

Heavy metals in water - suspended matter system in the Odra River

Ewa Adamiec, Edeltrauda Helios-Rybicka

University of Mining and Metallurgy, Faculty of Geology, Geophysics and Environmental Protection, Al. Mickiewicza 30, Kraków

The extensive investigations of total and mobile heavy metals concentrations in water and suspended matter (SPM) of the upper and middle Odra river were carried out over the years 1997 – 2000. The highest metal pollution of the Odra river spm was found with cadmium, zinc, lead and arsenic. The levels of water pollution vary in the wide ranges, depending on metal. Highest Cd, Cu and Zn concentrations in water were observed particularly in middle part of the Odra River at the Lubin - Legnica Cu-mining and processing region. Such high metals concentration is caused mainly due to agricultural and industrial activities such as: petrochemicals, petroleum refining, steel works foundries and non-ferrous metal-works (ADAMIEC, HELIOS-RYBICKA & BEHRENS 2000; HELIOS-RYBICKA 1996).

From all metals studied in suspended matter, Cd, Zn and As appear to be of particular concern because of the high level, 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.

1 Introduction

The study area covered about 70 % of the total Odra catchment area. 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 objectives of the study were: (1) to measure concentrations of heavy metals (Cd, Zn, Pb, Cu, Ni, Cr, Mn, Fe and As) for water and suspended matter in the upper and middle Odra river system. (2) To assess the level of contamination by comparison with the river solids classification or geochemical background standards, and to identify any need for monitoring (3) To estimate the mobility and potential bioavailability of metals in the river suspended matter.

2 Sampling and Methods

Totally over 100 samples were collected from both, water and suspended matter, from the upper and middle Odra river (516 km), in five samplings from November 1997 to May 2001. 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 (HELIOS-RYBICKA & KNÖCHEL 2000).

In order to assess the mobility and potential bioavailability of the metals in the suspended matter, the exchangeable and carbonatic bound metal fraction was estimated, using chemical extraction method proposed by KERSTEN & FÖRSTNER (1986). Metal concentrations were determined using ICP-MS and/or TXRF methods.

3 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 (RAMSEY 1993). During sampling in May 2000, the filed duplicates of water and spm 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.

For most elements measured in water samples (except arsenic) data quality control was satisfying. In a case of suspended matter, results of Cd, Ni, Cr, Cu measurements indicates an excellent precision. The analytical precision for Cd, Pb and particularly for Ni is not enough satisfying.

In order to estimate accuracy of the analytical method, reagent blanks and certified reference materials (Lake Sediment LSKD-4, riverin water 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.

4 Results and discussion

The heavy metals concentration in the Odra river water vary in the wide ranges. The statistical parameters are shown in table 1.

In order to estimate the Odra river water contamination with heavy metals, obtained results were assessed by LAWA classification for water (IRMER 2000). The results are presented in figure 1 (ADAMIEC & HELIOS-RYBICKA 2002a).

Highest values of arsenic in water were measured in samples taken in May 98, particularly in the upper Odra river at Krapkowice (8.10 µg/L), as well as at Brzeg Dolny and Nietków sampling points, at the Cu-mining and processing region.

Most of the samples are moderately to strongly and/or very strongly contaminated with Cd (fig.1). Taking into account four sampling campaigns, the Odra river water is characterized by slightly decreased with Cd contamination. Hig-

hest concentrations of Cd were observed in the water samples taken near Nietków and Krosno Odrzańskie.

Observed concentrations of Cr in water were rather stable (µg/L): 3.43 in May 98, 3.25 in November 98, 3.80 in June 99 and 4.35 in May 2000. Most of the samples can be classified from unpolluted to moderately polluted with Cr - classes I to II (fig. 1).

The level of contamination with Pb increased during the period 1998 – 2000. Highest concentrations of Pb in the Odra river water were detected in May 98 (7.84µg/L) at Nietków and in samples taken in November 98 in Brzeg Głogowski (5.67 µg/L) and in Obrzyca (5.40 µg/L).

Generally most of the water samples are moderately contaminated with Cu – LAWA class II.

The concentration of Ni in water is getting higher and higher taking into consideration following sampling campaigns. Highest concentration of Ni was measured in samples taken in November 98 in tributaries Osobłoga 36, 99 µg/L.

