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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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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.

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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 CaUO2(CO3)32–. 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
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 μg L\(^{-1}\), while variations can extend over four orders of magnitude (0.002–20 μg 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 to 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], estuarine [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 (e.g. PhreeQC, Minteq, JChem). 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\(_2\)OH\(^{-}\), UO\(_2\)(CO\(_3\))\(_2\)\(^{2-}\)) 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 the 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\(^{\textregistered}\)–100, Metsorb\(^{\textregistered}\) and Diphonix\(^{\textregistered}\) 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’Escarpière, 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 m\(^3\) s\(^{-1}\) and 101 m\(^3\) s\(^{-1}\), respectively (data provided by Department of Maine-et-Loire ANJOU).
The site of L’Ecarpière has a water treatment plant, which targets particularly at the removal of radium and uranium by the precipitation. This treatment involves the addition of BaCl₂ to precipitate radium by co-precipitation of Ba(Ra)SO₄ and the addition of lime to increase pH and to assist the precipitation of Fe(III) oxy-hydroxides, with co-precipitation of uranium and other mining related elements. The treated waters pass several precipitation basins and afterwards they are discharged into the river Moine. The quality of Moine river water was examined over 0.3 km course at three sampling stations-the upstream of the Moine river, the mining discharge water and at the confluence zone after the mining discharge (Fig. 2). The average flow rate of the river Moine during the sampling period was 7.1 m³ s⁻¹ (data provided by Department of Maine-et-Loire ANJOU). The discharge flow rate at the sampling spot (7) was approximately 60 m³ h⁻¹.

2.2. Filtration

The water samples were filtered in the field through a 0.45 μm and 0.22 μm pore-size membrane syringe filters (Chromafil). Those samples for trace metals analysis were acidified on-site with ultrapure HNO₃ and those for anions and major cations analysis were stored without treatment. Dissolved Organic Carbon (DOC) water samples were acidified with ultrapure H₃PO₄. Dissolved Inorganic Carbon (DIC) water samples were preserved using HgCl₂ and no air space was left in the bottles. The filtration field blanks were collected at the start and at the end of the sampling mission by passing MilliQ water through the membrane syringe filters.

The temperature, pH, Eh, dissolved O₂ and conductivity were measured in situ with VWR MU 6100H and WTW 3430 portable multi-parameter instruments and associated probes. Total alkalinity was measured titrimetrically using the Hach Digital Titrator and the measurements were done immediately on-site to prevent loss or gain of carbon dioxide or other gases when exposed to the atmosphere or to turbulence during the transport.

2.3. Ultrafiltration

The ultrafiltration used in this study was a MilliPore Pellicon² cassette filtering system with a Biomax MilliPore polyethersulfone membranes cut-off of 500 kDa, 100 kDa and 10 kDa (0.5 m² 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 using Eijkelkamp peristaltic pump. Afterwards, the samples were filtered first using a 500 kDa filter, and the collected permeate (<500 kDa) was ultrafiltered again, using a 100 kDa and 10 kDa filters, respectively. 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 on-line in a 50 mL glass tubes. The
permeate samples for trace metals and DOC analysis were acidified with ultrapure HNO₃ and H₃PO₄, respectively. The system was sequentially rinsed with MilliQ water, 0.01 M HNO₃ and 0.01 M NaOH solutions between each ultrafiltration cycle according to the procedure described by Guo et al. (2007). The ultrafiltration field blanks were collected at the start, in the middle and at the end of the ultrafiltration handling.

2.4. Speciation modelling

The thermodynamic geochemical speciation software PhreeQC was used to predict the U speciation and to assist with the interpretation of the results due to the lack of up to date approachable techniques which are able to measure individual uranium chemical species in solution [24]. A consistent database was based on the LLNL database, modified to include the set of uranium thermodynamic data selected by NEA (Table S1 in SI) [25,26].

