TOTAL AND MOBILE HEAVY METAL FORM IN SUSPENDED MATTER OF THE ODRA RIVER

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Abstract. The extensive investigations of total and mobile heavy metals concentrations in the suspended matter (SPM) of the upper and middle Odra river were carried out over the Years 1997 – 2000. Significant levels of contamination were found. The highest metal pollution of the Odra river was found with cadmium, zinc, lead and arsenic. From all metals studied, Cd appears to be of particular concern because of the high level and their high mobility. Studies of the Odra river system suggest, besides the determination of total metal concentration to evaluate the most mobile, and bioavailable metal fraction

Keywords. suspended matter, heavy metals, monitoring.

Introduction

The Odra River catchment area is 136 528 km^2 and 84.9 % of it lies in Poland. 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 and intensive crop production. 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 in the upper and middle Odra river system. (2) To assess the level of contamination by comparison LAWA classification (3) To estimate the mobility and potential bioavailability of metals in the river suspended matter. (4) To define frequency of SPM measurements and sampling points.

Sampling and Methods

In the Years 1997 - 2001 very wide and intensive investigations of the Odra river system were carried out within the framework of the International Odra Project. About 100 samples of suspended matter were collected from the upper and middle Odra river (516 km), during five samplings: November ’97, May ’98, November ’98, June ‘99 and May 2000.

The Odra river suspended matter samples have been separated from the river water on the membrane filters with porous of 0.45 μm diameter, and its concentration was established. The obtained samples were undergone an analytical procedure described earlier [1], [2].

In order to assess the mobility and potential bioavailability of the metals in the suspended, the exchangeable and carbonatic bound metal fraction was estimated, using chemical extraction method proposed by Kersten and Förstner [3]. Metal concentrations were determined using ICP-MS.

Data quality control

The analyses were subject to sampling and analytical quality program to describe random errors by Robust Analysis of Variance, with ROB2 program application [4]. During sampling in May 2000, the filed duplicates of SPM 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.

Results of Cd, Ni, Cr, Cu measurements indicates an 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 enough satisfying. Sampling variances for all samples are satisfying and not exceed 16% of total variances.

In order to estimate accuracy of the analytical method, reagent blanks and certified reference materials (Lake Sediment LSKD-4, 1643d) were used to assure criteria related to quality of the analytical results. Unambiguous of ICP-MS technique was confirmed in case of suspended matter by TXRF.

Heavy metal situation in the Odra River

Totally about 100 samples were collected from each of suspended particulate matter (SPM) in the upper and middle Odra river, in five samplings: 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 SPM concentration.

Tab. 1. Statistical parameters of heavy metals concentrations in the suspended particulate matter (SPM) *(from Chałupki to Krosno Odrzańskie)* of the upper and middle Odra river; SPM concentrations .

		As	Cd	Cr	Cu	Ni	Pb	Zn	Mn	Fe
SPM n= 101	SPM Conc. mg/l					mg/kg				
min	1,2	8,0	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	23,0	50,5	8,0	120	77,9	88,9	98,0	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

In the SPM samples taken in November '97, the concentration of Cd, Cr, Cu and Pb was higher 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 [2,9].

The results of metal concentrations determined in the suspended matter could be expressed in terms of LAWA classification [5]. Figure 2 shows the LAWA classifying metals contamination of the SPM in the upper and middle Odra river, for the two samplings. The obtained results showed that the strong to very strong contamination (classes III/IV and IV) of the suspended matter for almost all samples along the Odra river over two sampling periods. Only sporadically the class III was 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 been improved, and in 2000, class II - moderate contamination with Cu, Zn, and in the upper river section with Pb, was dominated.

Quality Assessment of the Odra River Suspended Matter

Figure 1 shows the LAWA [5] classifying metals contamination of the SPM in the upper and middle Odra river, for the two samplings. The obtained results showed that the strong to very strong contamination (classes III/IV and IV) of the suspended matter with Cd. Only sporadically the class III was stated, thus slight improvement of Cd contamination in the SPM from May 2000 could be observed.

