Accumulation of hexavalent uranium by highly organic soils

At the Needle's Eye Natural Analogue site, South-West Scotland

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Introduction

- **Nuclear power plants** have the potential to provide electricity with similar greenhouse gas emissions per unit electricity to those generated by wind farms
- However, nuclear power generation produces long-lived radionuclides, including **uranium (U),** that have the potential to evade waste containment barriers and contaminate near-surface soils.
- Investigations have been undertaken at the Needle's Eye Natural Analogue site in Southwest Scotland to investigate how **organic soils** impact the **mobility of (U)** in the far-field environment**.**

Background

- In the UK and globally, the general scientific consensus is that **high level nuclear waste**, such as **spent nuclear fuels** should be stored in a **Deep Geological Disposal Facility (GDF).**
- The design of a GDF (fig. 1) must take into account the potential mobility of radionuclides for **1000s of years into the future.**
- This includes considering the **mobility** of radionuclides **in the surface environment** for when they eventually escape the artificial barriers of the GDF

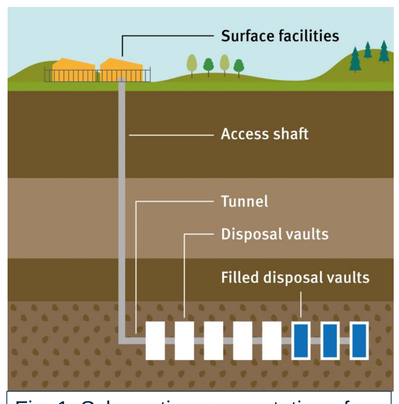

Fig. 1, Schematic representation of a GDF for nuclear waste[1].

Site Description and Methodology

- **Needle's Eye Natural Analogue Site:**
- A naturally occurring mineral U vein leaches U into organic soils
- U accumulates in the organic soils which act as a barrier to U mobility
- The site has complex biogeochemistry[2]

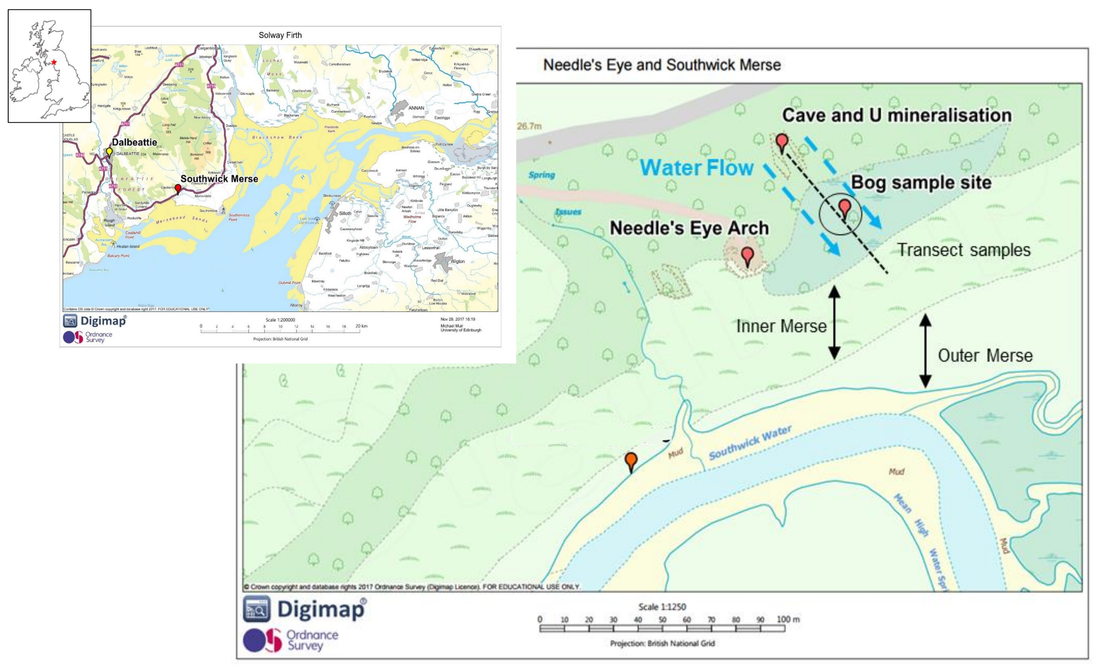

Fig. 2, Map showing the sample site and sampling transect

Sampling and analysis:

- Surface soil samples, soil cores and associated porewaters were collected along a transect (fig. 2).
- Concentrations of U and other elements were determined by ICP-OES or ICP-MS. Fe(II) was measured colorimetrically.
- U speciation was analysed by X-ray Absorption Spectroscopy (XAS)
- The properties of organic matter accumulating U in soils and porewaters were investigated using UV/Vis, FTIR and NMR spectroscopy.

Results

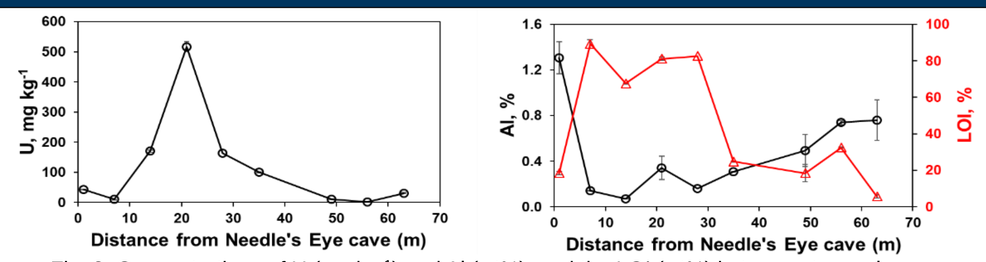

Fig. 3, Concentrations of U (mg kg^{-1}) and Al (wt%), and the LOI (wt%) in transect samples

- The U concentrations in near-surface soils varied along the transect, (fig. 3) with maximum values of **> 500 mg kg^{-1}** at ~20 m from the base of the mineralisation.
- The soils where U is accumulating had a **high organic matter content** (LOI~80%) and a **low mineral content** (e.g. Al <0.5 wt%)

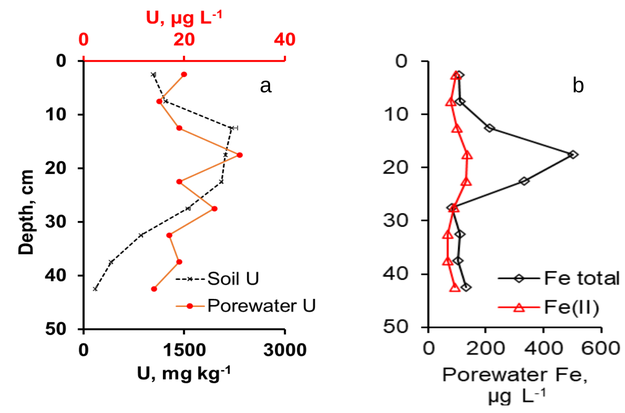

Fig. 4, a) Concentrations of U in soil (mg kg^{-1}) and porewater (mg L^{-1}), and b) Fe(II) and Fe(III) in porewater (mg L^{-1}) from core samples

- Fig. 4a shows the maximum soil U concentration of **~2,500 mg kg^{-1}** at ~20 cm depth and the concurrent maximum porewater U concentration of **~30 mg L^{-1}**
- Fig. 4b shows that the maximum porewater Fe concentration is also at ~20 cm; although the organic soils at this location are typically waterlogged, the waters at ~20 cm are most likely **oxygenated** since most of the Fe is **present as Fe(III)**.