2.5. Diffusive gradients in thin films

Milli-Q (ultra-pure) water (>18.2 MΩ cm, Millipore, USA) was used for the preparation of the solutions, gels, cleaning glassware and containers. All plastic equipment were pre-cleaned in 10% (v/v) HNO₃ (pro analysi, Merck, Germany) for at least 24 h and rinsed thoroughly with Milli-Q water. The polyacrylamide (PAM) diffusive gel (Δg = 0.4; 0.8; 1.2 mm) and Chelex®-100 resin gel (Δg = 0.4 mm; Biorad) were prepared according to the procedure described by Zhang and Davison (1995) [17]. Metsorb™ adsorbent gel (Δg = 0.4 mm; Graver Technologies) was prepared based on the protocol of Bennett et al. (2010) [20]. Diphonix® resin gel (Δg = 0.8 mm; Eichrom Technologies) was prepared according to Drozdzak et al. (2015) [21]. The preparation of various gels was carried out under laminar flow hood (class-100) in a clean room. The DGT samplers were supplied by DGT Research and assembled according to the protocol from Lancaster (www.dgtresearch.com). Concisely, the binding phase gel disc was placed on the bottom of a DGT device, with the binding phase side faced up. The binding phase gel was covered by a diffusive gel disc and then a Millipore Durapore membrane filter (0.45 μm, HVLP) was placed on a top of the gels. Assembled DGT samplers were stored at 4 °C in double zippered plastic bags, which contained several drops of 0.01 M NaNO₃.

The DGT device with Chelex®-100, Metsorb™, Diphonix® binding phase gels were deployed in 4 replicates at each sampling point for approximately 24–48 h, with the shorter DGT deployment time at sampling points with elevated U concentration. To assess the presence of the Diffusive Boundary Layer (DBL) at the former open pit (3), the DGT devices containing Chelex®-100 resin gel with different thicknesses of the diffusive layer (0.055, 0.095 and 0.135 cm) were deployed. The DGT devices were affixed to the water treatment station. "The water treatment station" should be included after "Fig. 2. Sampling stations at former mining site of L’Ecarpière (www.maps.google.com)."
several Perspex plates, which were specifically designed for deploying up to nine DGT devices. Then the DGT-Perspex units with the DGT devices facing towards the direction of the stream were attached to a rope and weighted to the river bed. Special caution was taken to prevent the DGT-Perspex units to be settled on the riverbed.

After deployment, the DGT devices were rinsed with MilliQ water and the DGT binding phase gels were peeled off from the DGT devices. The U accumulated on Chemlex®-100, Metersorb™, Diphenik® resin gels were eluted with 1 M HNO₃, 1 M HNO₃ and 1 M HEDPA, respectively [17,21,22]. The DGT field blanks (in triplicate) underwent all processes except the DGT deployment.

The DGT concentration of U accumulated on resin gel (C_DGT, ug L⁻¹) was calculated using Eq. (1) [17]:

\[ C_{DGT} = (M(Ag + σ))/DtA \]  

(1)

where M is accumulated mass of U on the binding phase gel disc (ng), t is the deployment time (s) and A is the exposure area of the DGT sampler (cm²), assumed to be equal to 3.8 cm², to account for lateral diffusion in the DGT device [23]. A is the thickness of the diffusion layer (cm) and σ is Diffusive Boundary Layer, that is determined experimentally for each set of deployment conditions or is assumed to be 0.23 mm in moderate to well mixed waters [23]. D is the temperature-corrected diffusion coefficient (cm² s⁻¹) using the Stokes-Einstein equation [17]. The uranium diffusion coefficients determined previously were applied to the DGT calculations in this study [21].

