Zn-Cd sulfides formation at the contact zone between organic-rich wetland and alkaline wastes

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A contact zone between organic-rich wetland and a wind-redeposited layer of alkaline tailings from Pb-Zn metallurgical processes has been studied. The study addresses elements (As, Fe, Pb, Zn, Cd, Tl, Ga) redistribution and new phases formation in a system of contrasting redox conditions.

Two cores ~50cm long were collected at sites differing in water saturation. Organic-rich material located directly beneath the wastes at 12-14 cm depth was selected. Several methods were applied (XRD, SEM, Mossbauer spectroscopy, ICP-MS, sequential extraction) to understand processes which govern metals behaviour and are responsible for their accumulation at the contact zone.

The waste material, composed of quartz (SiO_2), cerussite ($PbCO_3$), calcite ($CaCO_3$), hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}$ $4H_2O$) and low-crystalline FeOOH, contains up to 4.5% Pb, 6.7% Zn and 0.3% Cd. At the contact with the underlying organic material massive precipitates of FeOOH, Fe sulphates, and phosphates were observed on plant roots using SEM. They commonly contain traces of Al, Zn and Pb. XRD confirmed their amorphous state. Within the iron phases or covering decaying plant debris, numerous spheroids of Zn-Cd sulfides of a size <1μm were found. Commonly Cd dominates over Zn, but pure ZnS also occur. Conversely, Pb and Fe sulfides remained undetected. The observation consents with Mossbauer results indicating the only presence of ferric iron. Sequential extraction confirmed Cd occurrence in sulfides, Tl in both sulfides and FeOOH, and a general association of Pb and Ga with Fe and Al phases. Arsenic was exclusively incorporated in the Fe phases.

The selective precipitation of Zn-Cd sulfides was achieved by microbial sulfate reduction at microsites containing degradable organic matter and due to suppressed activity of iron, present in the ferric form. The investigation suggests that metal sulfides are much more common than suspected and are important hosts of potentially toxic metals in wetlands dominated by ferric iron precipitates.

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