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Natural attenuation of lead by microbial manganese oxides in a karst aquifer

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Lead is a toxic environmental contaminant associated with current and historic mine sites. Here we studied the natural attenuation of Pb in a limestone karst cave system (Mendip Hills, Somerset, UK) that receives drainage from the ancient Priddy Mineries. Extensive deposits of manganese oxides were observed to be forming on the cave walls and as coatings in the stream beds. Mn(IV) oxide minerals are highly reactive and can scavenge toxic metals from the environment such as Pb, As, Ni, Cr, Co, Cd via sorption and incorporation. Analysis of these cave crusts identified them as birnessite (δ-MnO_2), enriched in Pb (up to 56 wt%) and Zn (up to 11 wt%).

In the presence of oxygen aqueous Mn(II) is oxidised to Mn(IV), predominantly by heterotrophic bacteria and fungi due to the high activation energy of the reaction. Therefore we hypothesised that these cave crusts were actively being formed by microbial Mn(II)-oxidation. Microbial communities were characterised by 16S rRNA and ITS amplicon sequencing (llumina MiSeq). The birnessite deposits contained abundant and diverse prokaryotes and fungi, with ~5 % of prokaryotes and ~10 % of fungi closely related to known heterotrophic Mn(II)-oxidisers. Up to 17 % of prokaryote sequences were assigned to groups known as autotrophic ammonia and nitrite oxidisers, suggesting that nitrogen cycling may play an important role the cave crust microbial communities.

Heterotrophic Mn(II)-oxidising microorganisms were isolated from the birnessite cave crusts, and two isolates (*Streptomyces* sp. and *Phyllobacterium* sp.) could oxidise Mn(II) in the presence of 0.1 mM Pb. Both genera are known to be metal resistant, but this is the first time Mn(II) oxidation by *Phyllobacterium* sp. has been reported. Enrichment cultures of the cave crusts supplied with acetate stimulated Mn(II)-oxidation, but excess organics in the form of glucose generated aqueous Mn(II), likely via microbial Mn(IV)-reduction, and therefore organic carbon availability may control whether Mn(II) oxidation or Mn(IV) reduction occurs, with the formation of Mn(IV) oxides favoured under more C-limited conditions.

Together these results suggest that in this karst cave, microbial Mn(II)-oxidation contributes to the active sequestration and natural attenuation of Pb from contaminated waters.