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Isotopic investigation of the colloidal mobility of depleted uranium in a podzolic soil

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HIGHLIGHTS

- We investigated the colloidal transport of uranium in a contaminated site.
- We clearly shows the importance of colloids in uranium mobilization and migration.
- Mobilization of anthropogenic uranium is enhanced compared to native uranium.
- Smaller colloids are likely to dominate for the sorption of anthropogenic uranium.
- Native natural uranium is mainly associated with coarser fractions.

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ABSTRACT

The mobility and colloidal migration of uranium were investigated in a soil where limited amounts of anthropogenic uranium (depleted in the ^{235}U isotope) were deposited, adding to the naturally occurring uranium. The colloidal fraction was assumed to correspond to the operational fraction between 10 kDa and 1.2 μm after (ultra)filtration. Experimental leaching tests indicate that approximately 8–15% of uranium is desorbed from the soil. Significant enrichment of the leachate in the depleted uranium (DU) content indicates that uranium from recent anthropogenic DU deposit is weakly bound to soil aggregates and more mobile than geologically occurring natural uranium (NU). Moreover, 80% of uranium in leachates was located in the colloidal fractions. Nevertheless, the percentage of DU in the colloidal and dissolved fractions suggests that NU is mainly associated with the non-mobile coarser fractions of the soil. A field investigation revealed that the calculated percentages of DU in soil and groundwater samples result in the enhanced mobility of uranium downstream from the deposit area. Colloidal uranium represents between 10% and 32% of uranium in surface water and between 68% and 90% of uranium in groundwater where physicochemical parameters are similar to those of the leachates. Finally, as observed in batch leaching tests, the colloidal fractions of groundwater contain slightly less DU than the dissolved fraction, indicating that DU is primarily associated with macromolecules in dissolved fraction.

1. Introduction

Uranium is a natural trace element present in the environment and can be introduced by human activities, including agriculture, uranium mining, nuclear industry or military applications (Garnier-Laplace et al., 2001). Natural uranium (NU) is primarily composed of three isotopes, namely ^{234}U, ^{235}U and ^{238}U, with well-known relative abundances (Table 1). ^{236}U, produced through neutron capture by ^{235}U, occurs as a minor isotope ($^{236}U/^{238}U < 10^{-8}\%$). Types of depleted uranium (DU) are distinguishable by their isotopic and trace element compositions as signatures of their "nuclear history" (Hamilton, 2001). Of these types, two are used in shielding, armor-piercing munitions, or for diverse civilian and military purposes: (i) Non-reprocessed Depleted Uranium (NDU), a waste product remaining after extraction of the fissile isotope ^{235}U from natural uranium during enrichment processes, and (ii) Reprocessed Depleted Uranium (RDU), a waste product remaining after reprocessing of nuclear fuel from various types of reactors using either natural or enriched uranium as an energy source (Hamilton, 2001; Trueman et al., 2004). Like ^{236}U is produced during nuclear fission, RDU contains therefore ^{236}U in detectable quantity. This allows to identify RDU as a component of a commercially available standard solution of uranium (Richter et al., 1999b), making ^{236}U a convenient tracer for laboratory column and batch experiments mixing natural uranium and DU sources. The typical isotopic compositions for uranium in NDU and RDU are presented in Table 1.

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Table 1
Typical relative mass abundances, m_i^k, for uranium isotopes in natural uranium and in natural and reprocessed depleted uranium (DU) sources issued from the nuclear fuel cycle.

Isotope k	$^{234}U/^{238}U$ (mass.%) m_i^{234}	$^{235}U/^{238}U$ (mass.%) m_i^{235}	$^{236}U/^{238}U$(mass.%) m_i^{236}	Reference
Uranium type i				
Natural U	0.0055	0.72	10^{-8}–10^{-10}	(Buchholz et al., 2007; Zhao et al., 1994; Richter et al., 1999a)
Non-reprocessed DU				
(NDU)	0.001	0.2	<10^{-3}	(Bleise et al., 2003; Oliver et al., 2008b; Richter et al., 1999b; Trueman et al., 2004)
Reprocessed DU				
(RDU)	0.001	0.2–0.3	>2.10^{-3}	(Richter et al., 1999b; Danesi et al., 2003; Jia et al., 2006)

Fractionation of uranium isotopes exists in natural environments in relation to low-temperature hydrothermal redox processes, as observed in marine environments, uranium ores or speleothems. The anaerobic reduction of some soluble U (VI) species into insoluble U (IV) species in anoxic to euxinic (sulphidic) conditions is likely to induce fractionation of heavy U isotopes in precipitates, leading to $^{235}U/^{238}U$ variations below 10^{-5} (Weyer et al., 2008; Brennecka et al., 2010). This indicates that natural fractionation of U isotopes is negligible in comparison with the differences in isotopic composition of NU, NDU and RDU. Therefore, the isotopic composition of uranium is a powerful tool for radiological survey and impact assessment after DU contamination in soil or plants (Sansone et al., 2001; UNEP, 2001).