Concentration of Zn in water shows that average values of the individual sampling campaigns is rather high and vary in narrow ranges from 40.02 µg/L in June 99 up to 48.26 µg/L in November 98. Most of the samples are strongly contaminated. Samples taken in Cu-mining and smelting region are strongly and very strongly contaminated with Zn and highest concentrations were found in water samples taken in May 98.

Table 1: Statistical parameters of metals content in water of the upper and middle Odra River.

Parameters n=85	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Mn
					µg/L				
Minimum	0.376	<0.02	<0.21	0.550	0.259	<0.1	12.4	16.2	5.91
Maximum	8.10	0.867	12.7	54.6	27.2	7.84	535	1861	353
arithmetical average	2.33	0.140	4.78	8.24	5.34	1.77	55.4	250	73.3
geometrical average	1.91	0.075	3.74	5.81	4.01	1.41	45.9	165	55.2
median	1.75	0.082	3.93	5.65	4.20	1.45	43.0	154	54.5
std. deviation	1.70	0.186	3.00	8.64	4.34	1.26	57.6	298	58.5

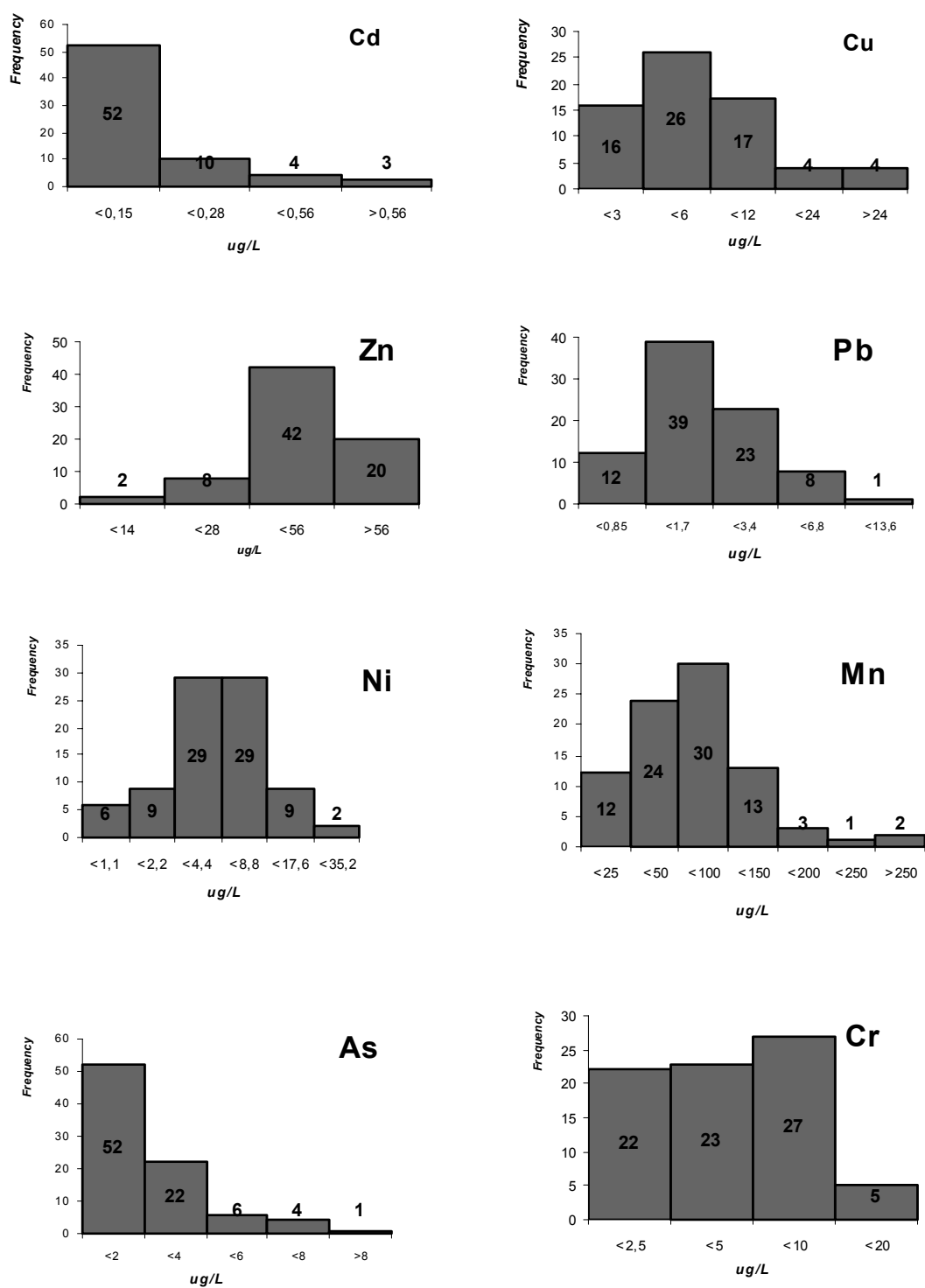


Figure 1: Occurrence of metals in water of the Odra River.

