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Evaluation of a titanium dioxide-based DGT technique for measuring inorganic uranium species in fresh and marine waters

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ABSTRACT

A new diffusive gradients in a thin film (DGT) technique for measuring dissolved uranium (U) in freshwater is reported. The new method utilises a previously described binding phase, Metsorb (a titanium dioxide based adsorbent). This binding phase was evaluated and compared to the well-established Chelex-DGT method. Batch experiments showed quantitative uptake ($100 \pm 3\%$) of dissolved U by Metsorb and an elution efficiency of 95% was obtained using a mixed eluent of 1 mol L^{-1} NaOH/1 mol L^{-1} H_2O_2. The mass of U accumulated by Metsorb was linear ($R^2 \geq 0.98$) with time across the pH range 3.0–8.1, validating the DGT measurement. The measured effective diffusion coefficients were highly dependent on pH, ranging from $2.74–4.81 \times 10^{-6}$ cm^2 s^{-1}, which were in reasonable agreement with values from the literature. Ionic strength showed no effect on the uptake of U, and thereby on diffusion coefficients, at $NaNO_3$ concentrations ≤ 0.01 mol L^{-1}, but caused the U concentration to be underestimated by 18% and 24% at 0.1 mol L^{-1} $NaNO_3$ and 0.7 mol L^{-1} $NaNO_3$, respectively. Deployment of Metsorb-DGT in synthetic freshwater resulted in reliable measurement of the dissolved U concentration ($C_{DGT}/C_{Sol} = 1.05$), whereas Chelex-DGT significantly underestimated the dissolved U concentration ($C_{DGT}/C_{Sol} = 0.76$). Metsorb-DGT was found to give reliable results after 8 h deployments in synthetic seawater but experienced competition effects with longer deployments. The Chelex-DGT was unable to measure U at all in synthetic seawater. A field deployment in a freshwater stream (Coomera River) confirmed the utility of the Metsorb-DGT method for measuring U in natural freshwaters, but performance of field deployments may require further evaluation due to the possibility of major changes in uranium speciation with pH and water composition. We recommend a filtered sample, of any water in which DGT measurements are to be made, be used to determine the appropriate diffusion coefficient under controlled laboratory conditions.

1. Introduction

Uranium (U) is present in natural waters due to weathering from the lithosphere, with concentrations ranging from 50 pM to 20 nM (12 ng L^{-1}–4.8 μg L^{-1}) in stream waters[1] and around 13.9 nmol kg^{-1} ($\sim$3.4 μg L^{-1}) in seawater [2]. Elevated levels of U occur in the environment due to U mining and processing, nuclear accidents, disposal of high-level nuclear waste, as well as testing, use and decommissioning of nuclear weapons [3]; long-lived U isotopes are a major source of environmental radiotoxicity [4]. As a non-essential trace metal and radionuclide, U toxicity is both chemical and radiological. While radiological toxicity is determined by the total U concentration and the isotopic composition, chemical toxicity is dependent on the chemical speciation [5]. As with most metals, U ions in natural waters form complexes with various organic and inorganic ligands. The U(VI) oxidation state, considered the most environmentally significant, is present as uranyl ions (UO_2^{2+}) that form stable complexes with hydroxide and carbonate as well as other anionic ligands (e.g. F^-, Cl^-, Br^-, and PO_4^{3-}) [6,7]. Due to this complexation, the speciation of U changes dramatically with pH [8], and is also dependent on the concentrations of the other anionic ligands, particularly Cl^- or PO_4^{3-}. The dependence of U speciation on environmental conditions has led to the recommendation that U concentrations be measured using in situ techniques to avoid the potential changes in speciation during transportation, preservation and pre-concentration [9].

The diffusive gradients in a thin film (DGT) technique is a kinetic passive sampler that facilitates measurement of time-weighted average concentrations of a range of elements in surface waters

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[10–14]. Passive samplers accumulate analytes in situ and allow quantification using sensitive laboratory instrumentation. Measurements using passive samplers are highly representative compared with those made on discrete grab samples [15], particularly in dynamic systems such as natural waters where analyte concentrations and speciation are known to vary substantially over several hours [16,17]. DGT measurements have been shown to record the effects of natural processes and anthropogenic sources that cause changes in metal concentrations and speciation [18]. The DGT technique uses an analyte-specific binding phase, which is generally immobilised in a hydrogel, to pre-concentrate the analyte, vastly improving detection limits and decreasing matrix interferences associated with many analytical measurements. Several DGT techniques with differing binding phases, have been described for uranium: Chelex-100, [4,8] dimethylaminoethyl substituted cellulose polymer membrane (Whatman DE81), [4,8] an anion exchange resin (Dowex 2×8–400 resin) [8] and Spheron-Oxin chelating ion-exchanger with anchored 8-hydroxyquinoline have all been used as DGT binding agents [5,8,9]. Li et al. [5,9] and Gregusova and Docekal [8] found that the concentration of U measured by DGT was dependent on the nature of the binding phase. Therefore, as U speciation changes significantly with pH and other factors, the DGT measurement for each binding phase also changes [8].

