EFFECTS OF ORGANIC MATTER ON THE SPECIATION OF URANIUM IN SOIL AND PLANT MATRICES

A.J. Bednar*, V.F. Medina, and S.L. Larson
US Army Engineer Research and Development Center
Vicksburg, MS 39180

D.S. Ulmer-Scholle and B.A. Frey
New Mexico Institute of Mining and Technology
Socorro, NM 87801

J.G. Moran
New Mexico State University
Las Cruses, NM 88003

ABSTRACT

Radionuclides are known to complex with organic matter, which can promote mobility in soil environments. This work focuses on interactions of depleted uranium with organic compounds using HPLC-ICP-MS to identify organouranium species in soil and plant materials. Nearly all of the uranium extracted from certain plant tissues is bound to organic ligands. These experiments suggest organic compounds may be a significant influence on the chemistry of uranium in the environment.

1. INTRODUCTION

Metal complexation with ligands has been known to affect physical and chemical properties of the affected metal (Nierop, et al., 2002). Natural organic matter (NOM), for example, contains functional groups that can form complexes with metals (Christensen et al., 1999; Chen et al., 2003). Radionuclides, in particular, have been studied and their interactions with NOM reported in the literature (Zhang et al., 1997; Lenhart et al., 2000, Pacheco and Havel, 2001).

Anthropogenic activities, such as mining, milling, and enrichment for nuclear fuel, can increase the potential mobility of uranium (Abdelouas et al., 1998). Additionally, the waste material from the enrichment process, isotopically 'depleted' uranium (DU), also finds uses, particularly in armor and armor piercing munitions (Chen and Yiacoumi, 2002; Sztajnkrycer and Otten, 2004). The United States Army does not use DU munitions for training, but does conduct testing, and DU has been historically used in military conflicts, which can result in the release of metallic DU into the environment (Sztajnkrycer and Otten, 2004). Although metallic uranium is essentially immobile, corrosion reactions can yield oxidized products (Chen and Yiacoumi, 2002), which can dissolve and complex with NOM. This work investigates the extent of organouranium complexes in various plant and soil matrices.

2. EXPERIMENTAL

An Agilent series 1100 High Pressure Liquid Chromatograph (HPLC) was used for all separations and was coupled to a Perkin Elmer Elan 6000 ICP-MS. Reagent grade chemicals and 18.2 $M\Omega \cdot cm$ deionized water were used for preparation of mobile phases, and all solutions were filtered (0.45 μm) prior to introduction into the instrument.

Molecular size exclusion (SE), or gel permeation, chromatography is an on-line size separation technique. A Shodex KW-803 SEC column was used to separate organouranium complexes based on molecular weight (hydrodynamic size). The mobile phase used in all experiments was 21 mM Tris buffer, (pH = 7) because of the protein molecular weight standards used to correlate elution time with molecular size. An ultraviolet-visible (UV) absorbance detector was added in-line prior to the ICP-MS to detect organic moieties. This dual detector capability allowed simultaneous determination of organic moieties that contain uranium and those that do not.

3. RESULTS AND DISCUSSION

Fig. 1 is a size exclusion chromatogram simultaneously using ICP-MS as an elemental specific detector for uranium and UV absorbance (230 nm), as a surrogate measurement for organic matter (SEC-UV-ICP-MS). The plant material in Fig. 1 is Indian Mustard from a phytoremediation study. Both inorganic and organouranium forms are seen in this plant material. The SEC-UV-ICP-MS chromatogram shown in Fig. 2 is of a cryptobiotic soil crust deionized water extract. These samples show the complex nature of the organouranium species extracted by deionized water. The soil crust sample contains a high level of uranium (~100 $\mu g/L$) with multiple inorganic and organouranium species. The

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uranium peak observed at ~6 min appears to be an inorganic colloidal form, as it did not have a significant UV signature, whereas the peaks observed at ~10-15 min consisted of uranium associated with the organic moieties.

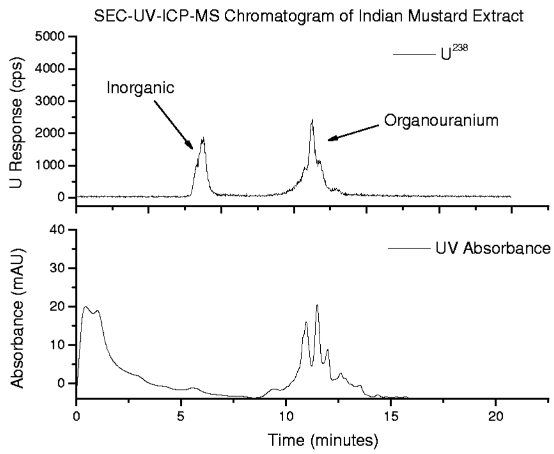

Fig. 1: Size exclusion chromatogram of organouranium complexes extracted from Indian Mustard plant material.

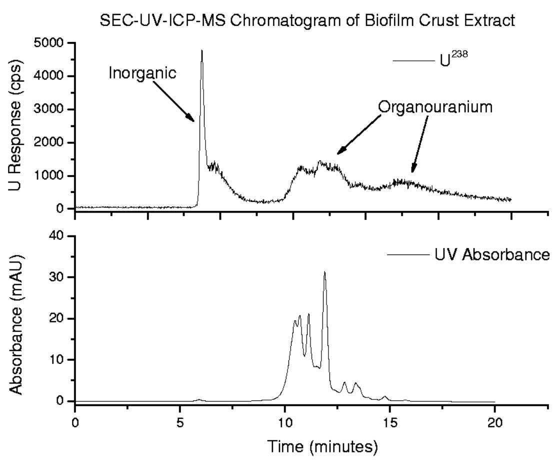

Fig. 2: Size exclusion chromatorgram of organouranium complexes extracted from soil crust material.

The most notable information gained from the SEC data in Figs. 1 and 2 was the distribution of uranium in these samples. Large molecules elute earlier than smaller ones as they are 'excluded' from pore spaces in the column packing. The data for the plant extract (Fig. 1) and the soil crust extract (Fig. 2) indicate that the inorganic uranium peaks (those without a large UV absorbance) were in particulate form and of a larger size than the organouranium complexes (because they elute first at about 6 minutes). Analysis of protein MW standards on this column with this mobile phase suggest the organouranium complexes eluting at 10-15 minutes have similar hydrodynamic size to ~ 3 kDa MW proteins.

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CONCLUSIONS

The experiments presented demonstrate that NOM interactions are important to the chemistry of uranium in natural systems. Size exclusion chromatography was used to investigate uranium binding with organic moieties in plant and soil extracts, and showed multiple inorganic and organouranium forms in natural samples. The results of this work indicate SEC is useful for studying binding of uranium to complex organic moieties found in nature.