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Distribution of Pollutants in the Odra River System Part IV. Heavy Metal Distribution in Water of the Upper and Middle Odra River, 1998–2000

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Abstract

The aims of this study were to asses an environmental condition and observe changes of heavy metal concentrations and distribution in water of the upper and middle Odra River. In order to estimate levels of heavy metal pollution in the upper and middle Odra River and its tributaries, in May and November 1998, June 1999 and May 2000, a total of 147 samples of river water were taken. Heavy metals (Zn, Pb, Cu, Cd, As, Cr, Ni, Mn, Fe) in the water samples were analysed by ICP-MS.

According to the LAWA classification, water in the Odra River and its tributaries are moderately to highly contaminated with heavy metals. High metals concentration is mainly due to agricultural and industrial activities such as petrochemicals, petroleum refining, steel works foundries and non-ferrous metal-works. The levels of pollution vary in wide ranges, depending on the metal. Highest Cd, Cu and Zn concentrations were observed particularly in middle part of the Odra River at the Lubin - Legnica Cu-mining and processing region.

Keywords: water, heavy metals, monitoring.

Introduction

In order to classify heavy metals pollution in upper and middle part of the Odra River and its tributaries, in May and November 1998, June 1999 and May 2000 85 samples of the Odra river water and 66 of its tributaries were taken for ICP-MS analysis. Complex estimation of water condition of the Odra River in years 1998-2000, worked out based on the results of studies carried out in framework of IOP showed, that heavy metals concentrations in water vary in the wide ranges depending on metals.

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Potential Sources of Pollution

There are many sources of pollution in the Odra River Catchment Area, mainly metallurgy and heavy industry . There are about 1700 potential sources of pollution in the Odra catchment area. About 700 significantly influence the condition of the Odra River and its tributaries. The main contributors of contamination with metals in the Odra River catchment area are industries such as petro-chemicals, petroleum refining, steel works foundries and non-ferrous metal-works [1]. It is obvious that industrial activities are important sources of heavy metal pollution

in the environment, resulting in high contamination of suspended matter. Heavy metals employed in major industry are present in Table 1 [2].

The most dangerous polluters in Silesia voivodeship are Łabędy Foundry in Gliwice, Silesia steel-works in Rybnik, coke-plant Radlin in Wodzisław Śląski, Knurów and Szczygłowice coal mines in Knurów, coal mine and coke-plant Dębieńsko in Czerwionka-Leszczyny, coal mine Krupiński, EMA-BRZEZIE Plant in Raciborz, POCH Chemical Plant in Gliwice.; RAFAKO (Racibórz)-steam factory, in Opole voivodeship; Chemical Factory in Kędzierzyn Koźle, metallurgical factory in Nysa, Opole, Ozimek. In Wrocław POLIFARB S.A- chemical plants, Wrocław heat power station, Hutmen S.A. Cooper Mining District (Lubin)-metallurgy activities, glass-works in Piechowice, Rokita (Brzeg), Wizów (Bolesławiec), Inorganic Chemicals (Kędzierzn Koźle), POLIFARB (Wrocław)- chemical plants, Paint Factory in Złoty Stok, Jelcz (Jelcz)-cars factory, tannery in Prochowice, and others [3].

Sampling and Methods

In order to estimate level of heavy metal pollution in the upper and middle Odra River and its tributaries, totally 147 samples of river water were taken. The samples were collected along the Odra River at the distance of about 516 km, from Olza town (close to the border with Czech Republic) to Krosno Odrzańskie. Respectively in May – 33, November 1998-37, June 1999 - 39 and in May 2000-38 samples were collected.

The Odra river water samples were filtrated on membrane filters of 0.45 μm diameter, farther on solutions were prepared following an analytical procedure described earlier [4]. Trace metals were analyzed by ICP-MS.

The analyses were subject to sampling and analytical quality program to describe random errors by Robust Analysis of Variance, with ROB2 program application [5]. In May 2000, the filed duplicates of water 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 (except arsenic) data quality control was satisfying. In order to estimate accuracy and bias of the analytical method, reagent blanks and certified reference material of river water 1643d was used to assure criteria related to quality of the analytical results. Unambiguous and unbiased ICP-MS technique was confirmed by TXRF.

