

Effects of natural organic matter on the speciation of uranium

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Introduction

Organic matter is known to complex metals and affects properties, such as sorption, mobility, and bioavailability. This work focuses on interactions of uranium with model organic compounds and complex plant extracts. Molecular weight cut-off filtration and size exclusion chromatography (SEC) with online UV absorption coupled to inductively coupled plasma mass spectrometry were used to qualitatively identify organouranium species in soil and plant materials.

Results and Discussion

An example size exclusion chromatogram (Figure 1) below shows that nearly half of the uranium extracted from the plant tissue grown in uranium containing soil is bound to organic ligands, as indicated by the concurrent ICP-MS and UV absorbance peaks.

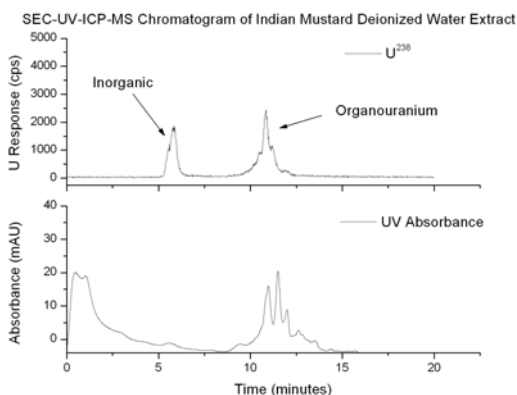


Figure 1: Size exclusion chromatogram of a plant extract.

Sorption studies indicate that humic acid can reduce uranium sorption to soils and can promote subsequent desorption of uranium. These experiments suggest organic compounds may be an important influence on the mobility and chemistry of uranium in the environment.

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Hg²⁺ bonding in soil humic acid and equilibrium partitioning in suspension

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Hg²⁺ bonds very strongly with natural organic matter (NOM) and NOM is important in the fate and transport of Hg. At environmentally realistic Hg/C ratios, Hg²⁺ is bonded to thiol S groups. X-ray absorption spectroscopy suggests that most of the Hg²⁺ is in 2-coordinate thiol S sites when Hg²⁺ is added to H⁺ saturated soil humic acid (HA) at less than 0.3 moles of Hg per mole of low oxidation state S (S_{red}). With more Hg²⁺, O (or N) sites also participate in the bonding. Because of the very strong bonding to thiol, it is not possible to investigate partitioning of Hg²⁺ into solution without using a competitive ligand. DTPA and EGTA do not bond Hg²⁺ with sufficient strength to compete with the S sites in soil HA but dl-penicillamine, a thiol ligand, can desorb Hg²⁺ from HA to attain equilibrium in 6 to 8 days. We conducted equilibrium experiments with IHSS Pahoee Peat HA varying the ratio of Hg to S_{red} from 1:1370 to 1:120, the ligand concentration from 0.25 to 5 mM, and the pH from 2 to 6. We determined K_{oc} ([HA-Hg]/[Hg²⁺]) and the apparent formation constant, K, for RS-Hg-SR sites. K_{oc} was affected by all of the variables but pH had the greatest impact and K_{oc} ranged from 10²² at pH 2 to 10³³ at pH 6. Variation in Hg loading and penicillamine concentration had little effect on K but the “constant” did increase linearly with pH from 10⁴¹ at pH 2 to 10⁴⁴ at pH 6. The slope of the plot of K vs. pH was 0.65. This suggests that at these low loadings, much less than in the XAFS study, 3-fold thiol sites might also participate in bonding with Hg²⁺. Results for six soil HA samples from a forest in Northern Minnesota and an associated SOM sample were consistent with the Pahoee Peat results.