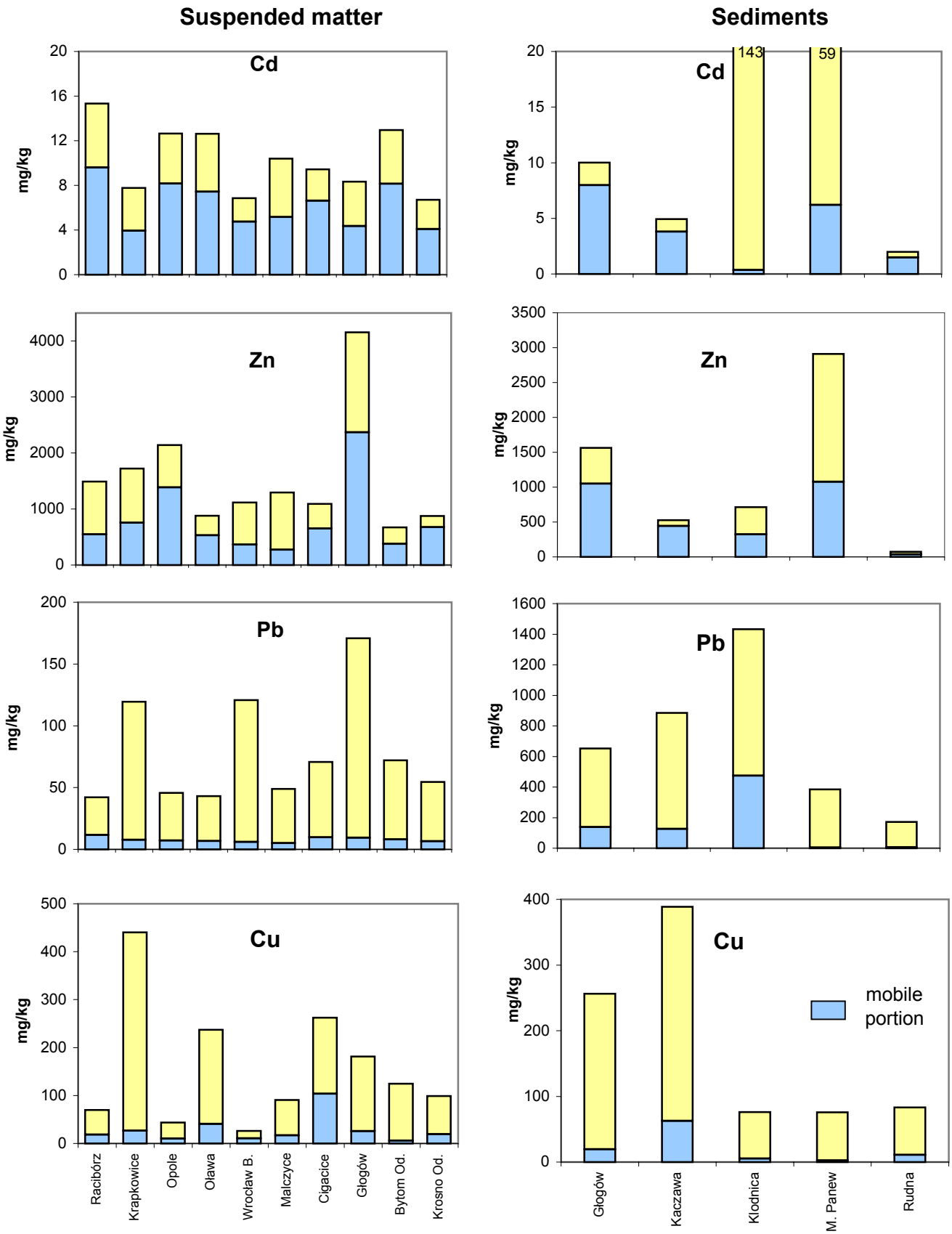
Distribution of As, Cd, Pb, Cu and Zn (arithmetical mean values of metal content in the samples from five sampling campaigns) with their "trend" lines for the bottom sediment, along the upper and middle Odra river.