2.6. Analysis

Trace metals analysis was performed using inductively coupled plasma sector field mass spectrometry (ICP-SF-MS, Element II, Thermo Fisher Scientific Bremen GmbH, Germany), equipped with ESI fast autosampler. Calibration was performed by external calibration, using Indium (2.5 µg L⁻¹ in 2% HNO₃) as an internal standard and 2% HNO₃ as a carrier solution. Analytical standard solutions were prepared from a 1000 mg L⁻¹ in 2% HNO₃ U stock solution (Johnson Matthey Materials Technology, UK) and a 1000 mg L⁻¹ in 2% HNO₃ multi-element solution (Merck, Germany). Certified river water standard reference materials- 1640a (National Institute of Standards and Technology) and SLRS-5 (National Research Council Canada) were used to validate the precision and accuracy of the instrumental analysis. Measured concentrations of all elements in 1640a and SLRS-5 were within the range of provided certified uncertainties. An average instrumental blank of 0.6 ng U L⁻¹ was obtained, resulting in a detection limit of 1.3 ng U L⁻¹ (determined as the average blank + 3 times standard deviation).

The concentration of major cations and anions were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optek Iris Advantage) and by ion chromatography (DIONEX DX 500), respectively. The concentrations of ammonium (NH₄⁺), nitrate and nitrite (NO₂⁻ + NO₃⁻), silicate (SiO₂⁴⁻) and phosphate (PO₄³⁻) were determined by automatic colorimetric methods (QuAAtro, Seal, Analytical). The concentrations of DOC were measured with a total organic carbon analyzer (HiPerTOC, Thermo) and DIC measurements were carried out using stable isotope ratio mass spectrometry (IRMS, Nu Perspective Instrument).

3. Results and discussion

3.1. Filtration and ultrafiltration

River waters were characterized as well oxygenated (dissolved O₂ -12.3 mg L⁻¹), neutral (pH ~7.5) and oxic (Eh ~330 mV ESH⁻¹) waters with low conductivity (~336 µS cm⁻¹). On the other hand the mining waters at the former open pit of Chardon (3) and at the mining discharge point of L’Ecarpière (7) were alkaline (pH ~8–9), characterized by higher major cations concentrations and thus very high conductivity (~2000 µS cm⁻¹ at (7) and ~3600 µS cm⁻¹ at (3)). However, the conductivity and the major ion composition at the downstream sampling stations of Moine (4) and Sevre Nantaise (5) rivers, were at the same level as at the upstream points, (2) and (1), respectively (Table S3 and S4). This indicates that the waters from the former open pit (3) and the mining discharge water (7) did not contribute appreciably to the chemistry of the receiving rivers.

The U concentrations in 0.45 µm, 0.2 µm, 500 kDa, 100 kDa, 10 kDa fractions at each sampling station of Chardon and L’Ecarpière mining sites are displayed in Fig. 3 and Fig. 4. The detailed spatial distribution and fractionation of major cations, anions, trace metals and DOC at each sampling point is also presented in Supplementary Information (Table S3 and Table S4). The total dissolved U concentration in control blank samples and at the upstream sampling points was below 1.5 µg L⁻¹, what indicates that the upstream sampling stations were not influenced by the mining activity. It also implies that the geochemical background U concentration is low and comparable to other natural waters [6,8]. The input from the former open pit (3) significantly increased the U concentration in the stream water of the Margerie (4), but no significant difference between the U concentration encountered at the downstream (5) and the upstream (1) of Sevre Nantaise was observed (Fig. 4). Likewise, the same pattern could be noticed at the L’Ecarpière mining site, where the U content at the confluence zone after the mining discharge (8) was relatively comparable to the one at the upstream sampling station of Moine river (6) (Fig. 3). Given the nature of U, this U decrease at two mining sites is due to a dilution and/or sorption predominantly with Fe(III)oxy-hydroxides in a less extent [27,28]. The precipitates containing Fe(III)oxy-hydroxides were visible in the discharge water flume at (7) and on the DGT devices.

