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Biogenic precipitation of manganese oxides and enrichment of heavy metals at acidic soil pH

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The precipitation of biogenic Mn oxides at acidic pH is rarely reported and poorly understood, compared to biogenic Mn oxide precipitation at near neutral conditions. Here we identified and investigated the precipitation of biogenic Mn oxides in acidic soil, and studied their role in the retention of heavy metals, at the former uranium mining site of Ronneburg, Germany. The site is characterized by acidic pH, low carbon content and high heavy metal loads including rare earth elements. Specifically, the Mn oxides were present in layers identified by detailed soil profiling and within these layers pH varied from 4.7 to 5.1, Eh varied from 640 to 660 mV and there were enriched total metal contents for Ba, Ni, Co, Cd and Zn in addition to high Mn levels. Using electron microprobe analysis, synchrotron X-ray diffraction and X-ray absorption spectroscopy, we identified poorly crystalline birnessite (δ-MnO_2) as the dominant Mn oxide in the Mn layers, present as coatings covering and cementing quartz grains. With geochemical modelling we found that the environmental conditions at the site were not favourable for chemical oxidation of Mn(II), and thus we performed 16S rDNA sequencing to isolate the bacterial strains present in the Mn layers. Bacterial phyla present in the Mn layers belonged to Firmicutes, Actinobacteria and Proteobacteria, and from these phyla we isolated six strains of Mn(II) oxidizing bacteria and confirmed their ability to oxidise Mn(II) in the laboratory. The biogenic Mn oxide layers act as a sink for metals and the bioavailability of these metals was much lower in the Mn layers than in adjacent layers, reflecting their preferential sorption to the biogenic Mn oxide. In this presentation we will report our findings, concluding that the formation of natural biogenic poorly crystalline birnessite can occur at acidic pH, resulting in the formation of a biogeochemical barrier which, in turn, can control the mobility and bioavailability of heavy metals in acidic soil environments.