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Uranium aqueous speciation in the vicinity of the former uranium mining sites using the diffusive gradients in thin films and ultrafiltration techniques



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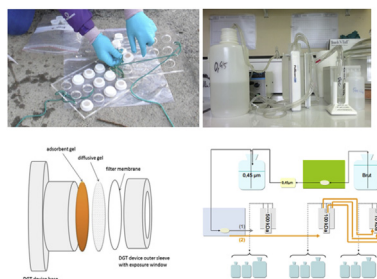
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HIGHLIGHTS

- The applicability of the DGT technique in the vicinity of former uranium mining sites was evaluated.
- The binding selectivity order of the binding phase is the imperative factor influencing the performance of the DGT method.
- There is a good agreement between U concentration measured by the DGT technique and 10 kDa ultrafiltrate.
- DGT technique can be used as an alternative to ultrafiltration method to determine a potentially U bioavailable pool.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of the Diffusive Gradients in Thin films (DGT) technique with Chelex[®]-100, Metsorb[™] and Diphonix[®] as binding phases was evaluated in the vicinity of the former uranium mining sites of Chardon and L'Ecarpière (Loire-Atlantique department in western France). This is the first time that the DGT technique with three different binding agents was employed for the aqueous U determination in the context of uranium mining environments. The fractionation and speciation of uranium were investigated using a multi-methodological approach using filtration (0.45 μm, 0.2 μm), ultrafiltration (500 kDa, 100 kDa and 10 kDa) coupled to geochemical speciation modelling (*PhreeQC*) and the DGT technique. The ultrafiltration data showed that at each sampling point uranium was present mostly in the 10 kDa *truly dissolved* fraction and the geochemical modelling speciation calculations indicated that U speciation was markedly predominated by $\text{CaUO}_2(\text{CO}_3)_2^-$. In natural waters, no significant difference was observed in terms of U uptake between Chelex[®]-100 and Metsorb[™], while similar or inferior U uptake was observed on Diphonix[®] resin. In turn, at mining influenced sampling spots, the U accumulation on DGT-Diphonix[®] was higher than on DGT-Chelex[®]-100 and DGT-Metsorb[™], probably because their performance was disturbed by the extreme composition of the mining waters. The use of Diphonix[®] resin leads to a significant advance in the application and development of the DGT technique for determination of U in mining influenced environments. This investigation demonstrated that such multi-technique approach

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provides a better picture of U speciation and enables to assess more accurately the potentially bioavailable U pool.

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1. Introduction

Uranium (U) is a primordial, naturally-occurring radioactive element that is present in aquatic environments at trace levels. The average background concentration of uranium in surface water in Europe is around $0.5 \mu\text{g L}^{-1}$, while variations can extend over four orders of magnitude ($0.002\text{--}20 \mu\text{g U L}^{-1}$) [1,2]. Nevertheless, several anthropogenic activities such as U exploration, mining and milling or industrial production of fertilizers increase uranium concentration in the environment. Uranium is known for its dual mode toxicity - radiological and chemical one, with the latter being of a particular concern. Although the radiological impact of uranium is determined by its total concentration and the isotope composition, the U nature, its bioavailability and toxicity are associated with a chemical speciation [1,3]. The bioavailable fraction of metal refers to the metal species, which are immediately available for absorption by a (micro)organism [3,4]. The bioavailable U fraction has not yet been conclusively determined, due to several factors such as inconsistencies in the operational definition of the bioavailable fraction, different methodologies employed as well as differences in the interpretation of the results.

