IMPACT OF ZN-PB MINING AND SMELTING INDUSTRY ON HEAVY METALS CONTAMINATION OF THE PRZEMSZA RIVER SEDIMENTS UPPER SILESIA, POLAND

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Abstract
The Przemsza river is classified as one of the most polluted rivers in Poland. It has been studied carefully for the purpose of determining the extent of heavy metals contamination caused by the Zn - Pb mining and smelting industry located in the area. The project involved studying the bottom sediments of the Przemsza River catchment area. The laboratory analysis included various techniques specially fitted to obtain maximum accuracy and precision. Throughout the entire studies, analytical methods i.e. ICP-MS and AAS have been used.
To investigate the river sediments, in general only fine size fraction was used for the analysis.
Our results showed high metals content, that reached [mg/kg]: 7000 of lead, 24500 of zinc and 300 of cadmium. It was obvious that the contamination levels are above the desired and set amounts, therefore further investigations were considered necessary. The results of the studied river sediment depth profiles showed that the concentration of metals was not stable over time. Depending on the depth, the concentrations [mg/kg] ranged: from 430 to 3500 of lead, 3400-34900 of zinc and 15-430 of cadmium and there is a very strong linear correlation between the content of these metals in the sediments. It is imperative that further studies should be carried out, as heavy metal contamination of river sediments is of great importance.

Introduction
The changes of heavy metal concentrations in the vertical profiles of sediments reflect past and present industry activity. The highest metal concentration usually occurs in the drainage basin affected by the excavation and processing of polmetallic ores (2,10).
In our work we investigated the Przemsza River which is located in the southern part of Poland, about 50 km north-east of Krakow. The river forms in Myslowice at the merging point of the Biała Przemsza River and the Czarna Przemsza River. The river discharges into the Vistula River. At about the 15th km the Matylda Channel runs into the Przemsza River, it discharges waters from one of the industrial plants into the river.
The Przemsza River is one of the most polluted rivers in Europe because is located within the most industrialized region in Poland. Industry at this scale has a vast effect on the heavy metal contamination in the river system. The river receives different types of discharges, namely; waters discharged from Zn-Pb ore processing plants, mine waters, meteoric water infiltrating waste dumps. These are considered to be the primary cause of pollution in the river (4,12). In prehistoric times, rocks found in the vicinity of the studied area had the concentration of [mg/kg]: 110 -Zn, 45 –Pb and 2-Cd. During the last 100-150 years, a sharp increase of concentration of heavy metals has been observed in the river (8). The concentration of Zn and Pb currently found in the bottom sediment is one to two magnitudes higher than the concentrations found in the deposits from the pre-industrial periods (5).

To investigate the river sediment, in general only fine grain fractions are used for the analysis.(6,7,9). In the investigation it was determined that heavy metals concentration increases with the decreasing grain-size fractions; in the finest fraction their amount was, in average, 8-19 times higher than in the raw sediment (1,11). In our study in the laboratory we used silty- clay fraction (below 63µm).
The main objectives we had were: (1) to determine the extent of Pb, Zn and Cd pollution in the vertical profile of the rivers, (2) to describe the correlation between heavy metals in the samples of the sediment depth profiles.

Methods

Sampling strategy: The sediment profiles were sampled using proper equipment and were taken at about 1m from the shore at depths from 10 to 65 cm, depending on the accessibility to the river and the characteristics of the river bed. The profiles were obtained from five points: the Biała Przemsza River (1BP), the Czarna Przemsza River (2CP), the Matylda Chanel (5M) and two points in the Przemsza River (7P and 8P) (Fig.1).
Analytical methods: The analysis performed on site included the measurement of pH and Eh.
The profiles were then sealed off from oxygen access using plastic wrap and placed in protective lining for transport. In the laboratory they were refrigerated until the analysis was performed. The profiles were then sliced into 2.5 cm segments and placed in separate containers. Further studies involved the determination of heavy metal content in the fraction <63um, a portion of each sample was sieved using polyethylene sieve. Only for 1BP sediment profile both the bulk samples and fraction < 63µm was investigated. The dried samples were subjected to extraction with conc. HNO_3 and H_2O_2 in Teflon bombs using microwave technique according to EPA 3051 standard procedure (3). Heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn) content was determined using the ICP-MS and AAS techniques.

