

## Heavy Metal Species in Sediments of Lake Süßer See, Germany

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**Introduction:** For about 800 years, the Mansfeld region in eastern Germany has been affected by the exploitation of heavy metals contamination from the copper shale outcrops at the western margin of the Mansfeld geosyncline structure. After the suspension of mining and smelting activities in the late 1980's, substantial amounts of additional waste forms of slag or "Theisenschlamm", a gas washing residue of the smelters have been exposed to the surface aqueous environment. Almost all streams in the mining region feed into one stream, the "Böse Sieben", which eventually flows into Lake Süßer See. Because the lake is the central sink for the Böse Sieben, the lake sediments have accumulated heavy metals.

**Methods and Materials:** We examined the heavy metal contents of the sediments in several vertical profiles lined up along the lake axis to obtain records of the dimensions of heavy metal contamination as a function of time. Furthermore, we studied the sediment metal speciation to determine their hazard potential with regard to remobilization and to discover the geochemical processes of heavy metal accumulation. Wet chemical methods (such as sediment digestions and selective extractions) were performed to determine bulk metal concentrations in the sediment. Several analytical techniques were utilized: X-ray diffraction, scanning electron microscopy (with EDS), microprobe X-ray fluorescence mapping (micro-XRF) and microprobe X-ray absorption near-edge structure (micro-XANES). In most cases, the EDS, XRF and XANES analyses were conducted on identical particles in a surface sediment sample and 30- $\mu\text{m}$  thick thin sections of the lake sediments were used for these studies.

**Results:** Maximum sediment metal concentrations were found to be as high as 5% Zn, 0.5% Pb and 0.5% Cu and these metal concentrations vary strongly within the vertical profiles. Highest concentrations can be found in a 30-cm thick layer within the upper 60-cm of the sediment profiles that represent a period of intensive mining and smelting activity between 1960 and 1980. The micro-XRF-based elemental images of the thin sections indicate that most of the heavy metals are concentrated in small  $\sim 20$   $\mu\text{m}$ -sized areas and that the contamination is heterogeneously distributed. The spectroscopic studies on several sediment samples collectively indicate that most of the heavy metals are bound in sulfides (ZnS, CuS,  $\text{Cu}_2\text{S}$ ,  $\text{CuFeS}_2$ ). For Zn, other phases are present, such as Zn(II)-carbonate or Zn(II)-hydroxycarbonate and possibly trace amounts of ZnO. The micro-XRF elemental imaging showed that some of the Pb was co-associated with Zn (possibly as a solid solution with ZnS). The micro-XANES spectra for Pb at these Zn-enriched regions and at Zn-depleted regions resembled that of PbS.

**Conclusions:** By combining micro-XANES, SEM-EDS and micro-XRF techniques on the identical samples we identified the host phases of the heavy metals on a micro-sample scale. This approach is a step forward in our attempt to identify the anthropogenic sources of the heavy metals contamination of the lake sediments.

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