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CONTENT OF SELECTED HEAVY METALS IN WATER AND RIVERBED SEDIMENTS OF THE UTRATA RIVER

The results of study of heavy metals content in water, suspended solids and bottom sediments of the Utrata River have been presented. The highest concentrations were observed for the dissolved form of Pb (0.35 mg/dm^3). All heavy metals under investigation were present in suspended solids (over 90%). Remarkable amount have also been found in sediments [mg/kg] Zn – 174, Cu – 76, Pb – 49, and Cd – 2.5. Water extracts showed lower concentrations, while EDTA extraction was several times more efficient (over 26%).

1. INTRODUCTION

Development of civilisation has led to introducing heavy metals into the natural environment in amounts remarkably excessing the natural load. Bottom sediments accumulate many elements, some of which are heavy metals, hazardous for natural environment, as well as animals and people. Their amount might be several orders of magnitude higher than in the water phase [1–5]. Heavy metals are considered to be stimulating, or – on the other hand – limiting factors for life activities. Metals as free cations and those bound to suspended solids and bed sediments of water bodies harm biocenosis. Depending on their concentration, oxidation number and tendency to create complexes, they might become toxic substances for all living organisms. Toxicity of metals is dependent on their form. The total contents of metals in environmental samples, eg. bottom sediments, wastewater sediments or soil, does not allow one to determine real danger imposed by their forms which can be absorbed by life forms like plants, or health hazard for animals and people [6–8].

Mobility of heavy metals and their availability for organisms can be estimated based on chemical indicators (fractionation analysis of sediments) and biological ones (estimation of heavy metals contents in plants and life forms inhabiting the area of

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sediments being analysed). Speciation and its analysis are most often used to carry out this kind of study, since they allow one to determine forms of heavy metals in environmental samples [9]. According to the IUPAC definition, speciation study leads to identification and/ or determination of one or more chemical forms of a given metal in a sample [10], and speciation is defined as determining specific forms and configurations which can be taken by a given element [11].

In studies of heavy metals in environmental samples, single (simple) extraction is applied. It simulates natural conditions for transfer of elements from a sample directly to solution [9, 12]. Procedures applied here simulate natural environmental phenomena (eg. acid rain), which enables estimation of bioavailability and mobility of heavy metals. Apart from single extraction, sequential extraction is used, enabling one to separate heavy metals into chemical forms that can be released to the solution in different environmental conditions. Application of sequential analysis allows estimation of percentages of mobile metal forms, available for plants [13–15]). When combined with modern statistical methods, the following factors can be assessed as well: bioavailability, migration, accumulation, biomagnification, toxicity, solubility or sorption [16].

2. MATERIALS AND METHODS

Sediment samples were taken along midstream of the Utrata River, within the borders of the town of Pruszków, from 11 sampling stands (Fig. 1) and additionally from collector sewer from heat and power plant, located nearby some of the sampling stands.

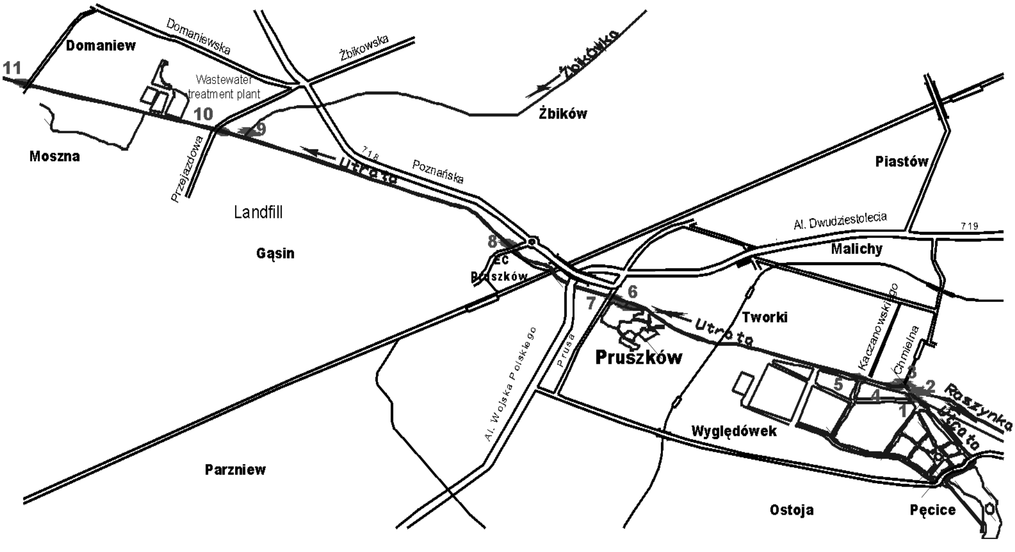

Fig. 1. Map of the Utrata River at the section of Pruszków town with location of sampling points (1–11)