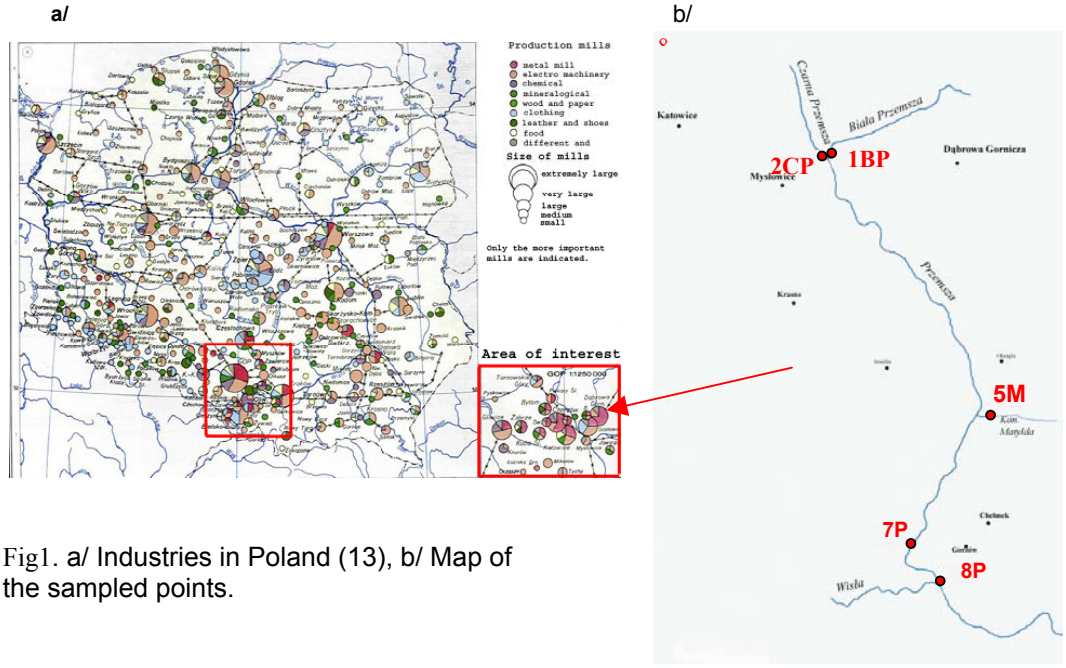


Fig1. a/ Industries in Poland (13), b/ Map of the sampled points.