A new binding phase, agglomerated nano-crystalline titanium oxide (anatase) based adsorbent (Metsorb), has recently been validated as a DGT adsorbent for the measurement of arsenic, selenium (IV), dissolved reactive phosphorus and aluminium in natural waters [19–22]. Due to its strong affinity for U adsorption [23,24], titanium dioxide has long been suggested as a potential adsorbent for U [25]. This study investigates the suitability of Metsorb as a DGT binding phase for the measurement of U in both synthetic and natural waters. Uptake and elution efficiencies were determined for a range of potential eluents. Time-series experiments were performed across a range of pH values in order to investigate the pH-dependency of the effective U diffusion coefficients. The accuracy of DGT to measure U solution concentrations was also assessed for a wide range of pH and ionic strength. The study subsequently focused on the ability of the Metsorb binding layer to determine U concentrations in synthetic fresh and marine waters relative to Chelex-DGT measurements used previously. Metsorb-DGT samplers were further deployed in situ with varying diffusive layer thickness in order to quantify the diffusive boundary layer thickness and thus enable accurate calculation of DGT-labile U.

2. Experimental

2.1. Reagents, materials and solutions

Deionised water (Milli-Q Element, $>18.2\ \mathrm{M\Omega}$ cm) was used to prepare all solutions. All chemicals were of analytical grade or higher and all plastic containers and DGT components were cleaned in 10% (v/v) HNO_3 for >24 h and rinsed thoroughly in deionised water. All sample handling and preparation was carried out in a class-100 laminar flow cabinet within a class-1000 clean room. All U solutions were prepared from $1000\ \mathrm{mg\ L^{-1}}$ stock solutions in 2% HNO_3 (High Purity Standards, USA) and subsequently adjusted to the appropriate pH (using $1\ \mathrm{mol\ L^{-1}}$ HNO_3 or NaOH) and ionic strength (using $NaNO_3$). These solutions were generally stirred vigorously for at least 24 h, to enable the total inorganic carbon in solution to equilibrate with atmospheric CO_2 prior to being used for other experiments, which were undertaken with the solution in contact with the atmosphere at all times.

For all experiments, DGT gels were exposed in triplicate. All U sample concentrations were preserved in HNO_3 at $\mathrm{pH} < 1.5$ and determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500a) with ^{238}U isotope used for quantification. Indium (m/z 115; $10\ \mu\mathrm{g\ L^{-1}}$) was used as an internal standard to compensate for instrument drift. Repeated measurements ($n=3$) of a seawater certified reference material (NASS-6 Seawater CRM) containing $\sim 3\ \mu\mathrm{g\ L^{-1}}$ U at 10 and 5 fold dilutions and no dilution, gave recoveries between 100 and 108% and relative standard deviations (RSD) $<1.5\%$. The instrument detection limit for U was $0.008\ \mu\mathrm{g\ U\ L^{-1}}$ and all samples measured were well above this concentration.

2.2. Preparation of binding and diffusive gels

Metsorb binding gels were prepared according to Bennett et al. [19] Briefly, 1 g of Metsorb HMRP (Graver Technologies) was added to 10 mL of polyacrylamide (PAM) gel stock, sonicated for 5 min, followed by mixing on a stirrer for a further 1 min. This procedure ensured an even distribution of Metsorb particles within the gel solution, prior to casting. The gels were set at 45 °C (>30 min), hydrated in deionised water for 24 h and stored in deionised water prior to assembly. Chelex binding gels and polyacrylamide diffusive gels were prepared according to Zhang and Davison [13], using the agarose-derived cross-linker purchased from DGT Research Ltd. (http://www.dgtresearch.com).

2.3. DGT assembly, deployment and analysis

DGT samplers were supplied by DGT Research Ltd and assembled as described previously [13]. Assembled DGT samplers were stored at 4 °C in doubled zip-lock plastic bags, with deionised water in both inner and outer bags to maintain humidity.