Ultrafiltration (UF) technique is often employed for the estimation of the bioavailable metal fraction, as this method allows precise determination of particulate, colloidal and truly dissolved fractions, using membranes with different cut-offs (e.g. 100 kDa, 10 kDa). This information is vital as metal bioavailability is considered be linked to the truly dissolved fraction, which is operationally defined as the phase with molecules smaller than 10 kDa (~5 nm) [5]. The ultrafiltration technique is neither limited by ionic strength nor by complexation equilibria and it has been used for the uranium speciation measurements in freshwater [6], estuaries [7] and in coastal seawaters [8]. Nevertheless, a vigorous and intricate handling protocol needs to be followed and possible contamination during transport and storage cannot be ruled out. Moreover, the ultrafiltration technique is an expensive, time-consuming and not user-friendly procedure, which might not represent temporal variations in metal concentration, because it is based on a grab-sampling. The alternative is to determine the distribution of metal species present in an aqueous solution by the geochemical speciation calculation codes (i.e. PhreeQC, Minteq, JChess). Afterwards, the bioavailable metal fraction is deduced by taking into account the toxicity of individual metal species. Generally, the uranyl ion and its complexes with hydroxides and carbonates (e.g. UO_2^{2+} , UO_2OH^+ , $\text{UO}_2(\text{CO}_3)_2^{\text{O}}_{(\text{aq})}$) are considered bioavailable and can be interpreted as the potentially toxic U species [9–12]. The toxicity of U complexes with phosphates and natural organic matter (humic and fulvic acids) is unclear, since the existing scientific evidence both support [13,14] and reject [15,16] the toxic effects of uranyl phosphates and U-organic complexes. However, this computational approach needs to be performed in conjunction with filtration or ultrafiltration techniques and it is only applicable in the environments close to pseudo-thermodynamic equilibrium.

An emerging tool for the estimation of the bioavailable metal fraction is the Diffusive Gradients in Thin Films (DGT) technique [17]. DGT is an *in situ* method that provides information about the time-averaged concentration of labile metal species in a solution.

The DGT technique is based on a simple device that accumulates solutes on a binding agent (i.e. a resin/adsorbent immobilized in a thin layer of a hydrogel) after passage through a hydrogel. The key role of the hydrogel is discrimination of metal species based on their size, lability and mobility (the so-called DGT-labile metal species). Afterwards, metal species are effectively immobilized and pre-concentrated on the binding phase gel, what in consequence facilitates the detection of very low concentrations of metals encountered under field conditions. The DGT technique has been employed for the purpose of the assessment of the metal bioavailability, because DGT imitates the diffusion limiting uptake conditions that are characteristic of a metal biouptake [18,19]. However, this is only applicable under some conditions, therefore the relationship between the metal uptake by plant/biota and on the DGT device should be evaluated taking into account the plant/biota species, the element of interest and its chemical form.

The most adequate methodology to estimate bioavailable metal fraction in the aqueous environment needs to involve not only computational and *in-situ* experimental approaches, but should also incorporate the results from naturalistic and ecological approaches, such as the monitoring research on the bio-indicator species. A considerable caution and profound knowledge of the limitations of analytical speciation methods is required when interpreting the bioavailable metal fraction data based only on chemical speciation, therefore the data obtained in this study will be operationally defined as a “potentially bioavailable pool”.

The primary aim of this study was to evaluate the applicability of DGT technique with Chelex[®]-100, Metsorb[™] and Diphonix[®] binding phases in both, natural and mining waters. The fractionation and speciation of U were carried out by filtration (0.45 μm , 0.2 μm), ultrafiltration (500 kDa, 100 kDa and 10 kDa) assisted with geochemical speciation modelling (PhreeQC) and the DGT technique in the vicinity of the former uranium mining sites. Moreover, the feasibility of the DGT technique for the estimation of a potentially bioavailable U pool was investigated based on the comparison of the U-DGT-labile and the 10 kDa *truly dissolved* U fractions.

2. Materials and methods

2.1. Field sites

The studied former uranium mines, Chardon and L'Ecarpière, are located in Pays de la Loire (Loire-Atlantique department) in western France. The field sampling was performed at high flow regime of water systems in January 2015. The mining site of Chardon consists of a former open pit that has been filled up with drainage waters from the underground mine and it is characterized by high salinity (i.e. 1.8×10^{-2} M NaCl). In order to prevent the pit from overflowing, during the winter months a part of the water is pumped into the stream Margerie, which is the tributary of the river Sevre Nantaise. Six sampling stations were located on 4 km of the Sevre Nantaise river's course, in order to investigate the downstream changes in a river after the mining waters have been discharged from the former open pit (Fig. 1). The average flow rate of the river Sevre Nantaise and the stream Margerie during the sampling period was $18.8 \text{ m}^3 \text{ s}^{-1}$ and $10.1 \text{ m}^3 \text{ s}^{-1}$, respectively (data provided by Department of Maine-et-Loire ANJOU).

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