Radionuclides, organic complexing agents and solid phases: Exploring their interactions

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Characterising the geochemistry and speciation of major contaminant radionuclides is crucial in order to understand their behaviour and migration in complex environmental systems. Organic complexing agents used in nuclear decontamination have been found to enhance migration of radionuclides at contaminated sites [1]; however, the mechanisms of the interactions in complex environments are poorly understood [2]. In this work, radionuclide speciation was explored alongside sorption behaviour, to identify ternary interactions between radionuclides, organic complexing agents and sand as a representative environmental solid phase.

Four key radionuclides encompassing different oxidation states (Cs and Sr as important fission products; Th and U(VI) as representative actinides) and three anthropogenic organic complexing agents with different denticities (EDTA, NTA and picolinic acid) were selected for this project. Electrospray ionisation–mass spectrometry (ESI–MS) was used to characterise the speciation of radionuclide complexes over the pH range 4 to 10. Interactions with sand were examined at circumneutral pH using inductively coupled plasma–mass spectrometry (ICP–MS) and dissolved organic carbon analysis.

The results showed that Sr, Th and U interacted with all three ligands and complexation affected their sorption to sand, even in the presence of a seven-fold excess of natural DOC. With EDTA and NTA the solution phase species were identified as: $[SrH_2EDTA]$ and $[SrNTA]^-$; $[ThEDTA]$ and $[ThNTA_2]^{2-}$; and $[(UO_2)_2EDTA]$ and $[UO_2NTA]^-$. These neutral and anionic species interacted with the sand to a greater extent than the uncomplexed radionuclides, thus complexation lowers radionuclide solubility. With picolinate, the cationic $[Cs_2Pic]^+$ and $[Sr_2Pic_3]^+$ species were observed by ESI–MS. The increased solubility of Cs was consistent with this species; however, picolinate did not impact on the sorption of Sr. These results will be explored in the context of sorption kinetics, emphasizing the mechanisms by which the organic co-contaminants affect radionuclide mobility in the environment.

[1] Means, J.L. *et al.* (1978) *Science* **200**, 1477-1481.
[2] Keith-Roach, M.J. (2008, in press) *Sci. Tot. Environ.*

Lithological and flow control of metals in a mountainous river basin, NE Portugal

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The distribution of Cd, Cr, Ni, Cu, Pb and Zn was investigated in fluvial waters and bottom sediments (<63μm fraction) in two different zones of the Corgo mountainous rural hydrographic basin (NE Portugal). These two zones correspond to relatively large valleys, originating from accumulation of Quaternary alluvial deposits on top of Cambrian rocks, in the Campeã Valley (Zone I), and on top of Hercynian granites, in the Vila Pouca de Aguiar Valley (Zone II). Both are agricultural valleys with low population density (Zone I-33 inhabitants/km^2; Zone II-146 inhabitants/km^2). Farmers mainly use manures, and in smaller quantities, phosphate fertilizers in agriculture. Two sampling campaigns were carried out: a) at the end of the wet period (WP) (May), in high-flow conditions; b) at the end of the dry period (DP) (October), in low-flow conditions. In sediment samples the potentially-available fraction and the residual fraction were analysed by a 3-step chemical sequential extraction procedure and *aqua regia* digestion, respectively.

The results show that in the sediment fractions Pb, Cu and Zn are similar in both zones; Cr and Ni are higher in the schist zone; and Cd is higher in the granite zone. In fluvial water, Cu and Zn are slightly higher in the DP in schists and slightly higher in the WP in granites; Pb occurs only in the DP and almost only in schists; Cd occurs almost only in the WP, with higher contents in schists; Cr and Ni are high in the DP in schists, and in the WP are slightly higher in granites.

The main observations resulting from the combination of data on dissolved and particulate metal contents point towards a general diluting effect for metals, except for Cd, in high flow conditions in the schist zone. A contribution of groundwater flow to summer river discharge, associated with a probable slower water flow in soils and sediments from this zone, resulting in an increase in pore water mineralization, should be considered. The higher levels of metals in water from the WP in the granite zone suggest an increase in weathering and transport in winter, with a contribution from finer sediments in suspension to the transport of associated metals. For Cd this behaviour is more noticeable.