

Heavy metals contamination of river sediments at the historical industrial areas in Poland

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Introduction: The main sources of heavy metal pollutions in the river systems are Cu-mining and smelting industry at the Lower Silesia, Zn-Pb mining and smelting industry at Upper Silesia and chemical industry in south-west Poland. During the last 100-150 years, a considerable increase of heavy metals concentration in the river sediments has been observed in those areas.

Methods: The bottom sediments and their cores were taken from the Odra and the Vistula Rivers and their tributaries. The $<20\mu\text{m}$ or $<63\mu\text{m}$ size fractions were used for analysis (digestion with conc. nitric acid or aqua regia in microwave oven). In order to assess the metal mobility in the selected sediment samples, the chemical and/or mineralogical forms of metals were determined, using indirect (sequential extraction method) and direct (X-Ray, SEM/EDX, TEM, microprobe) analytical methods. Metal concentration was determined by ICP-MS and AAS methods.

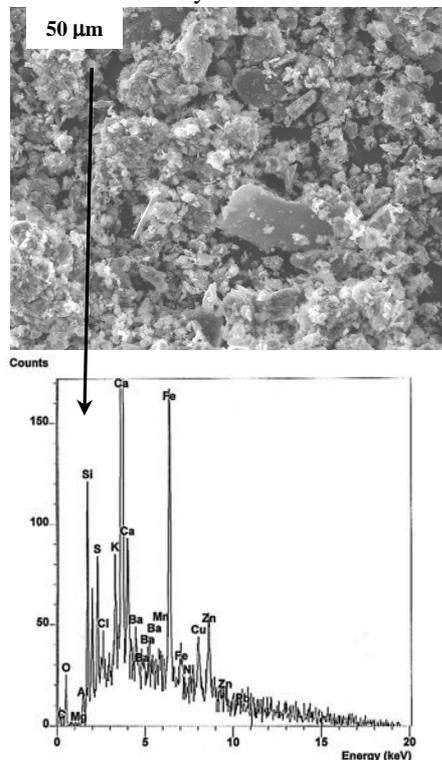


Fig. 1: SEM micrograph and X-ray energy dispersive spectrum for the Odra River sediment clay fraction at Cu-industry area.

Results: Concentration of metals and their mobility were studied in the sediments cores from the Odra and Vistula Rivers and their tributaries. The following range concentrations (mg/kg) of Cd (0.11-1400), Pb (30-19920), Cu (13-1185), Zn (168-62600) As (150-480) and Tl (0.72-59) were found in the sediments at the historical mining and smelting areas. Maximum concentrations of all these metals were found in the river sediments at the area of the Zn-Pb mining and smelting industry, while of Cu also at the Cu mining and smelting area. From studied metals, Cd and Zn seem to be of particular concern because of the high level, and their high mobility. The mobile forms of Cd and Zn reached for each up to 50% of their total amount. From SEM/EDX method is evident that considerable portions of Zn and Cu in sediments from metallic ores mining and smelting area occur as sulfides (Fig.1). In the surrounding of the chemical industry very high content of Cr was found in the sediments of the Vistula River tributary; the highest amounts (13430-17100 mg/kg) were stated at the 10–15cm depth of sediment cores. The main stable form of Cr was ferroan magnesiochromite, detected by XRD and SEM/EDX [1], which corresponds with high portion (~90%) of Cr bound with reducible fraction of sediments.

Discussion: The river sediments at the surrounding of mining and smelting industry are very strongly contaminated with metals, which can also migrate into the deeper sections of sediment cores [2]. Their sources could be geogenic (because of mineralization) and anthropogenic (because of processing and smelting activities). In some cases the metals could be transported into the river systems in the forms which appeared either in the raw material or in the wastes, but they can also undergo weathering processes and thus transform into more mobile forms, e.g. metal sulfides → metal sulfates, or chromates → Cr-oxides (spinel).

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References: [1] Helios Rybicka, Wilson (2000) *ESPR – Envir. Sci. & Pollut. Res.* 7 (1):7-13; [2] Helios Rybicka, Adamiec, Aleksander-Kwaterczak (2005) *Limnologia* 35 : 185-198.