Biostimulation approaches to generate recalcitrant uranium(IV) phosphate minerals

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Uranium-contaminated groundwater may be remediated by the addition of electron donors to stimulate the microbial reduction of aqueous U(VI) to insoluble U(IV) *in situ*. However, the susceptibility of microbially-precipitated U(IV) to oxidative remobilisation has raised concerns about the long-term viability of this technique. An alternative mechanism that has been assessed previously is to stimulate the microbial precipitation of U(VI) phosphates via the addition of glycerol phosphate under aerobic conditions, leading to phosphate release following microbial metabolism of the substrate. Here we selected a sediment sample from a UK nuclear site and stimulated the microbial community with 10 mM glycerol phosphate or glycerol under anaerobic conditions, to assess whether uranium phosphate precipitation could be a viable bioremediation strategy.

Results showed that U(VI) was rapidly removed from solution before and during the onset of Fe(III)-reducing conditions. Glycerol phosphate was broken down to release inorganic phosphate to solution, and millimolar quantities of the volatile fatty acids propionate and acetate were generated. U(VI) removal was markedly slower in the systems stimulated by glycerol addition, in which formate was the dominant volatile fatty acid. X-ray absorption spectroscopy revealed that glycerol phosphate stimulation promoted the formation of a U(IV)-phosphate mineral similar to ningyoite. This mineral was considerably more recalcitrant to oxidative remobilisation than the products of microbial U(VI) reduction in the absence of phosphate. Investigation of changes in the microbial ecology during glycerol phosphate biostimulation showed that *Pseudomonas* species were dominant during the early stages. A large increase in the abundance of bacteria closely related to *Pelosinus* species occurred between days 4 and 14, suggesting that they may have played a key role in uranium removal in these experiments.

This is this first time that U(IV) phosphate minerals have been generated via the biostimulation of sediments. This work therefore has significant implications for the long-term stewardship of uranium-contaminated groundwater.