Cd
Leachibility[%]
pH

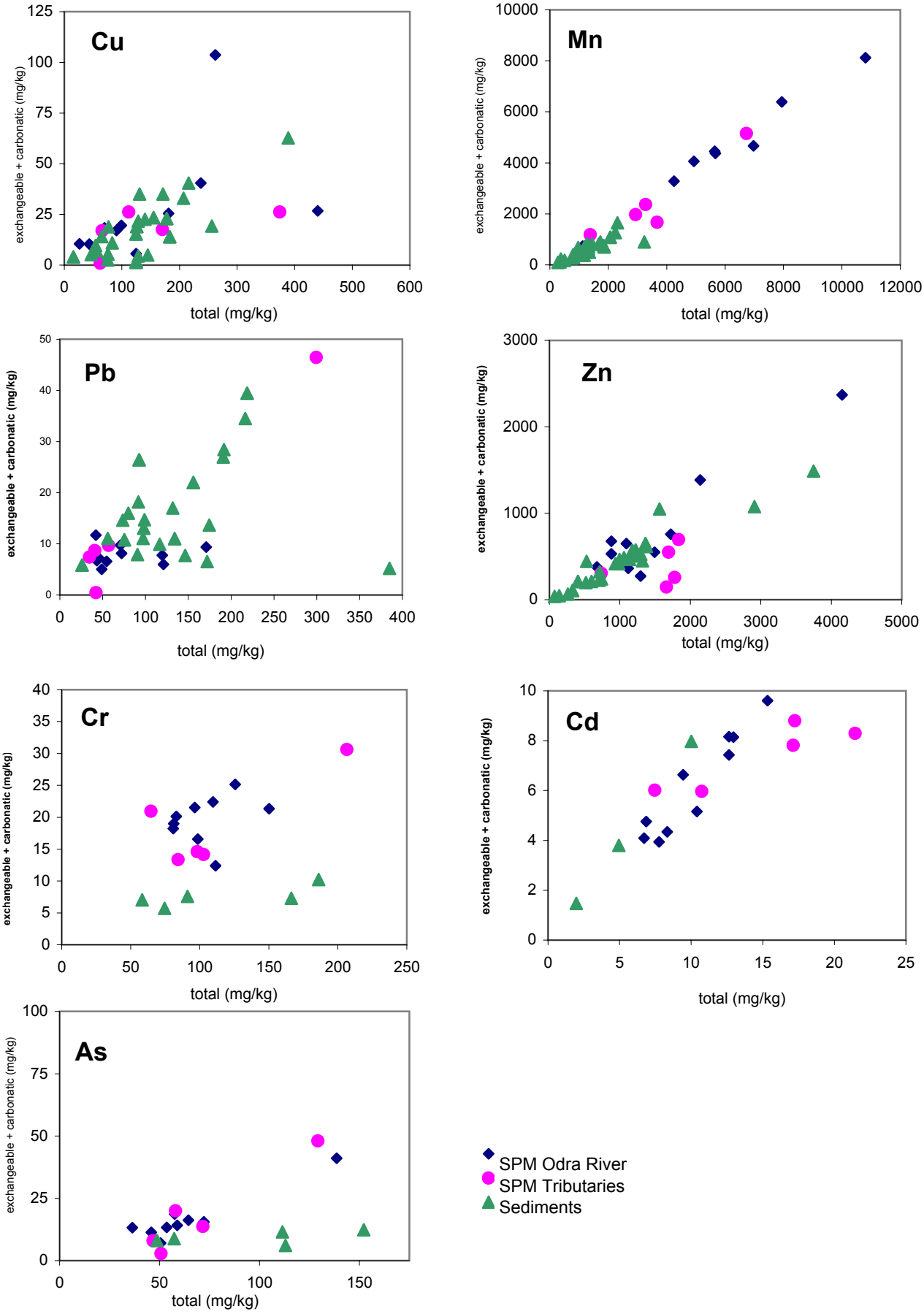

Cu
Leachibility[%]


Zn
Leachibility[%]
pH


Pb
Leachibility[%]



Total and mobile content of metals in the suspended matter and sediments samples of the Odra river.



Variation of the 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.

Conclusions

The studies were carried out within the International Odra Project, research activities of the Faculty of Geology, Geophysics and Environmental Protection at the University of Mining and Metallurgy in Krakow, and partly within the Jurzykowski Foundation.
The authors express also thanks and appreciation to the Polish-German Foundation for founding this research

1. **The detected levels of contamination, mainly Zn, Cu, Pb and Cd, in the most of PSM and sediment samples of the Odra river exceed the geochemical background or threshold values.**
2. **The highest metal pollution of the Odra river system was found with cadmium, zinc, lead and arsenic. The dilution, re–suspension, and re–deposition processes at extreme high the Odra river water events in July 1997 caused additional increase of metal concentrations in the PSM and sediments, immediately after flood.**
3. **Metals variability in the Odra river sediments was less significant if compare with PSM, thus the last component will be recommended for the chemical monitoring. Additional arguments for selection of PSM are: easy sampling procedure, better homogenity, less time consuming of sample preparation and its chemical digestion, and simpler matrix composition for ICP–MS method.**

4. **Cadmium, Zn and As appear to be of particular concern because of the high level, that appear to be bioavailable and their high mobility. However, from metal mobility procedures,**

- **buffer capacity of sediments – acidic metal leaching,**
- **extraction of exchangeable and carbonatic bound metals in solids, more favourable seems to be the last one, as one extraction step.**

5. **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. Particular in the PSM the carbonates play an important role in metal accumulation processes.**
6. **Besides total metal concentration, this well definite „mobilisation test" of metals in river solids, is recommend for monitoring purposes, allowing to evaluate the most mobile portion of metals, which can be easy release as soluble and bioavailable fraction. This mobile portion of metals are crucial for river quality assessment and remediation method selection, if require.**
7. **The results of four years, very wide studies of the Odra river system suggest, that for river monitoring purposes, the frequency and numbers of samples for chemical analysis of both water and solids - preferable PSM - could be reduce to twice a year, with few, correct selected sampling sites.**