Laboratory experiments were performed in 7 L of well-mixed experimental solution (using stirrers or aquarium pumps) into which DGT samplers were deployed. Temperature and pH of the exposure solution was monitored regularly using a combined pH/temperature probe (Five Go, Mettler Toledo). Conductivity was measured using a combination meter (TPE 90-FLMV). Two samples were collected at the start and end of the experiment and on every occasion that DGT samplers were removed from solution. One sample was digested in 2% HNO_3 for >24 h and was interpreted as a total (weak-acid soluble) U concentration while the other was filtered (0.45 μm) prior to preservation with acid (2 mL conc. HNO_3 per litre).

Following retrieval of the DGT devices, the binding gels were removed and eluted for at least 24 h. Elution efficiencies were determined as described previously. [12] Chelex gels were eluted in $1\ \mathrm{mol\ L^{-1}}$ HNO_3 for 24 h which was reported to have an elution efficiency of 89% [8]. While slightly higher efficiencies (96.2%) have been reported using concentrated HNO_3, [26] a higher dilution is also required before analysis making the measurement less sensitive. Metsorb gels were eluted in $1\ \mathrm{mol\ L^{-1}}$ NaOH/$1\ \mathrm{mol\ L^{-1}}$ H_2O_2 for at least 24 h, giving an elution efficiency of $95.2 \pm 0.4\%$. For seawater and field deployments, Chelex binding gels were rinsed in 5 mL deionised water for 1 h prior to elution to remove unbound salts. However, Metsorb binding gels were rinsed in 5 mL of $0.0001\ \mathrm{mol\ L^{-1}}$ HNO_3, instead of deionised water, prior to elution (see following section) due to the reduced variability in elution efficiency observed (RSD of 4% and 20% for 0.0001 M HNO_3 and deionised water, respectively). Not including the washing step has shown to reduce the elution efficiency of other analytes from Metsorb gels when using NaOH based eluents.[20]

Eluents were subsequently diluted 10-fold (2% HNO_3; Baseline, Seastar) prior to ICP-MS analysis. Time-averaged DGT measured U concentrations (C_{DGT}, $\mathrm{ng\ mL^{-1}} \cong \mu\mathrm{g\ L^{-1}}$) were calculated using

Eq. (1) [13]

$$C_{DGT} = Mg/DtA \tag{1}$$

where M is the mass of U in the binding gel (ng) corrected for the elution efficiency, Δg is the thickness of the diffusive layer (cm), D is the diffusion coefficient of U through the diffusive layer ($cm^2\ s^{-1}$), t is the duration of deployment (s) and A is the area of the sampling window exposed to solution (cm^2). The diffusion coefficient of U (determined by mass-time plots at 25 °C for various pH) was corrected for temperature using the Stokes–Einstein equation [13]. For seawater and high ionic strength solutions (> 1 mol L^{-1} $NaNO_3$) a corrective value of $0.9 \times D$ was employed as described previously [10].

2.4. Determining uptake and elution efficiencies

Uptake and elution efficiencies were assessed by exposing Metsorb binding gel discs in triplicate to solutions containing 5.00 mL of 20 μg U L^{-1} (prepared in 0.01 mol L^{-1} $NaNO_3$ at pH 7.0). These solutions were not exposed to the atmosphere beforehand, but were used immediately as they used binding gels instead of DGT apparatus and uptake was expected to be very quick. After 24 h, during which time the solutions were gently shaken, the gels were removed and the remaining solution acidified (to remove any U adsorbed to the containers) and analysed to determine the mass of U remaining in solution. Metsorb gels were eluted for 24 h in either 1 mol L^{-1} of HNO_3, HNO_3/H_2O_2, Na_2CO_3/H_2O_2 or $NaOH/H_2O_2$, diluted 10-fold and analysed by ICP-MS. Average elution efficiencies, i.e. the ratio between the amount of U eluted and the amount bound, are reported with the uncertainty ±1 SD of the mean.

2.5. Effect of deployment time and pH on DGT uptake

The accumulation of U over time by Metsorb-DGT samplers was evaluated by deploying triplicate DGT samplers in solutions initially of 20 μg U L^{-1} (prepared in 0.01 mol L^{-1} $NaNO_3$) for times ranging from ~4 to 48 h. The effect of solution pH on accumulation of U was investigated for time series experiments at pH 3.0, 3.5, 4.9, 6.0, 6.5, 7.0, 7.7 and 8.1. Solutions were adjusted to the desired pH using dilute HNO_3 and NaOH. Samplers were removed from solution after 4, 8, 12, 24 and 48 h, rinsed in deionised water and stored at 4 °C in sealed plastic bags until elution. A comparison was made between the mass of U accumulated and the predicted accumulation of U calculated using Eq. (1). Solution speciation was calculated using MINEQL (ver. 4.6) and equilibrium constants are given in the Supporting Information (SI).

