

## Redox controls on Tc, U, Np, and Pu behaviour in sediments

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Globally there is a substantial legacy of radioactively contaminated land. A fundamental understanding of the behaviour of redox active radionuclides is essential in innovating new *in situ* remediation technologies to assist in managing this legacy. An ongoing UK NERC funded research programme combines biogeochemical and geomicrobiological techniques to determine the redox cycling behaviour of the radionuclides Tc, U, Np and Pu in the soil sub-surface, under reducing and oxidising environmental conditions.

Here, we describe results from microcosm experiments performed on aquifer sediment samples representative of the Sellafield nuclear site, UK. Microcosms were spiked with Tc(VII)O<sub>4</sub><sup>-</sup> and the behaviour of Tc was monitored during bioreduction at both pH 5 and 7, with and without added nitrate (a common co-contaminant at nuclear sites). During anaerobic incubation over ~ 250 days, pH 5 microcosms with added NO<sub>3</sub><sup>-</sup> and pH 7 microcosms progressed through terminal electron accepting processes (TEAPs), and Tc(VII) was removed from solution *via* reduction to Tc(IV) during microbial Fe(III) reduction. In contrast, pH 5 microcosms without added NO<sub>3</sub><sup>-</sup> did not progress through the TEAPs and Tc(VII) was not removed from solution. Bioreduced sediments were then exposed to both air and nitrate to investigate Tc behaviour during redox cycling. X-ray absorption spectroscopy confirmed that hydrous Tc(IV)O<sub>2</sub> like phases were present in both the reduced and reoxidised sediments.

## Isotopic tracers of surface derived components in arsenic-rich shallow aquifers in Southern Asia

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In many areas of Southern Asia concentrations of arsenic in groundwater frequently exceed the WHO guideline value of 10µg/l. This has grave current and future health implications for millions of people [1]. Whilst it is widely agreed that arsenic is released through the reductive dissolution of iron oxides [2], the control/s on this mechanism is a subject of debate. It has been suggested that extensive pumping of shallow groundwaters in this region for irrigation purposes may have accelerated the rate of release of arsenic from the sediment [3]. This is because modern organic carbon is drawn into reducing aquifers where it acts as an electron donor in microbially mediated reactions, dissolving ferric oxide minerals and their sorbed As load [3]. In this study we assess the role of the hydrogeology on arsenic occurrence on a scale representative of that of the spatial variability of arsenic by taking 20 samples over a 5 km transect from the Hoogly River through the town of Chakdaha, West Bengal.

δ<sup>18</sup>O and δD, accompanied with noble gas data, will be used to assess the source of recharge to the aquifer and to trace the involvement of modern surface recharge in these groundwaters. δ<sup>13</sup>C will be used alongside these to assess the source of organic and inorganic carbon to these aquifer systems. This information will be supplemented at a later date by <sup>3</sup>H/<sup>3</sup>He, <sup>4</sup>He and <sup>14</sup>C groundwater dates to provide temporal control on the system. We will present our current progress in this analytical campaign. Combined, this information will be used to model and assess the role of the hydrogeological environment on the occurrence of arsenic in drinking water. If shown to be the case, more informed groundwater pumping practices may form part of future efforts to mitigate the effects of arsenic contamination in groundwater in southern Asia.

- [1] Charlet & Polya (2005) *Elements* 2(2), 91-96.  
[2] McArthur *et al* (2001) *Water Res Res* 39, 109-117.  
[3] Harvey *et al* (2002) *Science* 298, 1602-1606.