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DGT as a useful monitoring tool for radionuclides and trace metals in environments impacted by uranium mining: Case study of the Sagnes wetland in France

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HIGHLIGHTS

- The DGT technique was used to measure uranium, radium and other trace metals in the vicinity of a former uranium mining site and compared to ultrafiltration.
- A general good agreement was observed between the DGT fraction and the <10 kDa fraction.
- A novel DGT holder was constructed to measure porewater profiles in soils up to 75 cm depth.
- The soil DGT profiles can provide information on the lability of the metal complexes.

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ABSTRACT

The Diffusive Gradients in Thin films (DGT) technique was used to analyse U, ^{226}Ra and other trace metals in stream water and soil porewater in a wetland in France impacted by uranium mining. High resolution profiles of metals in soil porewater obtained by DGT could be measured for the first time up to a depth of 75 cm by the construction of a novel DGT holder. In stream water, the DGT technique was compared to speciation carried out by filtration (0.45 μm) and ultrafiltration (UF) (500 kDa/100 kDa/10 kDa) and DGT porewater profiles were compared with piezometer data obtained in a parallel study. An increase in the trace concentrations of dissolved (0.45 μm) and particulate U, ^{226}Ra, and elements such as Al, Fe, Mn and Ba was observed in the stream water as it passes through the bog as a results of mobilization from the wetland. The porewater results indicate DGT labile metals species to be present in porewater and mobilization of uranium and other elements linked to the presence of enriched clays. In stream water, colloids and particles govern the behavior of U, Al and Fe, whereas Mn, Ba and Ra are essentially transported as truly dissolved metal species with DGT labile concentrations accounting for 100% of the dissolved fraction. The combined approaches of DGT and UF allow us to obtain a better understanding on the biogeochemical processes involved in the retention and mobility of U and ^{226}Ra in the wetland.

1. Introduction

Between 1945 and 2001, uranium mining in France has led to the production of 76,000 t of uranium (U). Either mined as open pits or underground mines, these former sites also induced large amounts of rock wastes, mine tailings and mine waters coming from the underground mines. Downstream from these former mines, the influence of these radionuclides on ecosystems is linked to their bioavailability which depends on their speciation, meaning that it results from the combination of many parameters in the study system, such as water chemistry, nature of solid phases, presence of particles/colloids, presence of organic matter, *etc.* Therefore, in order to control the influence of former U mines on ecosystems, it has become relevant to assess bioavailability as well. Among the available techniques, the *in situ* technique Diffusive Gradient in Thin films (DGT) has been developed to mimic the

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biological cell membranes (Davison and Zhang, 1994). It measures a labile fraction of metals, metal species small enough to diffuse in the pores of a diffusive gel and species which can dissociate within the time of diffusion and bind to a resin gel. The DGT probe preconcentrates the analytes, thus making it possible to detect trace levels of contaminants without the need of filtering and preconcentrating large volumes of water. In recent years, the developed and application of the DGT technique has increased enormously, with a wide range of different resins used to trap the compound of interest. DGT can also be applied in sediments and soils in order to obtain high resolution porewater profiles and mobilization rates from the solid phase. The resolution that can be obtained by DGT (cm or mm scale) is much higher that using classical porewater sampling by piezometers (5–10 cm resolution; Wang et al., 2013, 2014). The DGT sediment probes are generally used to investigate processes occurring at the sediment water interface and are thus restricted to the top 10–15 cm of the sediments. In order to apply this technique up to a depth of 75 cm, a novel device constructed to hold 5 sediment DGT probes in series, in order to obtain a continuous profile over 75 cm depth (see Fig. S1 Supplementary information).

Wetlands often act as a sink for uranium and other trace metals, accumulating both metals of natural and anthropogenic origin (Phrommavanh et al., 2008; Regenspurg et al., 2010; Owen and Otten, 1995). For example, Schöner et al. reported a U content of up to 7500 μg/g within peat horizons in wetlands of the Thuringia and Saxony regions of German contaminated by seepage of mine tailings of former U mills (Schöner et al., 2009). Uranium and ^{226}Ra immobilization in wetlands is believed to involve sorption on Fe- and Mn- oxyhydroxides (Sajih et al., 2014) and on organic matter (Bordelet et al., 2013) as well as reductive precipitation of sparingly soluble U(IV) minerals. Due to the relatively high stability and low solubility of uraninite (UO_2) under reducing conditions at near-neutral pH, its formation as a result of (bio)reduction is considered an efficient strategy for U immobilization in sediments and soils. U(IV) —where it occurs in the environment— is generally expected to be a low mobility U species, in contrast to U(VI) species which are generally soluble and mobile.