The total dissolved Fe concentration did not differ significantly between the sampling stations and between each former mining site, except at the mining discharge point of L’Ecarpière (7). The lowest total dissolved Fe concentration was encountered in the mining waters at (7), what was probably due to the removal of Fe in the precipitation ponds. The majority of total dissolved Fe (80–90%) was present in >500 kDa fraction, therefore the presence of large Fe colloids of both origin, organic and inorganic, is evident [29–31].

The distribution of U species among different fractions (0.45 µm, 0.2 µm, 500 kDa, 100 kDa, 10 kDa) at different sampling points did not vary substantially except at the mining influenced sampling stations (Figs. 3 and 4). Precisely, a membrane filtrate (0.45 µm and <0.2 µm) U concentration at sampling spots directly influenced by the mining activity ((3) and (4) at Chardon and (7) and (8) at L’Ecarpière) markedly exceeded the ultrafiltrate U concentration. A paired t-test showed no statistically significant difference between 500 kDa, 100 kDa and 10 kDa fractions/ultrafiltrate samples in terms of U concentration at each sampling point at a specified alpha level of 0.05. At the upstream sampling point of L’Ecarpière (6), there was no significant difference between the U concentrations measured by 0.45 µm, 0.2 µm, 500 kDa, 100 kDa and 10 kDa fractions. In turn, at (7) and (8) approximately 40% of the total dissolved U was bound to large colloids (i.e. >500 kDa), which were probably a mixture of Fe(III)oxy-hydroxides, and aluminosilicates. Similarly, at all sampling spots of the mining site of Chardon, the majority of total dissolved U concentrations (70–90%) was observed in the 10 kDa truly dissolved fraction. Only in the alkaline waters of the former open pit (3), approximately 30% of U was in form of large colloids (>500 kDa).
The relative dominance of small organic molecules (<10 kDa) at all sampling points has been verified by DOC measurements (Fig. 5). Only at the upstream of Sevre Nantaise river (1), the colloidal organic carbon comprises a dominant fraction of the DOC pool (62%). It is well known that the U distribution is strongly influenced by the presence of DOC [7,32,33], however no significant correlation was found in this study. Along the river Sevre Nantaise, Margerie stream and Moine river, the DOC concentrations were rather moderate and constant, besides very low DOC content at the mining discharge point of mining site of L’Ecarpiere (7). The DOC concentration value ranged between 533.8 μM and 868.4 μM (with very low concentration of 198.4 μM at (7)). Hence, uranium is dominantly transported in the 10 kDa truly dissolved fraction in the vicinity of the former uranium mining sites of Chardon and L’Ecarpiere. The geochemical modelling speciation indicated that the inorganic U species (i.e. CaUO$_2$(CO$_3$)$_3$)$^{2-}$) predominates.

3.2. U- DGT labile speciation

The U concentration measured by DGT-Chelex$^\text{®}$-100, DGT-Metsorb$^\text{™}$ and DGT-Diphonix$^\text{®}$ is presented in Figs. 3 and 4. The U concentration estimated by a single DGT measurement and the average $C_{\text{DGT}}$ at each sampling point used for the statistical evaluation is displayed in Table S2 in the Supplementary Information.

The repeatability of the DGT method was expressed as the relative standard deviation of the $C_{\text{DGT}}$ values at each sampling point (4 replicates of each binding phase per sampling point, $n = 32$). The repeatability of DGT-Chelex$^\text{®}$-100 was estimated at 9.1% (with 3.9% min, and 24.5% max), DGT-Metsorb$^\text{™}$ at 7.9% (with 0.7% min, and 17.6% max) and DGT-Diphonix$^\text{®}$ at 8.1% (with 0.5% min, and 16.1% max). These results show a considerable variation in the repeatability between the binding phases and between the sampling points. Poorer repeatability was observed at the sampling points influenced by the mining activity, probably due to the spatial
and temporal heterogeneity of the mining influenced waters. The repeatability of the U-DGT measurements reported by other authors for the comparability is rather scarce, however in general, the precision of 10–15% is considered satisfactory [34,35].