Results and Discussion

The heavy metals concentration in the Odra river water vary in the wide ranges. The statistical parameters are shown in Table 2.

For comparison of the OdraRiver water metals pollution the content of selected metals in river waters from different regions are shown in Tables 3,4,5.

Published data show that highest concentrations of Cd, Cu and Zn were observed particularly in middle part of the Odra River at the Lubin-Legnica Cu-mining and processing region. The influence of dust emission from the "Głogów" Cu-smelter on heavy metals concentration in Agrocenoses was discussed by Pilc et al., [7]; the metals contents in surface water from this area are shown in Table 4 [7].

The heavy metal concentrations were also studied in 22 water samples from the river Flanders in Belgium. Earlier studies showed that this area was highly polluted. Obtained results are presented in Table 5 [8].

In order to estimate the Odra river water contamination with heavy metals, obtained results were assessed by LAWA classification for water [9]. These results are presented in Fig. 1.

Table 1. Heavy metals employed in major industries [2].

	As	Cd	Cr	Cu	Fe	Mn	Pb	Ni	Zn
Pulp, paper mills,			x	x			x	x	x
Organic chemicals, petrochemicals	x	x	x		x	x	x		x
Alkalis, chlorine, inorganic chemicals	x	x	x		x	x	x		x
Fertilisers	x	x	x	x	x		x	x	x
Petroleum refining		x	x	x	x		x	x	x
Basic steel works foundries	x	x	x	x	x	x	x	x	x
Basic nonferrous metal works, foundries	x	x	x	x			x		x
Motor vehicles, aircraft plating		x	x	x				x	
Flat glass, cement, asbestos products			x						
Textile mill products			x						
Leather tanning			x						
Steam generation power plants			x						x

Table 2. Statistical parameters of metals concentrations in water of the upper and middle Odra River.

Parameters	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Mn
n=85	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

Table 3. Content of Cr and Ni in river waters from different countries [6].

River/Country	Poland	Germany	Russia (Siberia)	Italy	USA
Chromium (μg/L)	1-73	2.5-15.5	>10	0.1-1.2	-
Nickel (μg/L)	2-75	8.9-24	-	-	0-71

Average concentration of As in water for all sampling campaigns is 2.38 μg/L. Results of As concentration in water show average values for individual campaigns as follows (μg/L): 3.49 in May 98, 1,75 in November 98, 1.41 in June 99 and 1.58 in May 2000. 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.

Analyzed concentration of Cd in water shows average values of the individual campaigns from 0.03 (June 99) to 0.15 (May 98). In 25 water samples the concentration of Cd was below limit of determination. Most of the samples are moderately to strongly and/or very strongly contaminated with Cd (Fig.1). Taking into account four sampling campaigns, Odra river water is characterized by slightly decreased with Cd contamination. Highest concentrations of Cd were observed in the water samples taken near Nietków and Krosno Odrzańskie.

Chromium in water shows average content of 7.27 μg/L. In 8 water samples the Cr concentration was below limit of determination. 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. Concentration of Pb in water show average values of the individual campaigns as follows (μg/L): 1.04 in May, 1.52 in November 98, 1.46 in June 99 and 1.62 in May 2000. Highest concentrations of Pb in Odra river water were detected in May 98 (7.84 μg/L) at Nietków and in samples taken in November 98 in Brzeg Głogowski (5.67 μg/L) and in Obrzyca (5.40 μg/L).

Concentrations of Cu in water show average values of the individual campaigns from 4.05 μg/L in May 98 up to 7.28 μg/L in May 2000. It seems that Cu contamination in water increases. Significantly high concentration was

Table 4. Metal content in surface water sampled in the villages of Bogomice and Grodziec Mały [7].

Metal μg/L	Bogomice	Grodziec Mały
copper	16 (7-31)	10 (5-16)
Lead	38 (17-62)	31 (26-40)
Zinc	42 (16-92)	78 (24-120)
Cadmium	4 (1-7)	4 (1-8)

Table 5. Heavy metal concentrations in water from the river Flanders [8].