Sediment samples were taken with Kajak probe by KC Denmark Research Equipment, from top layer of bottom sediments, on the depth of 10–15 cm below the sediment surface. The total of 28 water samples and 24 sediment samples were collected.

Water samples were filtered on filter drains. Suspension left on drains was mineralised with acid mixture of HNO_3 and $HClO_4$ (3:1). Sediment samples were dried at room temperature. Air dry deposit was thoroughly stirred and sieved, getting the fraction < 1 mm. One gram of sediments was weighed out from dried and sieved samples, to be mineralized with the acid mixture. After mineralization of the suspension and sediments, the following heavy metals were determined in the filtrate (water) and in solutions: Fe, Mn, Zn, Cu, Pb, Cd. To determine the total content of heavy metals in water, graphite furnace atomic absorption spectrometry (GFAAS) was used, while in mineralized solutions – flame atomic absorption spectrometry (FAAS). Effects of metal extraction from bottom sediments were compared for distilled water and 0.1 M EDTA solution. The extraction was carried out for 1 h after adding reagents in the ratio of 10 g of sediments/100 cm^3 solution. Extracts after filtration were analysed to determine the content of heavy metals.

3. RESULTS AND DISCUSSION

Water and bottom sediment quality were analysed in the period of 2003–2006 in the Utrata River [17]. The results of the study showed that water quality varies and depends on the place of collecting samples. Characteristics of water was slighlty basic (pH 7.1–8.0). Higher values of pH were observed downriver. River waters were well aerated. Closer to collector sewers of the heat and power generation plant, water was oversaturated with air and showed high manganese index (62 mg/dm^3). Manganese index values increased (over 10 mg/dm^3) downriver, from sampling stand 6. The analysed waters were highly mineralized, which is proved by high value of electrical conductivity (average 947 µS/cm). Analyses of the depths of the river show various contents of suspended solids in sampling stands as well as depending on period of research. Higher values were observed in winter period, lower ones in spring. Riverbed sediments were slightly basic (pH 7–7.6). Main ingredients of sediments were mineral substances, accounting for 86.2%. According to Stangenberg classification, these sediments can be classified as mineral sediments. The highest concentration of organic matter was observed in sediments taken from sampling stands 1–5 (19.4%), while the lowest in the area around sites 8 and 9 (5.4%). Reasearch sites upriver were situated within agricultural area, while sites from 6 to 11 in urban, highly industrialized area. Study of metals dissolved in water and bound in the suspension showed significant differences between sampling stands. Lead occurred in the highest concentrations in a dissolved form (0.35 mg/dm^3). The lowest concentration in water was determined for Cd (0.01mg/dm^3). Ranges, medians and average contents for heavy metals are given in Table 1.

Table 1

Concentration of metals in the depths of the river [mg/dm^3]

Concentration	Fe	Mn	Zn	Cu	Pb	Cd
Average	0.09	0.02	0.04	0.07	0.35	0.01
Median	0.06	0.01	0.02	0.07	0.32	0.01
Minimum	0.03	0.01	0.01	0.06	0.27	0.01
Maximum	0.21	0.14	0.10	0.08	0.49	0.03

Contents of metals in suspension accounted for ca. 99% for iron, manganese and zinc, while for copper, lead and cadmium ca. 91% (Table 2). Lead was the least bounded with suspension and it was present mainly in a dissolved form. The process of bounding metals in water depends, among others, on temperature, amount of suspension, biological activity of organisms [17–19] as well as geological base. In many cases, reaction of solution is important as well. In slightly basic reaction, metal ions (especially zinc) change into slighlty soluble forms, which at the same time tend to adsorb on suspensions [20].