The analysis of variance using Holm-Sidak method for multiple pairwise comparisons was applied to assess binding phases’ performance. The Grubbs test was used to detect the presence of the outliers. At sampling points not influenced by the mining activity, no significant difference was obtained in terms of U uptake on Chelex®-100 and Metsorb™, while similar or inferior U uptake on Diphonix® in comparison was observed. It was found that there is a statistically significant difference between different DGT devices at the former open pit (3), where the U accumulation on DGT-Diphonix® was markedly higher than on DGT-Chelex®-100 and DGT-Metsorb™. In turn, at the downstream of the stream Margerie (4) and at the mining discharge water point of L’Ecarnière (7), the U uptake on Chelex®-100 was significantly higher than on Diphonix® and Metsorb™, which produced similar results. Surprisingly, U labile concentration estimated by Chelex®-100 at (7) of L’Ecarnière was notably greater than total dissolved (0.45 μmol) U concentration.

The equivocal performance of DGT-Chelex®-100, DGT-Metsorb™ and DGT-Diphonix® is strongly interrelated to the complex composition of natural waters and to the specific chemistry of the mining environments. Several studies correlated the discrepancies in metal uptake on different DGT devices to the distribution of metal species and/or the functional properties of the DGT binding phases [36–38]. However, the extensive laboratory investigation [21] demonstrated that CaUO$_2$(CO$_3$)$_3$$^{2-}$, which constitutes approximately 100% of all U species at all sampling points, is quantitatively accumulated on the DGT devices irrespectively of the functional properties of Chelex®-100, Metsorb™, Diphonix®. Other factors such as pH, ionic strength or the U capacity of the DGT binding layers had probably a minor influence on the observed discrepancies in the U uptake on different DGT devices. The pH at all sampling spots was neutral and ionic strength was of 0.003 M, except at the former open pit (3) and at the mining discharge point (7), where surface waters were slightly alkaline with ionic strength of 0.04 M. Neither effect of pH nor ionic strength of this range, on the U uptake on DGT-Chelex®-100, DGT-Metsorb™ and DGT-Diphonix® was observed under laboratory conditions [21]. It is also unlikely that the saturation of either DGT binding layer was achieved and negatively affects the U accumulation on DGT-Chelex®-100, DGT- Metsorb™ and DGT-Diphonix® under field conditions. The maximum U capacities exhibited by Chelex®-100, Metsorb™, Diphonix® binding phase gel discs are 1.05 μmol, 1.05 μmol and 10.5 μmol, respectively [21]. The mass of U accumulated on Chelex®-100, Metsorb™, Diphonix® at the former open pit ([U$_{0.45}$ μmol L$^{-1}$] = 1.1 mg L$^{-1}$), were $1.3 \times 10^{-2}$ μmol U, $1.4 \times 10^{-2}$ μmol U and $1.7 \times 10^{-2}$ μmol, respectively.

Presumably, the U uptake is hampered by the presence of other co-adsorbing analytes, which can compete individually and/or collectively for the binding sites of the adsorbent and in consequence rearrange the selectivity order of the DGT binding layer towards uranium [36,39,40]. Furthermore, Wazne et al. [41] and Jafrezic-Renault et al. [42] highlighted the twofold competition effect of the aqueous carbonate on the U uptake on the titanium dioxide based adsorbent (i.e. Metsorb™). Under some conditions, the aqueous carbonate will compete with U species for the binding sites of the adsorbent, but it can also compete with the binding sites of the adsorbent to complex uranium.