Heavy metals μg/L	Range concentration	Mean values
As	2.0 to 14.3	6.1
Cd	0.16 to 2.14	0.6
Cr	2.0 to 336.8	26.3
Cu	3.3 to 60.5	13.9
Ni	5.3 to 30.6	11.4
Pb	2.3 to 52.5	14.1
Zn	89 to 521	202.8

detected in November 98 in sample taken in Nowa Sól - 54.56 μg/L. Generally most of the water samples are moderately contaminated - LAWA class II.

The concentration of Ni in water is getting higher and higher, taking into consideration following sampling campaigns. The average content of Ni in water for individual sampling campaigns amounts to the following (μg/L): 1.86 in May 98, 4.65 in November 98, 5.56 in June 99 and 5.15 in May 2000. Most of the water samples are moderately to strongly contaminated with Ni. Highest concentration of Ni was measured in samples taken in November 98 in tributaries Osobłoga 36.99 μg/L.

Concentrations of Zn in water shows that average val-

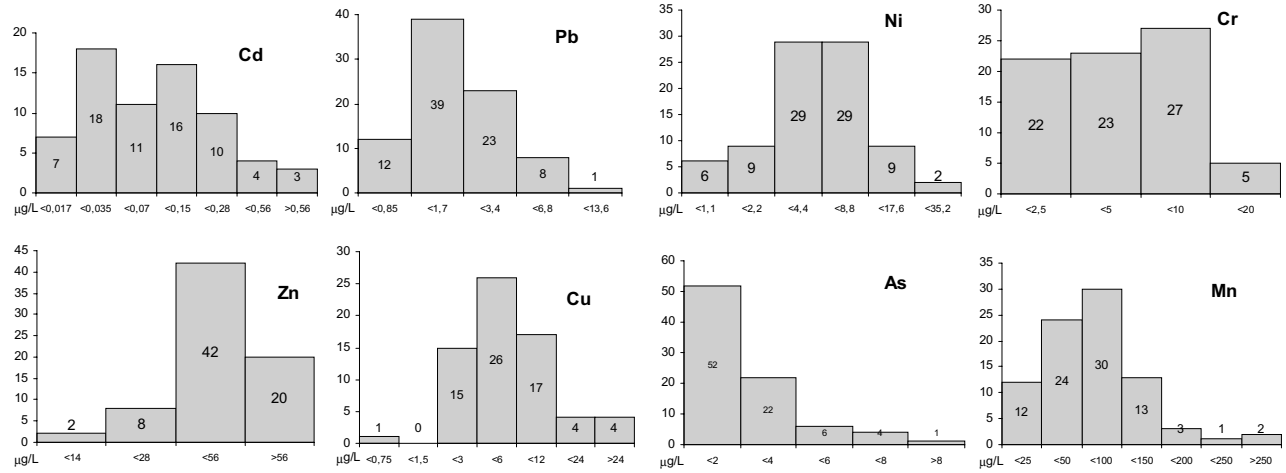

Fig.1. Frequency distribution of heavy metals concentrations in water of the Odra River with LAWA classes application.