2.6. Measurement of diffusion coefficients

Diffusion coefficients were determined from mass accumulation over time experiments for each pH. The diffusion coefficients (D, $cm^2\ s^{-1}$) were calculated using the slope (α) of the linear regression of U accumulated in the DGT sampler over time, the diffusive layer thickness (Δg, cm), the area of the diffusive layer (A, cm^2) and the concentration of the U solution (C, ng mL^{-1}) (Eq. (2)).

$$D = \alpha g/AC \tag{2}$$

2.7. Effect of Ionic strength on DGT measurement

The effect of ionic strength on the accumulation of U by Metsorb DGT was assessed by deploying triplicate samplers in solutions with varying concentrations of $NaNO_3$ (0.0001, 0.001, 0.01, 0.1 and 0.7 mol L^{-1} $NaNO_3$). DGT samplers were deployed for 24 h in 20 μg U L^{-1} at pH 8.0 ± 0.1.

2.8. DGT deployment in synthetic freshwater and coastal seawater

Time-series deployments (up to 4 days) of Metsorb-DGT and Chelex-DGT samplers in synthetic freshwater (spiked with 20 μg U L^{-1}) and seawater collected from a local beach (spiked with 25 μg U L^{-1}) were carried out in the laboratory to investigate the performance of both adsorbents under realistic matrices and to provide a comparison with the established Chelex-DGT technique. The synthetic freshwater compositions was similar to that described by Langmuir [27]. Samplers were removed after approximately 8, 24, 48, 74 and 96 h, rinsed in deionised water and stored at 4 °C in sealed plastic bags until ICP-MS analysis. DGT-labile U concentrations were determined using Eq. (1) and compared to 0.45 μm filtered solution concentrations.

2.9. Freshwater field deployments

Triplicate Metsorb-DGT samplers containing varying diffusive layer thickness (0.05, 0.09 and 0.13 cm) were deployed at a fast flowing freshwater (Coomera River, Queensland). Temperature, conductivity/salinity and pH were measure daily on site (TPS 90-FLMV), and filtered grab samples (0.45 μm) were collected daily and stored at < 4 °C until analysis. At the end of the deployment period, DGT samplers were removed and rinsed thoroughly with deionised water, sealed in acid washed plastic bags and stored at 4 °C until elution and subsequent analysis. The detection limit of the Metsorb-DGT sampler (calculated from blank DGT values) is 0.003 μg U L^{-1}. As shown by Warken et al. [28], deployment of DGT samplers with diffusive layers of varying thickness enables determination of the thickness of the filed diffusive boundary layer (δ) based on Eq. (3).

$$1/M = \Delta g/DC_{DGT}At + \delta/DC_{DGT}At \tag{3}$$

A plot of $1/M$ versus Δg is a straight line with a slope (m) of $1/(DC_{DGT}At)$ and intercept (b) of $\delta/(DC_{DGT}At)$. Therefore, δ (Eq. (4)) and C_{DGT} (Eq. (5)) can be calculated according to

$$\delta = b/m \tag{4}$$

$$C_{DGT} = (1/mDAt) \tag{5}$$

When the thickness of the DBL was included in the DGT calculations, a value of 3.8 cm^2 was used for the sampling area, A, as described by Warnken et al. [28].

3. Results and discussion

3.1. Uptake and elution efficiency

The U uptake and elution efficiencies of the Metsorb binding gel were evaluated by exposing the gels to a solution of known volume (5 mL) and concentration (20 μg U L^{-1}). The average U uptake efficiency using the Metsorb binding gel was 100 ± 3%; no measurable uranium remained in solution. Metsorb gels were subsequently eluted using one of the following eluents (all 1 mol L^{-1}): HNO_3; HNO_3/H_2O_2; Na_2CO_3/H_2O_2; or $NaOH/H_2O_2$. The presence of H_2O_2 enhanced the elution efficiency when using HNO_3 (83.2 ± 3.1%) compared to 77.1 ± 3.0% using HNO_3 alone. However, the combination of H_2O_2 with either Na_2CO_3 or NaOH eluted significantly greater quantities of U from the Metsorb binding gel (88.7 ± 1.4% and 95.2 ± 0.4% for Na_2CO_3/H_2O_2 and $NaOH/H_2O_2$, respectively) and was substantially more reproducible as indicated by the low standard deviations. The H_2O_2 is thought to be effective because some of the U^{VI} was likely to be photo-reduced by the titanium oxide to uraninite ($U^{IV}O_{2(S)}$) during uptake [29,30], which is then re-oxidised by the peroxide allowing more efficient elution.