Table 2

Concentrations of metals in suspension [mg/dm^3]

Concentration	Fe	Mn	Zn	Cu	Pb	Cd
Average	47.46	3.71	6.93	0.73	3.42	0.13
Median	35.86	2.02	6.87	0.59	3.59	0.13
Minimum	15.76	0.79	3.83	0.15	1.62	0.09
Maximum	95.49	21.36	11.13	1.79	4.27	0.17

Bottom sediments of the Utrata River analyzed in this study were characterised by high content of heavy metals. Content range (in mg/kg) was: for zinc 71–338, copper 8.2–281, lead 49.6–111.6 and cadmium 1.25–4.39, respectively. The values of average contents of metals allowed one to arrange them in order of occurence, depending on their concentrations, in the following way: Zn > Cu > Pb > Cd (Fig. 2. Table 3).

For the analyzed sediments, the most distinctive area was the one located in the neighbourhood of municipal waste and heat and power generation plant. Sediments sampled there were characterised by the lowest reactivity, while their conductivity was many times higher than the values measured in other stands. For these sediments, the highest concentrations of metals were determined (Fig. 2).

Total content of heavy metals in bottom sediments is used only to estimate the level of pollution. It cannot be the basis to determine concentrations of elements that are potentially bioavailable. This kind of estimate can be based on the results of single or sequential extraction. Extraction allows one to identify metal forms and assess their mobility in aquatic environment. Bioavailability of metals usually depends on particular factors: reaction (pH), electrical conductivity of organic matter, oxidizing-reducing properties, as well as heavy metals characteristics and their initial form.

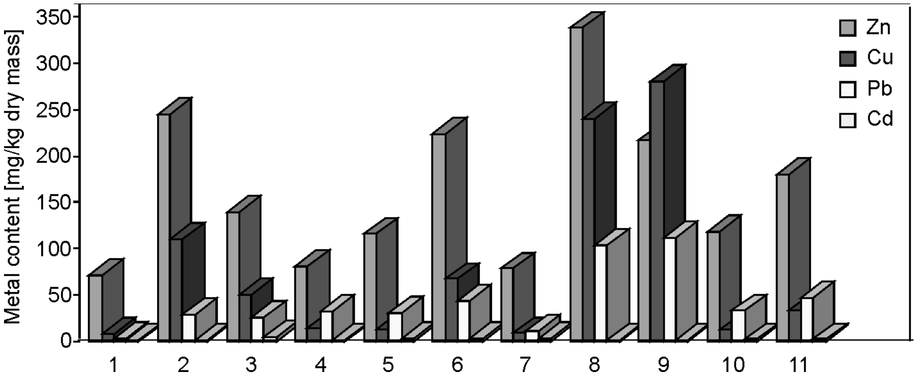

Fig. 2. Concentration of heavy metals in riverbed sediments of the Utrata River

Table 3

Concentrations of heavy metals in riverbed sediments [mg/kg d.w.]

Concentration	Fe	Mn	Zn	Cu	Pb	Cd
Average	9651.65	392.67	164.52	76.44	49.70	2.52
Median	3819.74	110.38	151.87	33.36	31.92	2.45
Minimum	987.98	26.92	71.13	8.21	23.60	1.25
Maximum	36382.21	1536.21	338.36	281.25	111.63	4.39

In laboratory-scale tests, effects of Zn, Cu, Pb and Cd extraction from sediments were compared for those with the use of EDTA and H_2O. The results prove that adding 0.1 M EDTA to sediments leads to the transfer of metals deposited in sediments into the solution. Results for metals extracted with EDTA were much higher than those for solutions with distilled water (Fig. 3).

Applying 0.1 M EDTA led to the release of 45–189 mg/kg Zn, 7–68 mg/kg Cu, 6–100 mg/kg Pb and 0.5–2.0 mg/kg Cd from the sediments, which accounted for 34, 40, 37 and 26% of the total contents of Zn, Cu, Pb and Cd, respectively. The highest increase of solubility was observed for sediments taken in the last part of the analysed river area. Much lower, but still noticeable values were measured for sediment extraction with distilled water. Lead and cadmium were released to the environment the most efficiently (18% and 7.7% respectively), the lowest efficiency was that for zinc (1.2%) and copper (3.5%). After using water and EDTA, it was observed that metals occurring in sediments are intensively washed out, which makes them more bioavailable. Taking into account slight concentrations of metals in depths of the river and their high content in riverbed sediments, the effectiveness of metal transfer from sediments into water might be high. Presence of complexing substances (eg., EDTA), mobilizing metals into water solution, is a significant threat to aqueous biocenosis. Plants absorb chelated metals in motion intensely, which results in their concentration in biomass exceeding the demand [21].

