

Speciation of Uranium in a Polluted Site: a TRLFS study.

Vannapha Phrommavanh¹, Thomas Vercoouter², Michaël Descostes^{1,3}, Catherine Beaucaire¹ J.P. Gaudet⁴

¹Laboratory for measurement and modelling of the migration of radionuclides,

²Laboratory of speciation of radionuclides and molecules, CEA Saclay DEN-DANS/DPC/SECR/, F-91191 Gif-sur-Yvette cedex

³UMR 8587 CEA – Université d'Evry – CNRS (France)

⁴CNRS-INPG-IRD-UJF-LTHE, BP 53, F-38041 Grenoble Cedex 09

The uranium speciation in a polluted soil was investigated to assess the possible impact on geo- and biosphere. During winter, uranium was found to be mostly under the +VI oxidation state, which is potentially mobile, while it was reduced into less soluble U(IV) species in summer. These observations were correlated with changes of the redox potential due to the activity of sulphate-reducing bacteria. The potential migration of uranium is also highly dependent on its aqueous speciation, particularly concerning U(VI). In this work, the speciation of U(VI) was investigated in real samples by using time-resolved laser-induced fluorescence spectroscopy (TRLFS) and speciation calculations. We show that U(VI) speciation can be determined in carbonate-rich solutions and at ambient temperature by using TRLFS on chemically-treated samples, to remove U(VI)-fluorescence-quenching molecules such as organics.

No U(VI) was detected by TRLFS in the samples collected during the summer period, while the uranyl ion would mainly form calcium carbonate complexes in the winter-collected samples. The relative concentrations of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ will be discussed according to TRLFS results on synthetic carbonate solutions. These complexes have similar fluorescence features. They are usually hardly detected at ambient temperature by TRLFS equipped with a nanosecond-pulse excitation laser because of their fluorescence in the nanosecond time scale. However, we show in the present work that, despite their very short fluorescence lifetimes, U(VI) carbonate species can be quantitatively measured at low concentration by applying a proper signal treatment.