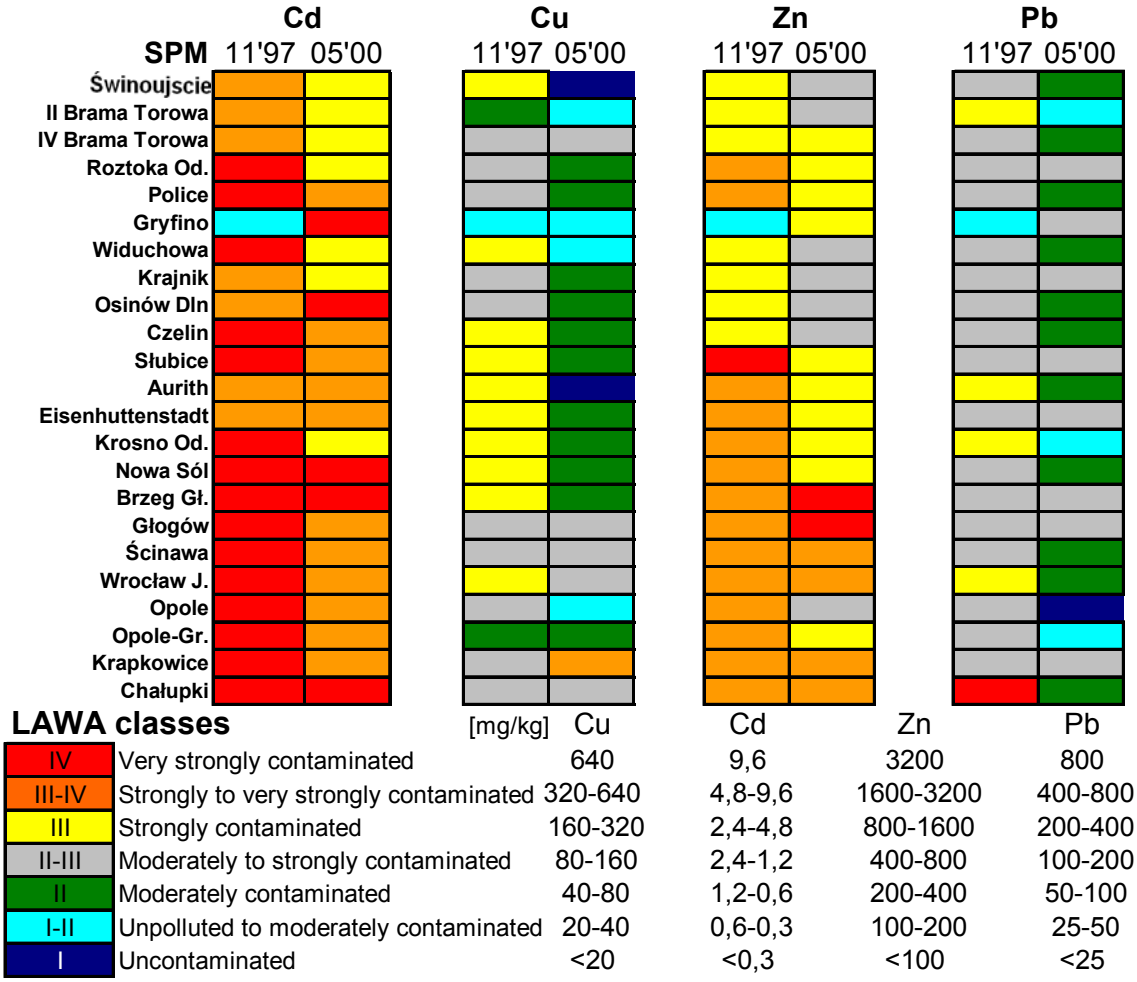

Fig 1. Metals (Cu, Cd, Zn, Pb) in suspended matter.

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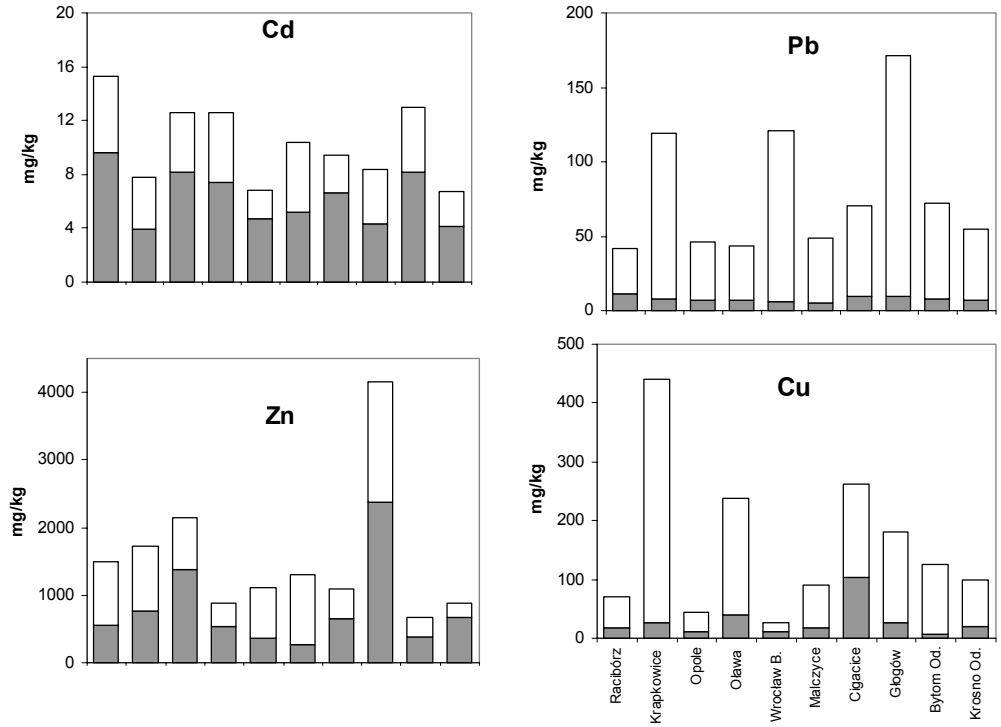
The pattern of spatial variation of the metals in the river solids indicates that a variety of sources might be responsible for the contamination; very intensive, historical and current mining and smelting activities probably being the most important.

Metals mobility in the Odra river solids

To estimate the mobility and potential bioavailability of metals in the river spm, the exchangeable (pH 7) and 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 [3], [6], [7]. Following the discussion on speciation analysis and/or fractionation of elements carried out by Tempelton et al, [8]. 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 2 shows the sum of exchangeable and bound with carbonates portion of Cd, Zn, Pb Cu and As, in the selected suspended matter samples.

First results of extraction of the exchangeable metals and bound with carbonates seems to be



more suitable for the 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, well definite, and allow to omit significant differences between strong and poor buffer capacity of sediments, and thus their very variable metal release, which arise if acidic leaching used.

Conclusions

1. The detected levels of metal contamination, mainly Zn, Cu, Pb and Cd, in the most of suspended matter were found to exceed the geochemical background. 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 at extreme high the Odra river water events in July 1997 have caused additional increase of metal concentrations in the suspended matter immediately after flood.
2. From all elements studied, cadmium, zinc and arsenic appear to be of particular concern because of the high level, that appear to be bioavailable and their high mobility.
3. 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 suspended matter - could be reduce to twice a year, with few, correct selected sampling sites.

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..

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