

# AS, CD AND ZN IN WATER OF THE ODRA RIVER

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## Abstract

Study were focused on an environmental condition of the upper and middle Odra River. The aim of the researches were to observe heavy metals distribution in water and preparation of the model.

In order to estimate level of heavy metal pollution in the upper and middle Odra River and its tributaries, in May and November 1998, June 1999 and May 2000, about 150 samples of riverin water were taken. Metals in the water samples were analysed with ICP-MS application.

According to the LAWA classification, water in the Odra River and its tributaries are moderately to high contaminated with heavy metals. 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 in the researched area. The levels of pollution vary in the wide ranges, depending on metal. Highest Cd and Zn concentrations were observed particularly in middle part of the Odra River at the Lubin – Legnica Cu-mining and processing region.

## 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 totally 85 samples of the Odra river water and 66 of its tributaries were taken for ICP-MS analysis. The results of complex estimation of water condition of the Odra River in years 1998-2000 showed, that heavy metals concentrations in water vary in the wide ranges depending on metals.

There are many sources of pollution in the Odra River Catchment Area, mainly metallurgy and heavy industries activities which 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 petrochemicals, 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 environment, resulting in high contamination of suspended matter. Heavy metals employed in major industry are presented in table 1 [2].

**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

The most dangerous polluters in Silesia voivodeship are „Łabędy Foundry” in Gliwice, „Silesia Steel-works” in Rybnik, Coking-plant „Radlin” in Wodzisław Œl’ski, Coal mining

Coal mining „Krupiński”, „EMA -BRZEZIE” Plant in Raciborz, Chemical Plant POCH in Gliwice.; RAFAKO (Racibórz) -steam factory, in Opole voivodeship; Chemical Factory in Kędzierzyn Koźle, metallurgical factory in Nysa, Opole, Ozimek. In Wrocław w POLIFARB S.A - chemical plants, Heat power station ‘Wrocław’, Hutmen S.A. Cooper Mining District (Lubin) -metallurgy activities, Glass - works in Piechowice, Rokita (Brzeg), Wizów (Bolesławiec), Inorganic Chemicals (Kędzierzyn Koźle), POLIFARB (Wrocław)- chemical plants, Paint Factory in Złoty Stok, Jelcz (Jelcz) -cars factory, tannery in Prochowice and others [3].

## Sampling and methods

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 the membrane filters with porous of 0.45 μm diameter, further on solutions were prepared followed 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 riverin water 1643d was used to as sure criteria related to quality of the analytical results. Unambiguous and unbiased of 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 showed in table 2.

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

Parameters	As	Cd	Zn
n=85	ug/L		
Minimum	0,376	<0,02	12,4
Maximum	8,10	0,867	535
arithmetical average	2,33	0,140	55,4
geometrical average	1,91	0,075	45,9
median	1,75	0,082	43,0
std. deviation	1,70	0,186	57,6

Published data show that highest concentrations of Cd 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 Agroecosystems was discussed by Pilc et al., [7]; the metals contents in surface water from this area are show in table 3 [7].

**Table 3. Metal content in surface water sampled in villages Bogomice and Grodziec Mały [7].**

Metal i g/L	Bogomice	Grodziec Mały
Zinc	42 (16–92)	78 (24–120)
Cadmium	4 (1–7)	4 (1–8)

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 4. [8].

**Table 4. Heavy metal concentrations in water from the river Flanders [8].**

Heavy metals (i g/L)	Range concentration	Mean values
As	2,0 to 14,3	6,1
Cd	0,16–2,14	0,6
Zn	89–521	202,8

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

Average concentration of As in water for all sampling campaigns is 2,38  $\mu$ g/L. Results of As concentration in water show average values for individual campaigns as follows ( $\mu$ g/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  $\mu$ g/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 about 0,05 (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, the 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.

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  $\mu$ g/L in June 99 up to 48,26  $\mu$ g/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. The highest value was identified for the Odra river water sample taken in G<sup>3</sup>ogów (535  $\mu$ g/L).

## 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 exceed the LAWA target values i.e., for Cd – 0,07  $\mu$ g/L and Zn – 14  $\mu$ g/L.
2. Highest Cd 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 the 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 and As on sampling season.

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## Captions of figures.

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

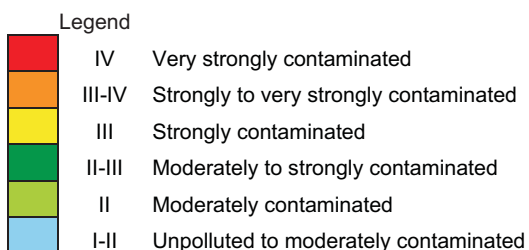
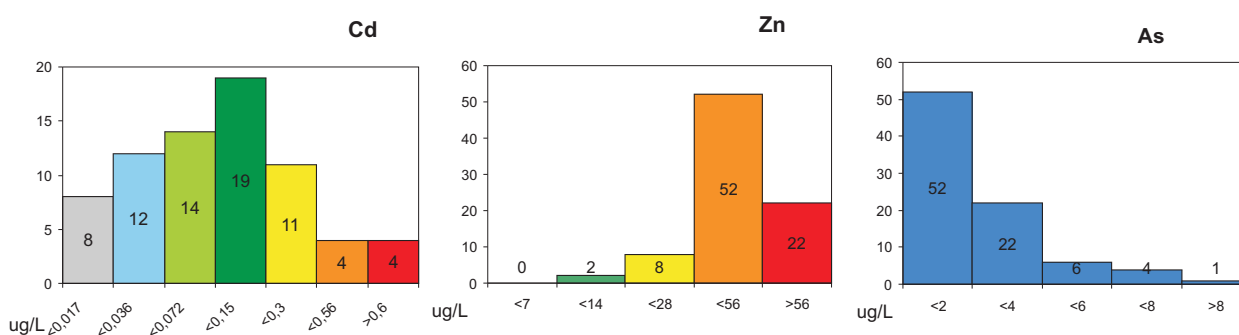


Fig. 2 Distribution of Cd, As and Zn stated in water samples of the Odra River for four sampling campaigns.