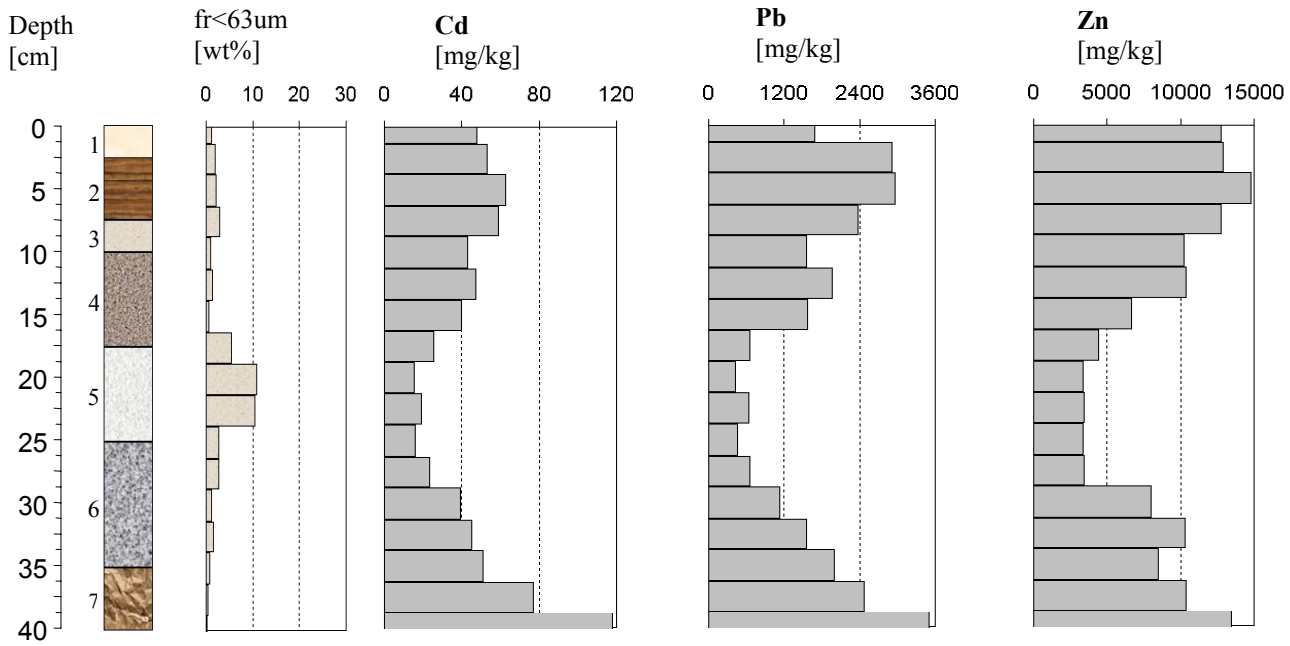
Results and discussion

Upon completion of the measurements at the sampling site, the pH values can be rendered neutral, or close to neutral (5.9-7.2). The Eh is negative in most places (from +70 to – 300 [mV]), which means that reducing conditions are prevailing in the sediment profiles sampled. The profiles consist generally of sandy-silty sediments with poor lamination.
The results of studied sediments showed that contents of heavy metals especially Cd, Pb, and Zn in most cases exceeded the geochemical background even in the deep profile sections often 100 and even 1000 more times. The concentration of metals was not stable over time. Depending on the depth, the concentrations [mg/kg] ranged: from 430 to 3500 of lead, 3400-34900 of zinc and 15-430 of cadmium For this metals higher concentrations were noticed in sediment of the Biała Przemsza River (1BP) and the Przemsza River (8P) (Fig.2). In the Matylda Channel (5M) which is not a natural

river system, amounts of metals were the highest, concentration of Pb reached 17 640 [mg/kg] and Zn 62 600 [mg/kg]. The Biała Przemsza River and the Matylda Channel are two major ways by which the Przemsza River gets polluted with trace metals.
Our investigation of the bulk sample and fraction below 63μm of the Biała Przemsza River (1BP) showed the same results as Sikora and coauthors (1,11) demonstrated in their experiment. Fine particles (fraction <63 um) contain greater amount of heavy metals than the bulk sample: for Cd is from 1,5 to 17, for Pb from 3 to 56 and for Zn from 3 to 36 times more. There is no linear correlation between the metal concentration in the fraction <63um and in the bulk samples.
The correlation between the heavy metals was tested in every sediment profile. There is a very strong linear correlation between the concentrations of lead, zinc and cadmium in most of the vertical profiles (Table1). Their correlation coefficients are greater than 0.8, indicating that these heavy metals might be discharged from the same pollution sources and had identical depositional activities. The strongest correlation was stated for the profile from the Biała Przemsza River. This may be due to the fact that the Biała Przemsza River runs very close to the mining and smelting area and is directly contaminated with the trace metals.