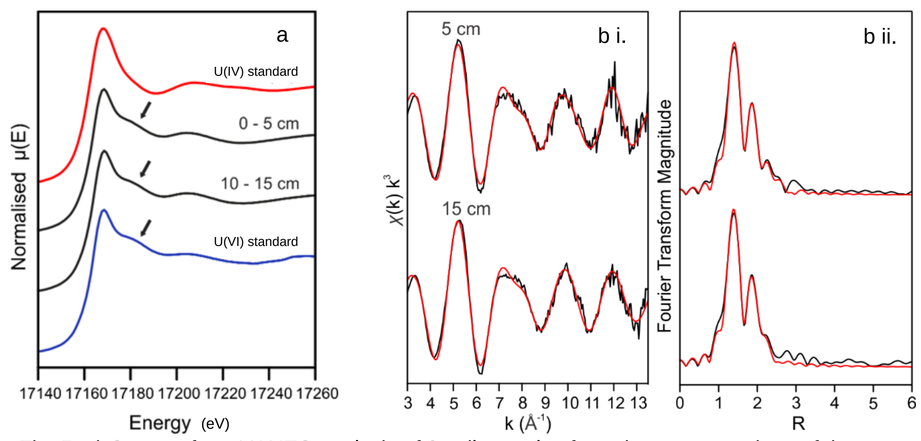

Fig. 5, a) Spectra from XANES analysis of 2 soil samples from the upper sections of the core profile, and b) EXAFS spectra of the same samples

- Analysis by XANES spectroscopy (fig. 5a) showed that U in the upper section of the profile was predominantly **present as U(VI)**
- EXAFS analysis (fig. 5b) showed that U(VI) was directly associated with oxygen bound to carbon atoms.

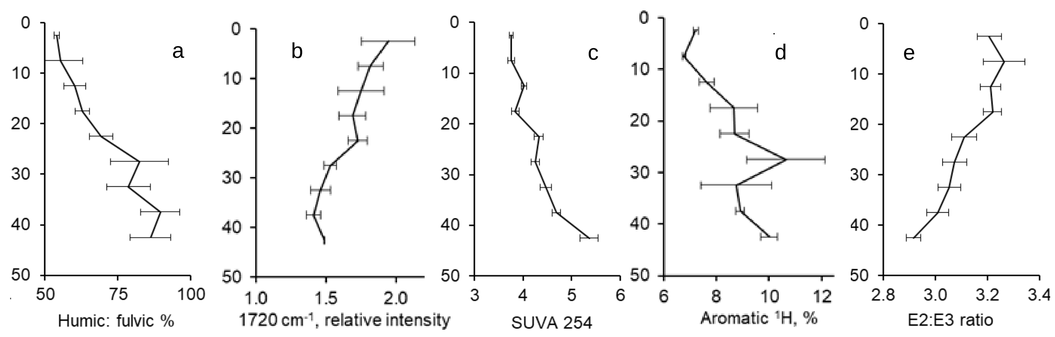

Fig. 6, Results of spectroscopic soil organic matter characterization

- Organic matter characterization by UV/Vis, FTIR and NMR spectroscopy (fig. 6) showed that the organic matter in the region of U accumulation had relatively **high fulvic acid content** (a) with **carboxylic acid** functional groups (b).
- The **aromaticity** (c, d) and **humification** (a, e) of the soil organic matter increased with depth, showing increasing OM degradation.

Conclusions

- U is seen to accumulate to **very high concentrations (~2500 mg kg^{-1})** in highly organic soils
- **U(VI)** is present in the upper sections of the soil profile, **despite waterlogged conditions**
- U(VI) is **directly associated with the oxygen functional groups** of **organic compounds**
- The **soil organic matter** (SOM) where U accumulates has **high carboxylic acid** and **fulvic acid** content
- Further down the soil profile the SOM is **more humified** with **higher aromaticity**

Acknowledgements

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References: [1]Long, J., 2019. "Deep thinking…. Regulating geological disposal" [Webpage]. *Blog: Creating a better place*. URL https://environmentagency.blog.gov.uk/2019/02/04/deep-thinking-regulating-geological-disposal/ (accessed 7.3.22); [2]Fuller, A.J., Leary, P., Gray, N.D., Davies, H.S., Mosselmans, J.F.W., Cox, F., Robinson, C.H., Pittman, J.K., Mccann, C.M., **Muir, M.R.,** Graham, M.C., Utsunomiya, S., Bower, W.R., Morris, K., Shaw, S., Bots, P., Livens, F.R., Law, G.T.W., 2020. Organic complexation of U (VI) in reducing soils at a natural analogue site : Implications for uranium transport. Chemosphere 254, 126859. https://doi.org/10.1016/j.chemosphere.2020.126859