

# Interactions Between Anionic Radionuclides ( $^{129}\text{I}$ , $^{79}\text{Se}$ and $^{99}\text{Tc}$ ) and Geocolloids

Heather Sanders, Liz Bailey, Scott Young, Neil Crout

NERC SCIENCE OF THE ENVIRONMENT

TREE



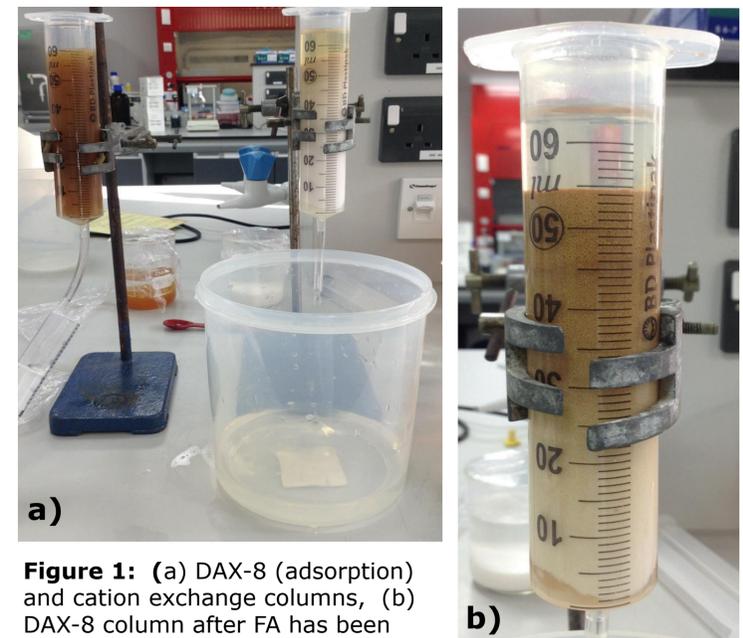
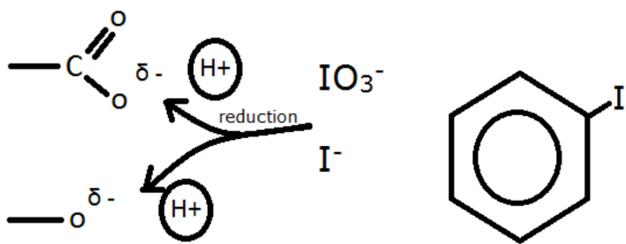
## Overview

The aim of this work is to develop predictive models for the fate of  $^{129}\text{I}$ ,  $^{79}\text{Se}$  and  $^{99}\text{Tc}$  in soils and aquatic systems by resolving underlying mechanisms and reaction rates.

There is a substantial gap in our understanding of the immediate and longer-term reactions of selected radionuclides in terrestrial and aquatic systems. This project will address these reaction mechanisms between selected radionuclides ( $^{129}\text{I}$ ,  $^{79}\text{Se}$  and  $^{99}\text{Tc}$ ) and soil components. Time-dependent changes in speciation will be monitored as the isotopes are progressively incorporated into native soil organic pools in order to elucidate reaction rates and mechanisms. Results will be quantified using geochemical speciation models and by direct measurement of mass/charge balance. A model will be developed predicting the fate of I, Se and Tc released from underground sources (e.g. radioactive waste repositories) and aurally deposited loads.

## Background

Soil organic matter is predominantly composed of humus, 80% of which is accounted for by negatively charged humic substances. It is recognised that iodine, selenium and technetium species can be converted to relatively stable organic forms in soil through interaction with soil humic acid, providing a means by which they can become fixed in non-bioavailable forms. The mechanisms associated with these interactions are poorly understood and there is little quantitative data from which to assess reaction rates and the inherent stability of the resulting organic complexes<sup>[1]</sup>. For example, inorganic iodine may undergo both reduction (of iodate,  $\text{IO}_3^-$ ) and oxidation (of iodide,  $\text{I}^-$ ) to more reactive species (e.g.  $\text{I}_2$  or  $\text{HOI}$ <sup>[2]</sup>) prior to bonding with carbon in aromatic moieties within humic acid. Initial redox interactions with metallic species ( $\text{Mn}^{\text{II}}$ ,  $\text{Mn}^{\text{IV}}$ ) on oxides or with quinone/hydroquinone groups on the surface of negatively charged humic molecules are likely to be highly pH-dependent. Such a range of possible reaction sequences presents a complex barrier to describing the formation-kinetics and stability of humic-isotope interactions.