There are several publications that tackle the issue of the selectivity order of Chelex®-100 and Metsorb™ as adsorbents and as the DGT binding layers. According to our knowledge, there is no investigation on the selectivity order of Chelex®-100, Metsorb™ and Diphonix® that includes uranium as the analyte of interest. The extensive laboratory investigations and in situ field studies demonstrated the complexity and non-applicability of a selectivity order of a specific binding phase under every environmental condition [43–45]. Commonly, only the effect of a few co-adsorbing analytes at particular pH on the uptake of the metal of interest on the DGT binding phase is assessed, consequently those findings might not be adequate under environmental conditions, especially in mining waters. The actual selectivity order of the DGT binding phase depends on several parameters and can vary from one system to another, thus possible competition of the metal of interest with other co-adsorbing analytes should be tested under conditions of a particular mining system [46,47].

It is generally accepted, that the selection of the efficient eluent for specific DGT binding phase should be analyte-oriented. Therefore, the elution procedures applied here for the U extraction might...
not be applicable for other analytes, but they still might be accumulated on Chelex\textsuperscript{®}-100, Metsorb\textsuperscript{TM} and Diphonix\textsuperscript{®}. For instance, Bennett et al. (2010), Panther et al. (2011) and Price et al. (2013) used 1 M NaOH to elute As, Se, V, P from DGT-Metsorb\textsuperscript{TM}, while in this study 1 M HNO\textsubscript{3} as an eluent was utilized [20,44,48]. Chiarizia et al. (1994) employed 0.33 M H\textsubscript{2}O\textsubscript{2}/1 M NaOH mixture to elute Cr from Diphonix\textsuperscript{®} resin, while in this study 1 M HEDPA as efficient eluent for DGT- Diphonix\textsuperscript{®} was applied [49]. Consequently, the estimated As, Se, V, Cr and other metals uptake on Chelex\textsuperscript{®}-100, Metsorb\textsuperscript{TM} and Diphonix\textsuperscript{®} might not reflect accurately their accumulation on the DGT devices. In all probability, the reason behind a diminished U uptake on DGT-Diphonix\textsuperscript{®} is a synergistic effect of a near neutral pH and highly complex composition of aquatic systems. Chiarizia and Horwitz (1994) and Chiarizia et al. (1997) highlighted that at circumneutral pH, the gem-diphosphonate groups of Diphonix\textsuperscript{®} resin can dissociate the uranyl species; hence the neutral U species should be still sorbed, although less efficiently than the positively charged complexes [49,50]. It has been also pointed out that the uptake of negatively charged uranyl carbonates species into the cationic exchange resin is likely to be significantly suppressed because of the Donnan potential. Drozdzak et al. (2015) demonstrated no effect of U species distribution on U uptake on Diphonix\textsuperscript{®} over wide pH range of 3–9 under laboratory conditions; however those findings in case of highly complex matrix of natural waters might not be fully pertained. The performance of Chelex\textsuperscript{®}-100 and Metsorb\textsuperscript{TM} binding phases is clearly affected by the extreme conditions encountered in mining influenced environments. Mitigated or possibly agrandized U uptake on Chelex\textsuperscript{®}-100 and Metsorb\textsuperscript{TM} is most likely associated with very high concentrations of major cations, anions and other metals typical for mining environments, such as Zn, Mn, Ba or Sr. A small variance between the replicates of cations, anions and other metals typical for mining environments, is most likely associated with very high concentrations of major cumneutral pH, the gem-diphosphonate groups of Diphonix\textsuperscript{®} resin was observed regardless of the milieu of a sampling point, while the repeatability of the Chelex\textsuperscript{®}-100 and Metsorb\textsuperscript{TM} was negatively affected at sampling stations influenced by the former uranium mining activity. Precisely, at least one of the replicates of Chelex\textsuperscript{®}-100 and Metsorb\textsuperscript{TM} has been identified as an outlier and excluded from the DGT data interpretation at mining influenced sampling points. Diphonix\textsuperscript{®} resin was designed and used mainly for the preconcentration of actinides and the removal of uranium from the radioactive wastewater [51]. Therefore, it can be presumed, that given all the above mentioned aspects, the U–DGT labile concentration measured by the DGT-Diphonix\textsuperscript{®} method provides the most reliable results at sampling points directly influenced by the mining activity. 