A wetland in central France located adjacent to a former U mine was impacted by mining activity for several decades. A recent study showed that there were areas within the wetland with U concentrations of up to 4000 μg/g (Moulin, 2008). The geochemistry of uranium has intensively been investigated at this site in several projects which were performed in parallel to the present study (Bordelet et al. (2013), Wang et al., 2013, 2014). Bordelet et al. (2013) demonstrated in sorption experiments that the peat soil had a very high retention for U (over 90%) resulting from both the sorption on organic matter as on mineral phases. Wang et al. (2013) showed the presence of U(IV) in soil as a non-crystalline species bound to amorphous Al–P–Fe–Si aggregates and in porewater as a species associated with Fe and organic matter colloids. An increase in the trace levels of U, ^{226}Ra and other trace metals in stream water passing through the wetland was observed indicating a release from the wetland Phrommavanh et al., 2013.

The main objective of this work was to determine whether the technique of Diffusive Gradients in Thin Films (DGT; www.dgtresearch.com) could be used as a monitoring tool for both the stream water as the peat soil. The DGT technique together with filtration and ultrafiltration techniques was thus applied in the stream water flowing through the bog in order to characterize the transport of natural U and ^{226}Ra, *i.e.* particles, colloids, dissolved species, and to compare ultrafiltration (UF) and DGT results in mining impacted environments. Both techniques discriminate on size, but in contrast to UF which is an equilibrium technique, DGT also depends on the kinetics of dissociation of the metal ligand complexes as they must be able to dissociate within the time of diffusion. Several studies have been performed on the comparison of DGT and UF (Forsberg et al., 2006; Öhlander et al., 2012) as on the DGT lability of the UF fraction (Österlund et al., 2012; Liu et al., 2013). The DGT soil probes were placed in the vicinity of the piezometers in order to compare the data obtained by those two approaches. Comparison between the two methods provides useful information on the remobilization from the solid phase as well as the lability of the metal-ligand complexes in the porewaters.

The DGT technique is applied for the determination of U, ^{226}Ra, Ba, Al, Fe, Mn and U in the water and soils. Ba, Al, Fe and Mn were trapped on Chelex© resin and ^{226}Ra on MnO_2 adsorbent gel (Leermakers et al., 2009).

2. Material and methods

2.1. Study site

The studied wetland is located in central France, the Limousin region, a part of Massif Central, where igneous rocks such as granite dominate (see Boekhout et al., 2015 for typical description). The Sagnes wetland is a river fed, topogeneous peat bog with a stream (Ruisseau des Sagnes) flowing through the top soil. The wetland has been affected by the storage of waste rock piles from the former open-pit and underground U mining site located north of the wetland. The uranium rich clays from the former settling pond have dispersed into the wetland, the lowest topographic point (see Wang et al., 2013, 2014 for further descriptions) (Fig. 1).

2.2. Water sampling

Surface waters were sampled during three sampling campaigns (April 2011, Nov 2011 and July 2012) from upstream to downstream of the wetland up to entrance of the lake. Physico-chemical parameters such as pH, Eh, dissolved O_2, conductivity and temperature were measured *in situ* (VWR MU 6100H and WTW 3430 portable multi-parameter instruments).

Filtrations and ultrafiltrations (UF) were performed immediately on site. For dissolved metals, samples were filtered through 0.45 μm membrane syringe filters (Chromafil). For particulate metals a 1 L water sample was collected and 200–500 mL was filtered through a 0.45 μm Polyvinylfluoride (PVDF) 0.45 μm filters (Durapore, Millipore). A water sample was collected at the start of the DGT deployment, in the middle and at the end of the 3 day deployment. UF were performed in July 2012 for the sampling points S1, S2, S3 and Downstream sampling spots, and for Blank and Post-Blank (with ultrapure water before and after processing samples).

The ultrafiltration used in this study was a cross flow MilliPore Pellicon®2 cassette filtering system with Biomax MilliPore polyethersulfone membranes cut-off of 500 kDa, 100 kDa and 10 kDa (with a 0.5 m^2 filter area). The water samples were collected in 5 L acid-clean plastic bottles and then filtered immediately through a 0.45 μm cellulose acetate filter on line using a peristaltic pump. Ultrafiltration was performed on the 0.45 μm fraction to separate the 500 kDa fraction, and the collected permeate (<500 kDa) was ultrafiltrated again, to separate the 100 kDa and 10 kDa fractions simultaneously. In order to achieve a good recovery, a high cross-flow ratio was maintained at each step. Approximately 0.5 L of water was passed through the filter and discarded before the filtrate was collected. The permeate samples for trace metals and DOC analysis were acidified with ultrapure HNO_3 and H_3PO_4, respectively. Between each sample, the system was sequentially rinsed with MilliQ water, 0.01 M HNO_3 and 0.01 M NaOH solutions according to the procedure described by Guo and Santschi (2006).