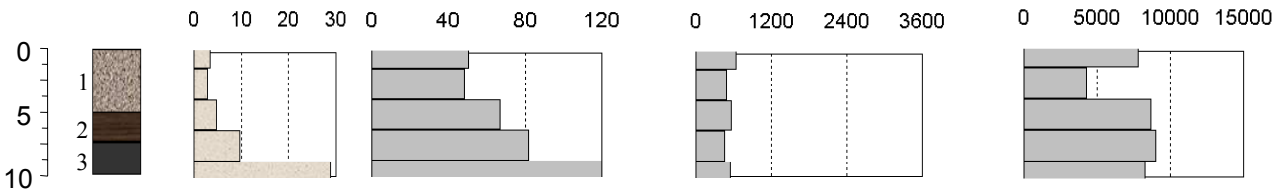
Fig 2 Distribution of the heavy metals in the sediment profiles

a/ the Biała Przemsza River



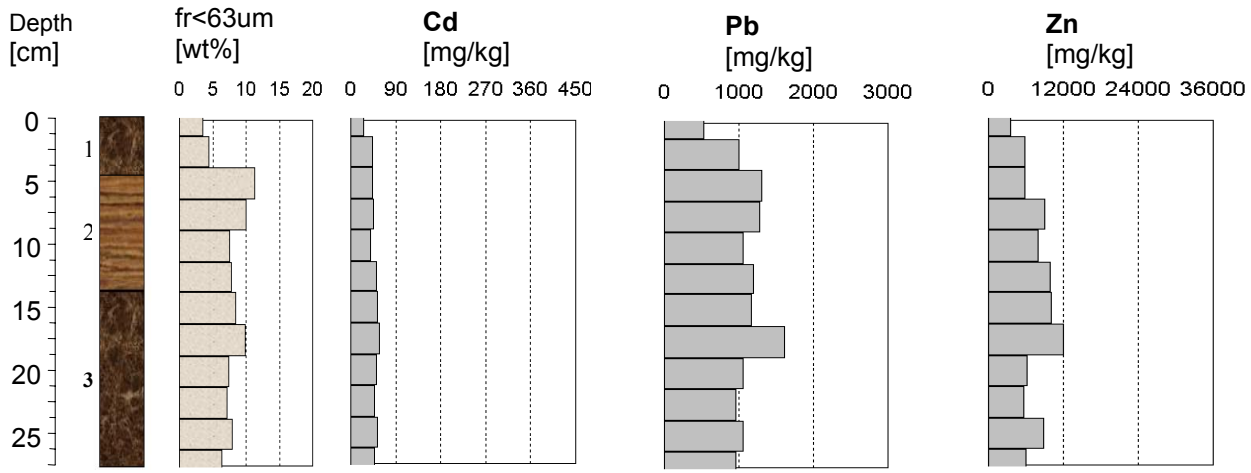
1.light medium-grained sand 2. medium-grained sand with some roots 3. fine- grained sand 4. dark medium-grained sand 5.dark fine- grained sand 6. dark coarse- grained sand 7. loosely bonded coarse- grained sand