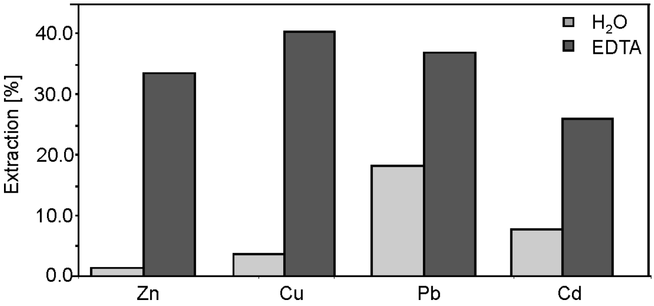

Fig. 3. Percentage of extraction of metals from sediments into water and EDTA

In Poland, there are not legally biding regulations referring to classification of bottom sediments which would comply with commonly used categorization of polluting elements. The only estimate is the one carried out while monitoring quality of inland surface waters. It is based on geochemical criteria and estimates sediment quality in terms of its pollution with detrimental organic elements and heavy metals. The first Polish geochemical classification of riverbed sediments and lake bed sediments was made by the Polish Geological Institute and is used in State Environmental Monitoring. Sediments were divided into 3 classes according to their metal content, based on geochemical criteria [22]) (Table 4).

Table 4

Classification of water sediments based on geochemical criteria

Metal [mg/kg]	Geochemical background	Class I slightly polluted sediments	Class II moderately polluted sediments	Class III polluted sediments
Cadmium (Cd)	<0.5	<1	<5	<20
Copper (Cu)	6	<20	<100	<200
Lead (Pb)	10	<50	<200	<500
Zink (Zn)	48	<200	<1000	<2000

According to this classification, sediments from the Utrata River, referring to the metal contents, can be assessed mainly as slightly or moderately polluted. The sediments are polluted mainly with copper and cadmium. The content of Cu, at majority of sampling stands, exceeded the value set for class II. The analysis of the results of the research led to the conclusion that a high proportion of the sediments is contaminated with cadmium, in some cases the concentrations exceeded the values for class II. The content of zinc and lead were slightly lower. Their content was usually classified as belonging to class II, sometimes class I.

It is impossible to determine the contents of metals in sediments being safe for organisms, using geochemical criteria. The USA and Canada have introduced criteria enabling assessment of ecotoxicity of waste. They are based on two critical (limiting) values of the treshold effect level (TEL) – the content of a given element, above which its toxic effect can be observed and probable effect level (PEL) – the content of a given element, above which its toxic effect on organisms is often observed. Having analysed the sediments in terms of their ecotoxicity, it can be claimed that generally they can impose danger to aquatic life. Cadmium content in all the samples exceeded TEL (0.7 mg/kg), and usually it exceeded also PEL (3.5 mg/kg). The concentrations of other analysed metals were higher than TEL (Cu – 36 and Pb – 35mg/kg) only in a few sampling stands in the industrialized area. They tended to slightly exceed PEL (Cu 197, Pb 91, Zn 315 mg/kg).

4. CONCLUSIONS

The high content of heavy metals in the surface layer of sediments showed continuous inflow of pollution to the waters of the Utrata River. Their source might be surface run-offs from the river basin, from nearby roads and from the collector sewers.

Concentrations of analysed metals were low in the depths of the river. The most dissolved forms were determined for lead. Over 90% of contamination was connected to suspension. The riverbed sediments of the Utrata River are most polluted with cadmium and zinc, while copper and lead were in lower concentrations.

The total content of metals in sediments can be applied only to assess their level of contamination. It is not useful to assess the mobility or bioavailability of metals in the environment. This estimate can be done based on concentration values determined in speciation analysis. Extraction of metals into water and EDTA solution carried out for the purpose of this study proved that Zn, Cu, Pb and Cd get into dissolved forms easily and they become more bioavailable for organisms inhabiting the Utrata River. Metals in sediments are easily washed out into water phase. It is especially noticeable in the case of lead and cadmium.

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