3.3. Ultrafiltration and DGT The comparison of the U concentration in the 10 kDa ultrafiltration permeates and the DGT-labile U concentration is presented in Figs. 3 and 4. There is a good agreement in respect of the U concentration measured by those two techniques. The observed discrepancies are probably due to the differences between the operationally-defined fraction measured by each method and the artifacts influencing each measurement. Ultrafiltration is a laboratory-based technique that discriminates metal species only by their size. The water samples for the analysis are collected usually by a single grab sampling and the relevant fractionation is performed immediately to minimize the speciation changes associated with sample collection and storage. The pore size (i.e. cut-off) of the ultrafiltration membranes is specified by the manufacturer; however the actual rejection rate depends not only on a nominal molecular weight, but also on the structure and the properties of metal species. Moreover, the real cut-off of the membrane differs by approximately 10–20\% from the manufacturer-defined one. Therefore, a certain percentage of metal species with higher molecular weight might breakthrough the ultrafiltration membrane, and in turn, it is also possible that some metal species with lower molecular weight might be retained by the membrane [5]. Favre-Régullion et al. (2005) and Guo et al. (2007) also emphasized a high possibility of an artifactual rejection or retention of large anionic species, such as, UO\textsubscript{2}(CO\textsubscript{3})\textsubscript{2}\textsuperscript{2–} or CaUO\textsubscript{2}(CO\textsubscript{3})\textsubscript{2}\textsuperscript{2–}, due to the negatively charged ultrafiltration membranes [5,52]. In consequence, this might lead to a significant underestimation of the 10 kDa truly dissolved U fraction. The imperative feature of the DGT technique is its ability to provide an in situ, time-averaged estimation of labile metal concentration. Metal species are discriminated by their size, lability, mobility. Although, a straightforward comparison of the molecular sizes expressed in a hydrodynamic diameter (i.e. nm) and a molecular weight (i.e. kDa) is rather cumbersome, it can be assumed that the open pore of a diffusible gel (i.e. 5 nm) used in this study, corresponds to the 10–13 kDa cut-off membrane [5]. Generally speaking, only the metal species smaller than the pore size of a hydrogel, labile enough to dissociate over the deployment time and able to bind effectively on the DGT binding phase, will be retained by the DGT device. It is also of a paramount importance to emphasize several attributes that can influence the precision of the DGT measurement, thus might influence an accurate comparison of DGT and ultrafiltration. The extensive laboratory investigation on the uncertainty of the DGT measurement has been performed by Knutsson et al. (2014) and Kreuzeder et al. (2015) [34,53]. Several parameters such as elution factor, diffusion layer thickness, DGT blank, analyte signal intensity and so forth, were taken into account. It is noteworthy, that other contributors might also deteriorate the accuracy of the DGT measurement under field conditions. The U concentration measured by the DGT technique is a sum of both, labile inorganic and organic species, however \textit{C}_{\textit{DGT}} in this study was calculated using mean value of the diffusion coefficient of inorganic U species (Eq. (1)). Drozdzak et al. (2015) have shown no effect of a distribution of inorganic U species on the effective U diffusion coefficient. However U-organic bearing complexes that might also contribute to the mass of U accumulated on the DGT binding layer, diffuse much slower than the inorganic U species, hence \textit{D}_{\textit{org}} will not correlate well with \textit{D}_{\textit{org}}. Quantitative discrimination between inorganic and organic metal complexes can be achieved by a parallel deployment of the DGT devices with different pore sizes of the diffusive gel (Zhang and Davison, 2000). Up to date, no investigation on the diffusion coefficient of organic U complexes has been conducted. Nevertheless, in this study neither tremendous difference between the DGT and the ultrafiltration data nor any trend in diminished U–DGT labile concentration was observed, which indicates that the DGT calculation strategy (i.e. using only \textit{D}_{\textit{org}}) was legitimate. Indeed, the geochemical modelling speciation indicated that the inorganic U species (i.e. CaUO\textsubscript{2}(CO\textsubscript{3})\textsubscript{2}\textsuperscript{2–}) prevail. There is a good agreement between the DGT–measured and the 10 kDa-ultrafiltrate U concentrations, given all the differences between the fractions and the artifacts and limitations of each method. At all sampling spots in the vicinity of the former mining sites of Chardon, the U concentration estimated by the 10 kDa ultrafiltrate was higher or equal to the DGT–measured one. This suggests that the uranyl species with low molecular weight, which predominate at each sampling spot, can pass through the 10 kDa membrane and the open pore of the DGT diffusive layer, but they do not have sufficient dissociation rate to be accumulated on the DGT device. Likewise, similar behaviour was observed in the vicinity of the mining site of L’Ecarpière, with the exception at the mining discharge station (7), where the 10 kDa-ultrafiltrate U
We thank the Hercules Foundation for financing the ICP-SF-MS instrument (UABR/11/010). Furthermore the authors thank Graver Technologies (www.gravertech.com) for providing the Metsorb™ adsorbent.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.aca.2016.01.052.