b/ the Czarna Przemsza River



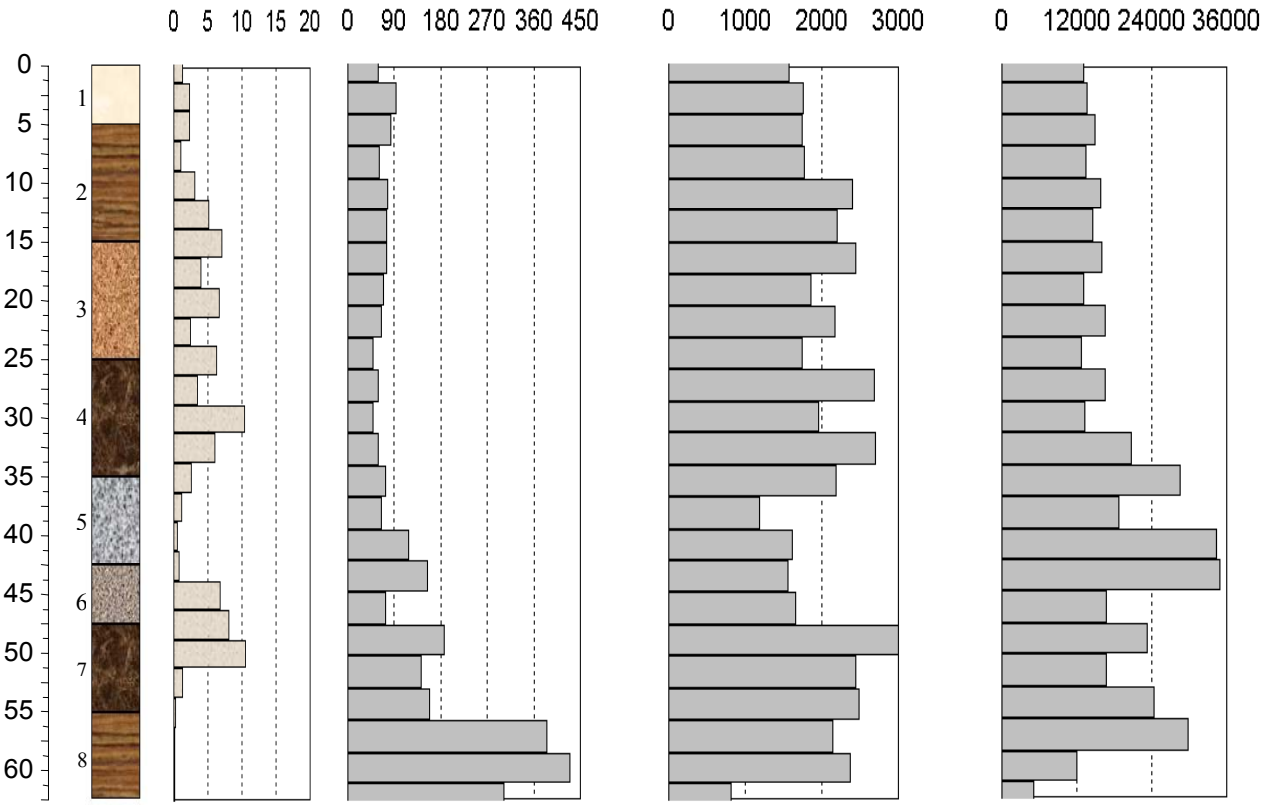
1.dark medium-grained sand 2. dark fine- grained sand 3.silty-clay

c/ the Przemsza River (7P)



1. fine- grained sand 2. silty –clay dark with some roots 3 fine- grained sandy-clay

d/ the Przemsza River (8P)



1. light medium-grained sand 2. medium-grained sand with some organic particles 3. fine- grained sand with some roots and red grain 4. dark fine- grained sandy clay 5. gray medium-grained sand 6. fine-grained sand 7.silty clay 8. medium-grained sand with bit of organic material.

Table 1 Determination coefficient (R) of the linear dependences between the heavy metal concentration in the sediment profiles

R	Localization											
	Biała Przemsza 1BP (n=17)			Czarna Przemsza 2CP (n=5)			Przemsza 7P (n=12)			Przemsza 8P (n=24)		
	Cd	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**
Cd	x	**0.91**	**0.78**	x	-0.21	0.51	x	0.76	0.74	x	0.01	0.09
Pb	x	x	**0.90**	x	x	0.19	x	x	0.79	x	x	0.18
Zn	x	x	x	x	x	x	x	x	x	x	x	x

Conclusions,

The Przemsza river system is a perfect example of an affected river environment. The studied river system lies in a region of high industrial activity, mainly mining and smelting. The results of the studied river sediment depth profiles showed that the concentration of metals was very high and not stable over time, the contents of heavy metals especially Cd, Pb, and Zn in most cases exceeded the geochemical background even in the deep profile sections. There is a very strong linear correlation between the concentrations of lead, zinc and cadmium in most of vertical profiles indicating that these heavy metals might be discharged from the same pollution sources and had identical depositional activities. Fine particles (fraction <63 um) contain greater amount of heavy metals than the bulk sample: for Cd is from 1,5 to 17, for Pb from 3 to 56 and for Zn from 3 to 36 times more. There is no linear correlation between the metal concentration in the fraction <63um and in the bulk samples.

Even though some of the plants have been shut down, there is continuous discharge into the river, which contaminates it to a great extent. For this day, water itself does not pose an alarm as to the extent of contamination with heavy metals. It is the bottom sediment that does so. That is exactly why this research project was based on analysis of the sediment profiles. It is imperative that further studies should be carried out, as heavy metal contamination is of great importance.

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