Many studies have examined the properties, use, health effects and mobility of DU (Bleise et al., 2003; Briner, 2010; Handley-Sidhu et al., 2010; Graham et al., 2011). However, the role of colloids in the mobility of uranium in the environment is not completely understood. The reduced mobility of uranium in soils and groundwater is mainly observed when the system is at thermodynamic equilibrium or under steady-state flow (Barnett et al., 2000; Donat, 2010). Sorption onto mineral surfaces is then implicated as mediating this reduced mobility. However, it is now recognized that colloids act as vehicles for a rapid and long-range migration of uranium in subsurface and groundwaters (Artinger et al., 2002; Mibus et al., 2007). The presence of colloids in the environment warrants their consideration in the study of uranium mobility. Inorganic colloids can play a major role in colloidal transport processes (Jackson et al., 2005; Claveranne-Lamolère, 2010). Moreover, the colloidal organic complexes can enhance uranium migration (Ranville et al., 2007; Graham et al., 2008; Crançon et al., 2010; Bryan et al., 2012). Additionally, humic substances can be adsorbed onto soil nanominerals, forming organic coatings that are likely to change their charge and reactivity toward uranium (Murphy et al., 1992; Labonne-Wall et al., 1997; Shen, 1999). However, interactions between uranium and colloids are site-specific, and the proportions of total uranium associated with colloids ranges from 0% to 100% (Bednar et al., 2007; Arnold et al., 2011). Moreover, the proportion of remobilized uranium may be increased in soil or interstitial waters when changes arise in flow velocity or water chemistry. For example, a drop in ionic strength may lead to a partial reversibility of the sorption reactions or limited remobilization of the uranium bound to colloids (Gabriel, 1998; Crançon et al., 2010). Therefore, the acquisition of data under controlled conditions is important to further understand the fate of uranium in environmental media.

The aim of this study was to determine the role of the colloidal phase on the mobilization and mobility of uranium in a podzolic soil. Site investigations were conducted in a soil where limited amounts of DU were deposited, adding to the naturally occurring uranium. To examine the mobilization processes for uranium in soil, laboratory batch leaching experiments were conducted using a common isotopic uranium spiking method, which is fast and easy to conduct with controlled and repeatable experimental conditions. In addition, on-site mobility of uranium was assessed from groundwater and surface water sampling and uranium isotope analysis.

2. Materials and methods

2.1. Field work

The study site is located in the wetlands of Landes Gascony, France. Pyrotechnic experiments in the context of military activities using DU have led to metallic deposits on the surface of a podzolic soil situated on poorly mineralized fluvio-eolian sands. These deposits were then continuously exposed to weathering. The studied soil area overlies a surficial and shallow sandy aquifer. The main chemical and mineralogical properties of the soil and aquifer were previously reported (Crançon and van der Lee, 2003). The soil (taken outside of the DU-deposition area) exhibited a low NU content (typically lower than 1 mg kg^{-1}, which is typical of the NU background concentration for this region) and strong spatial and vertical homogeneity, except in spodic horizons where the uranium content can reach approximately 4 mg kg^{-1} (Crançon et al., 2010). The regional geochemical background in subsurface and groundwaters is characterized by very low uranium concentrations, typically lower than 0.1 μg L^{-1}. These values are among the lowest found in natural waters (Reimann and Caritat, 1998). Fig. 1 depicts a map of the site and sampling points.

The DU content in soil decreases sharply with depth. An artificial pond (point M) is located close to a drain crossing the DU-deposition area from east to west (Fig. 1). The pond and the drain are supplied by the drainage of soils and a shallow aquifer. The drain may be occasionally fed by the pond water at the specific junction location.

Surface and subsurface water samples were collected from the DU-deposition area in ponds, drains and boreholes during a high flow period. 2 L of water were collected for each sample in square bottle 1 L HDPE, and stored at 2 °C until analysis. Pond water samples (point M) were collected in the immediate surroundings of the DU-deposition area. Drain water samples were collected upstream (point A), in the DU-deposition area (point C) and downstream (point E) of the site. Groundwater was sampled upstream (borehole P2, standing for geochemical background and also acting as a control site) and in the immediate surroundings (borehole P0) of the DU-deposition area at about 30 cm depth. Boreholes designed for site monitoring are approximately 15 years old.

O horizons are quite inexistent in the soils from the studies site. Soil samples were collected in the DU-deposition area (Fig. 1) in horizon E (the most superficial soil horizon) at around 40 cm depth. For that, a 1-m deep vertical trench was dug. Soil samples were stored at a temperature of 5 °C in plastic bags.

2.2. Sample analysis

For sample filtration, regenerated cellulose filters with a 1.2-μm cut off from Millipore (Bedford, MA, USA) were used as separation between particular and colloidal fraction. Ultrafiltration was