Time-resolved in-situ detection of newly formed secondary Mn and Fe oxides using a SQUID gradiometer technique

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The post U mining area near Ronneburg (Thuringia, Germany) provides a powerful study site to investigate the formation of secondary Fe and Mn oxides/-hydroxides in an acidic soil. Those secondary phases identified in the field as birnessite, todorokite and goethite act as heavy metal scavengers (e.g. for Cd, Co, Cu, Ni, Zn) and therefore contribute to natural attenuation processes. To understand the formation of those phases under acidic conditions a novel lysimeter approach was designed to monitor relevant processes in-situ.

To mimic field relevant conditions the design was chosen to allow continuous flow of contaminated groundwater through the substrate from the bottom to the top in the lysimeter by a mariotte´s bottle. All materials for the lysimeter (soil, groundwater) were taken directly from the field. Time- and spatially-resolved measurements of the newly formed phases were performed by a highly sensitive SQUID (Superconducting Quantum Interference Device) technique for the first time on such a small scale. In combination with hydrogeochemical investigations (chemistry of the soil solution, pH, Eh, etc.) the processes of secondary mineral formation could be revealed in the lysimeter after 9 months of experiment. Thereby, three secondary mineral phases could be detected: a salt crust, iron oxides and manganese oxide. The precipitation of a salt crust at the top of the lysimeter could be identified to be epsomite the same evaporite than the one found in the field indicating similar processes. The formation of Fe oxides (goethite) in the lysimeter could be proven as dissolution and re-precipitation process according to predominant pH/Eh conditions. For the Mn oxides it seems to be a more complex interaction of the groundwater and soil material with bacteria and organic matter. However, similar mineral structures (MnO_2) than the ones in the field were formed.