Table 2: Statistical parameters of heavy metals concentrations in the suspended particulate matter (SPM; from *Chalupki to Krosno Odrzańskie*) of the upper and middle Odra river; SPM concentrations.

SPM n= 101	SPM Conc. mg/l	As	Cd	Cr	Cu	Ni	Pb	Zn	Mn	Fe
		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

5 Suspended particulate matter

Totally about 100 samples 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 were taken for analysis. Table 2 shows the statistical parameters of metal contents obtained for all of the SPM samples.

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 (ADAMIEC & HELIOS-RYBICKA 2000; ADAMIEC & HELIOS-RYBICKA 2002b).

The results of metal concentrations determined in the suspended matter could be expressed in terms of LAWA classification (RAMSEY 1993). 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.

6 Conclusions

Results of the study carried out starting in May 98 showed that water samples have been strongly contaminated with cadmium, zinc and copper. The detected levels of the metal concentrations were found exceed the LAWA target values i.e., for Cd: 0.072 µg/L, Zn: 14 µg/L, Cu: 4 µg/L (ADAMIEC & HELIOS-RYBICKA 2002b). In case of Ni about 50% of the samples have concentration higher than target value 4,4 µg/L. Taking into considerations Cr – 93% and Pb – 85 % of the samples do not exceed target levels - 10 µg/L and 3.4 µg/L, respectively.

Highest Cd, Cu and Zn concentrations were observed particularly in the middle Odra River water and suspended matter, at the Lubin – Legnica Cu-mining and processing region. Generally the level of the metal contamination in the Odra river depends on the elements, sampling points for most of the metals and for Zn, As and Cr in water on sampling season.

The detected levels of metal contamination, mainly Zn, Cu, Pb and Cd, in the most of suspended matter 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. From the metals that were studied, Cd seems to be of particular concern because of high level and their high mobility in suspended matter, along river course. Particular in the suspended matter the carbonates play an important role in the accumulation processes of metals. 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