**Figure 1:** (a) DAX-8 (adsorption) and cation exchange columns, (b) DAX-8 column after FA has been adsorbed.

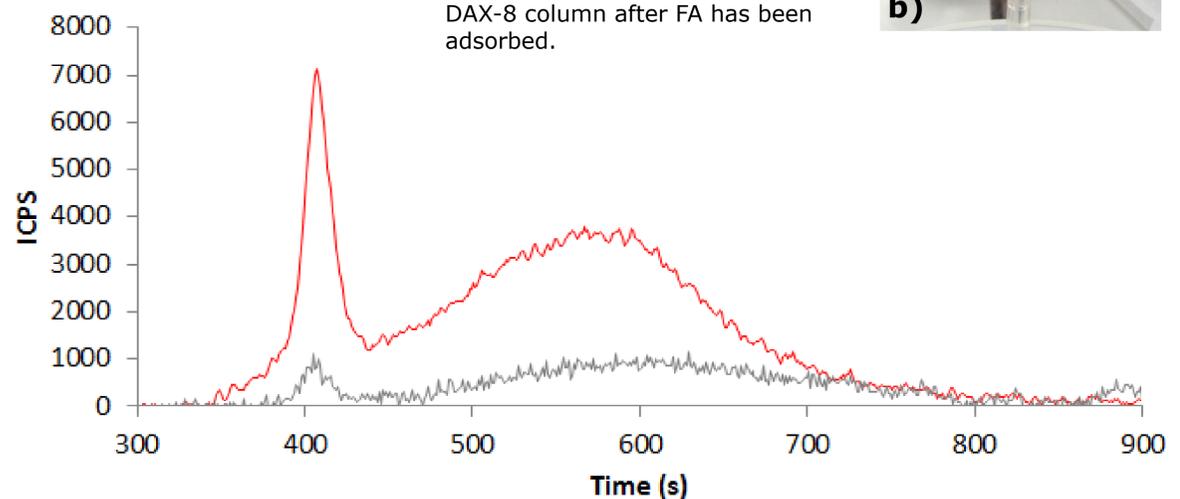
## Approach

To investigate these interactions humic acid (HA) and fulvic acid (FA) fractions must be first extracted from soil, separated and purified:

- HA and FA fractions are extracted using alkali and then separated after acidification which precipitates HA.
- The HA fraction is then washed before dialysis and freeze drying.
- The FA fraction is passed through an adsorption (DAX-8) and then a cation exchange column, before freeze drying (Figure 1 a & b).

A typical experimental protocol involves batch-incubation of the isotopes with HA and FA solutions at a range of temperatures, ionic strengths and pH values in order to generate variable electrostatic charge on the HA and FA molecules, quantifiable via the WHAM(VII) geochemical speciation model.

Time-dependent changes in speciation (chemical form and redox status), will be monitored as the spiked isotopes are progressively incorporated into native organic pools. The principal approach will be the application of 'size-exclusion chromatography' coupled to ICP-MS (SEC-ICPMS) to observe the time-dependent changes in speciation as the isotopes are progressively incorporated (Figure 2). X-ray Absorption Spectroscopy (XAS) may also be used to obtain solid phases speciation information (e.g. Figure 3).

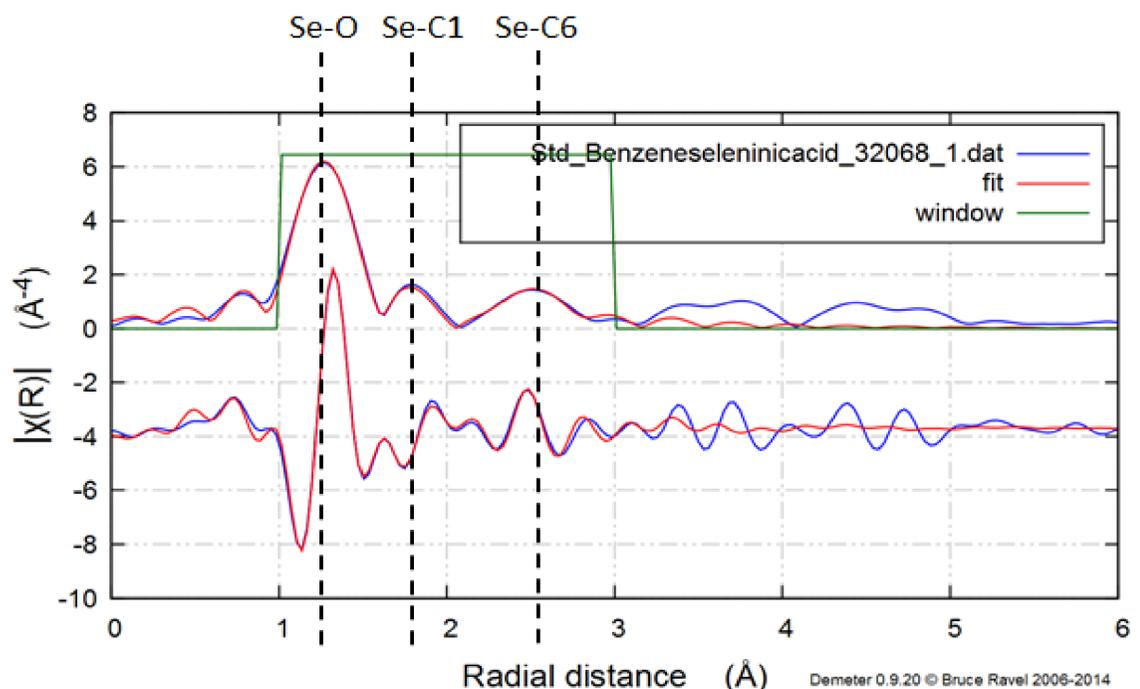


**Figure 2:** Organic-I chromatogram for  $^{127}\text{I}$  (red line) and  $^{129}\text{I}$  (grey line) for a HA solution spiked with iodide and iodate and incubated for 77 days.

## References

[1] Shetaya, WH, Young, SD, Watts, MJ, Ander, EL and Bailey, EH. 2012. *Geochim et Cosmochim Acta* 77, 457-473.

[2] Francois R. 1987. *Geochim. Cosmochim. Acta* 51, 2417-2427.



**Figure 3.** EXAFS spectra for selenium standard in the form of benzene seleninic acid.