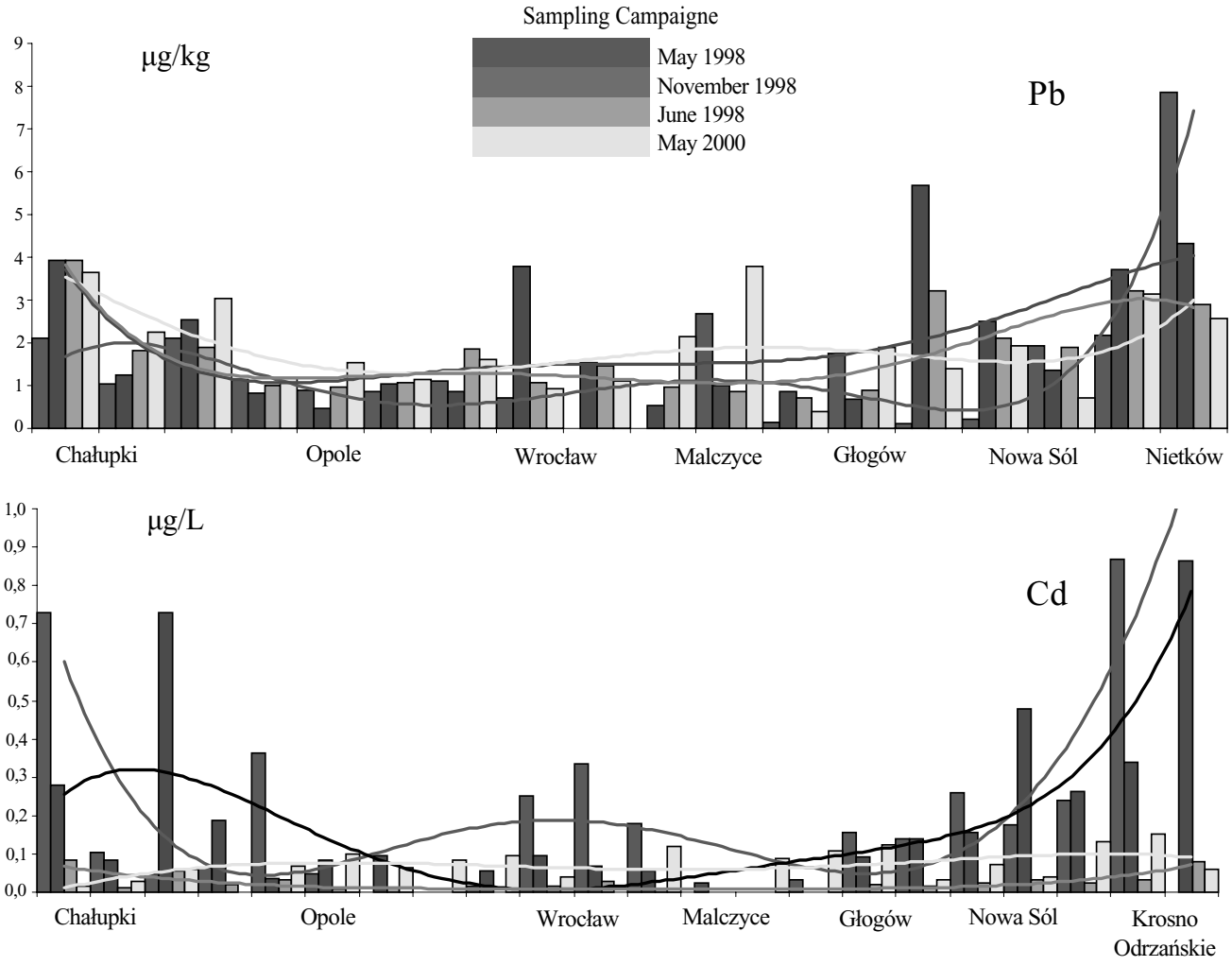

Fig. 2. Distribution of Cd and Pb stated in water samples of the Odra River for four sampling campaigns.

ues of the individual sampling campaigns is rather high and varies 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 the 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. The highest value was identified for the Odra river water sample taken in Głogów (535 μg/L).

Analyzed concentrations of Mn in water increases significantly, taking into account successive sampling campaigns, and amounted in May 98 - 42.3 μg/L, in November 98 – 47.8 μg/L, in June 99 – 57.3 μg/L and 84.0 in May 2000.

The obtained results showed that the concentration of Pb, Ni and Mn among sampling points for all four sampling periods were more stable than observed for Cd, As and Cr. Fig. 2 shows distribution of Cd and Pb stated in water samples of the Odra River for four sampling campaigns.

Conclusions

1. 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 to exceed the LAWA target values, i.e. for Cd - 0.072 μg/L, Zn – 14 μg/L, Cu – 4 μg/L. In the case of Ni about 50% of the samples have concentrations 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.

2. Highest Cd, Cu and Zn concentrations were observed particularly in the middle Odra River water, at the Lubin – Legnica Cu - mining and processing region. From the metals that were studied, Cd seems to be of particular concern because of high level in water, along river course.

3. Generally, the level of metal contamination in water of the Odra river and its tributaries depends on the elements, sampling points for most of the metals and for Zn, As and Cr on sampling season.

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