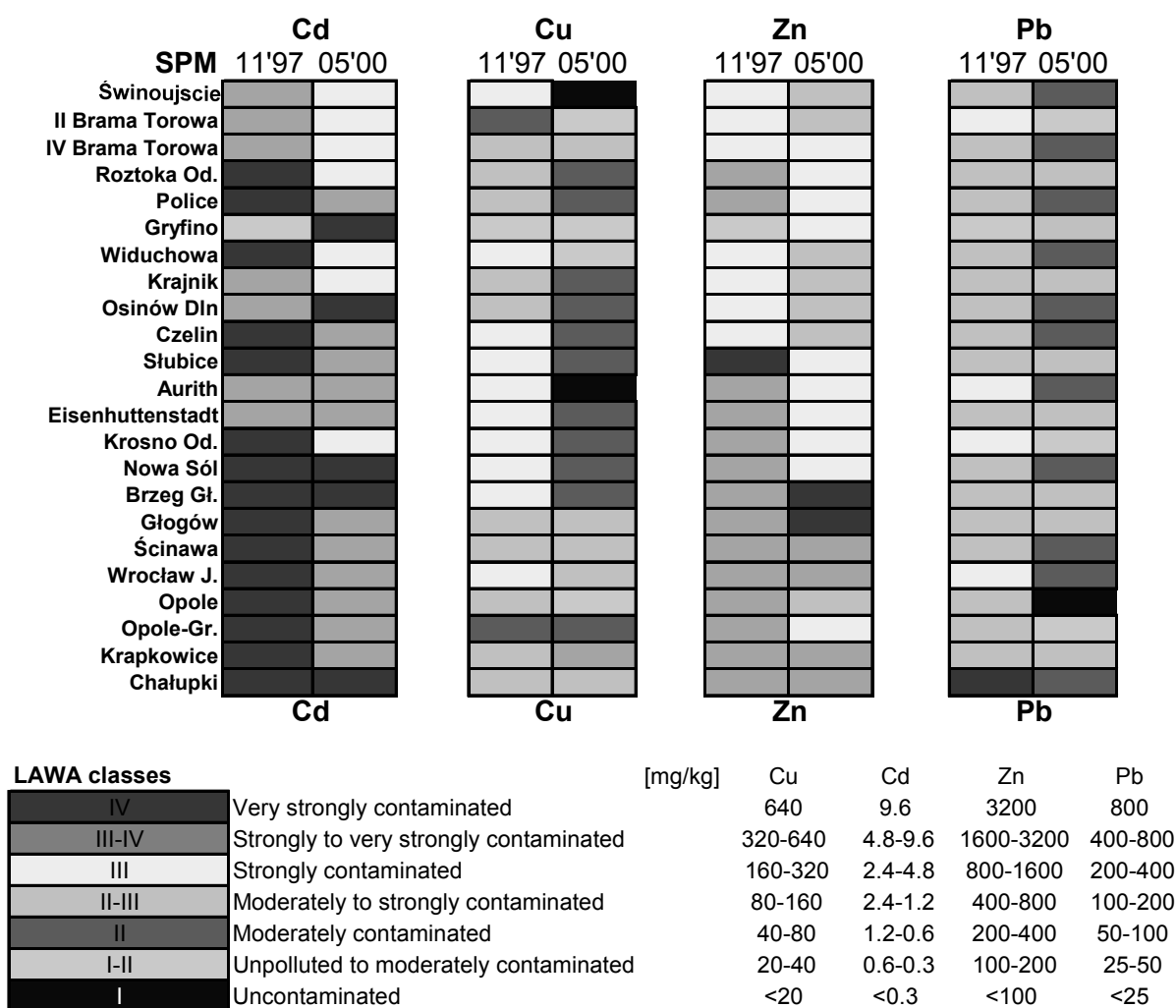


Figure 2: The heavy metals situation in the Odra River suspended matter and bottom sediments from November 1997 and May 2000, expressed in LAWA classes.

concentrations in the suspended matter immediately after flood

References

- ADAMIEC E., HELIOS-RYBICKA, E. & BEHRENS, K. (2000): Heavy metals in water and suspended matter in the Odra River after the flood in 1997. Intern Research Conference. Physicochemical problems of natural waters ecology. Szczecin, Poland, pp. 20.
- HELIOS-RYBICKA, E. (1996): Environmental impact of mining and smelting industries in Poland. In: Environ. Geochem. Health. Geol. Soc. Sp. Publ. 113, pp 183–193.
- HELIOS-RYBICKA, E. & KNÖCHEL, A. (2000): Crucial load in the river Odra – impacts of floods on the situation of hazardous substances. IBMBF Symposium, Elbeforschung, Gewässer Landschaften, 21, pp 79–99.
- KERSTEN, M. & FÖRSTNER, U. (1986): Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. Water Sci. Technol. 18, pp 121-130.
- RAMSEY, M.H. (1993): Sampling and analytical quality control (SAX) for improved error estimation in the measurement of Pb in the environment using robust analysis of variance. App. Geochem. 2, pp 149-153.
- IRMER, U. (2000): Requirements for the Implementation of the EC Water Framework Directive in Germany. Sediment Assessment in European River Basins. ISSN 1431–2409. BfG, 22 26-37.

- ADAMIEC, E. & HELIOS-RYBICKA, E. (2000): Changes of heavy metals concentrations in suspended matter of the Odra river after the flood in 1997. Proc. of 5th Intern. Symp. Exhib. on Environmental Contamination in Central and Eastern Europe. Prague, Sept. 2000. pp 7.
- ADAMIEC, E. & HELIOS-RYBICKA, E. (2002a): Heavy metals distribution in water of the upper and middle Odra river in period 1998 – 2000. Part IV International Odra Project. Polish Journal of Environmental Studies. Vol 11, No 6, 669-673.
- ADAMIEC, E. & HELIOS-RYBICKA, E. (2002b): Assessment of total and mobile heavy metals content in the suspended matter and sediments of the Odra river system recommendations for river chemical monitoring. Part IV International Odra Project. Polish Journal of Environmental Studies. Vol 11, No 6, 675, 688.