References

[21] J. Drozdzak, M. Leermakers, Y. Gao, V. Phrommavanl, M. Descotes, Evaluation and application of diffusive gradients in thin films (DGT) technique using concentration was lower than the DGT labile U concentration. Most likely, the observed discrepancy is correlated to the highly complex matrix of the mining discharge water and temporal variation in the U concentration over the DGT deployment time, nevertheless diurnal variations in streams with similar pH ranges might be possible as well [54].

DGT has considerable benefits over ultrafiltration technique as it provides an information about the dynamic supply of metal species from the medium [18]. Other features, such as robustness, pre-concentration and in situ abilities are worth-mentioning as well. Furthermore, the application of the DGT technique allows obtaining more precise estimation of the potentially bioavailable U pool and the nature of the uranyl complexes in natural and mining influenced water systems. This study accentuates a high potential of the DGT technique as an alternative to ultrafiltration method for the purposes of the determination of the potentially bioavailable metal fraction.

4. Conclusions and perspectives

This is the first time that the feasibility of the DGT technique with Chelex®-100, Metsorb™ and Diphonix® as binding agents for the determination of labile U species was evaluated under field conditions. The application of Diphonix® resin leads to a significant advance in the development of the DGT technique for the measurement of U in uranium mining environments. The performance of DGT-Diphonix® is not disturbed by highly complex matrix with elevated levels of major cations, anions and other metals such as Zn, Mn or Sr.

This work disclosed that it is a prerequisite to perform an exhaustive laboratory characterization of the DGT binding phase layer prior to undertaking an in situ fieldwork, what was performed previously by Drozdzak et al. (2015). The comprehension of the optimal working parameters of the DGT technique under specific field conditions ensures a reliable and precise metal speciation measurement. Moreover, such a combination of the comprehensive DGT laboratory investigation and in situ field studies promote a better understanding of the applicability of the DGT technique as a water speciation tool in aqueous environments.

It is likely that this research has environmental significance as it demonstrates the capability of DGT to predict the potentially bioavailable U fraction. Furthermore, it shows that the multi-technique approach, which integrates ultrafiltration combined with the computational modelling speciation and the DGT technique provides a deep insight into the U speciation in mining influenced environments and the measurement of the potentially bioavailable U fraction. Finally, this study contributes to the overall understanding of the feasibility of the DGT technique as a monitoring tool for the environmental research within the scope of the Water Framework Directive.

The future work should assess the applicability of DGT-Diphonix® technique for the measurement of other co-adsorbing analytes usually encountered under field conditions. The study on the variability of the DGT technique with different DGT binding phases is required as well. Furthermore, more research should be devoted to study the relationship between the DGT measured concentration and the response of the biota in the aquatic environments, including mining influenced waters.

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