The elution efficiency of U from the Metsorb binding gel using 1 mol L^{-1} NaOH/ H_2O_2 was comparable and often an improvement on previously observed elution efficiencies for U DGT using Chelex (89% using 1 mol L^{-1} HNO_3 [8], 67.8% using 2 mol L^{-1} HNO_3 [9], and 96.2% using concentrated HNO_3 [26]), Dowex resin gel (86.3% using 10% HNO_3 [5]) and Whatman DE 81 membrane (87.7% using 2 mol L^{-1} HNO_3 [9]) binding layers. For this reason and due to the very good reproducibility obtained, 1 mol L^{-1} NaOH/1 mol $L^{-1}H_2O_2$ was selected as the eluent for all Metsorb-DGT samplers used throughout this study.

3.2. Accumulation of mass over time

For a DGT binding phase to be valid for a particular analyte it must demonstrate a linearity of mass accumulated over the deployment time. The linearity of U accumulation using Metsorb-DGT samplers was assessed over 48 h in solutions ranging from pH 3.0–8.1. Mass accumulation over time was linear for each experiment with R^2 values ≥0.98 obtained at each pH (Fig. 1; the data for pH 3.5 and 6.5 are not shown). This confirms that the Metsorb-DGT functioned in accord with the assumptions of the DGT equation (Eq. (1)) and that U species were being taken up irreversibly at each of the pH values. This is an important result as it is likely that the adsorption of uranium to TiO_2 would vary with pH due to the change in distribution of charged species (Fig. 2). However, as the mass vs. time plots are all linear this means that the uptake efficiencies and capacities are high enough for the DGT equation to still be valid over the pH range 3.0–8.1, with uptake being irreversible, at least over 48 h and with simple solution matrices.

These linear mass vs. time relationships were obtained despite the fact that the 0.45 µm-filterable U concentrations at several pH values varied considerably from the initial 20.0 µg U L^{-1} added (Table 1). Uranium concentrations decreased from 19.9 to 1.5 µg U L^{-1} with increasing pH from 3.0–6.0 and increased again as pH increased from 6.0–8.1. There was no evidence in the experimental solution of a precipitate forming and the 0.45 µm-filterable and total U measurements always agreed within experimental error. Furthermore, speciation modelling (MINEQL) indicated that formation of insoluble U species should be insignificant under each of the conditions used. The significant decrease of dissolved U concentration at circumneutral pH is most likely due to the dominance of neutral U species within this pH range (Fig. 2), which may be adsorbed to and absorbed into the plastic container and other materials present. These U losses from the test solutions, however, did not affect the validity of the DGT performance as the linear mass vs. time relationships demonstrate.

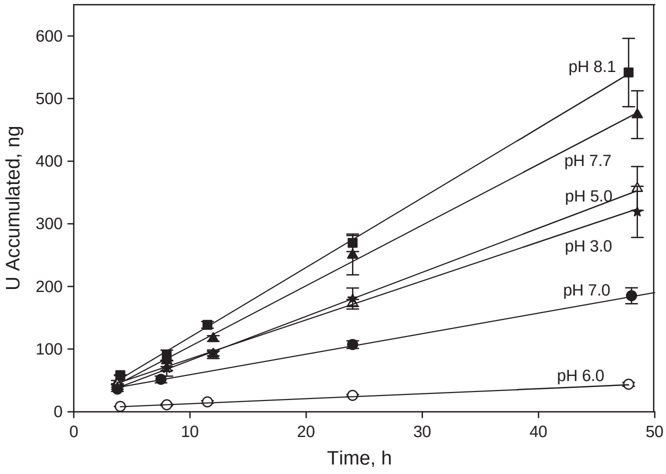

Fig. 1. Mass of U accumulated by Metsorb samplers (n=3, mean ± 1 standard deviation) as a function of time at various pH in 0.01 mol L^{-1} $NaNO_3$. [U] for each pH is given in Table 1. Regression lines are shown for most pH values (all R^2 values were ≥0.98).

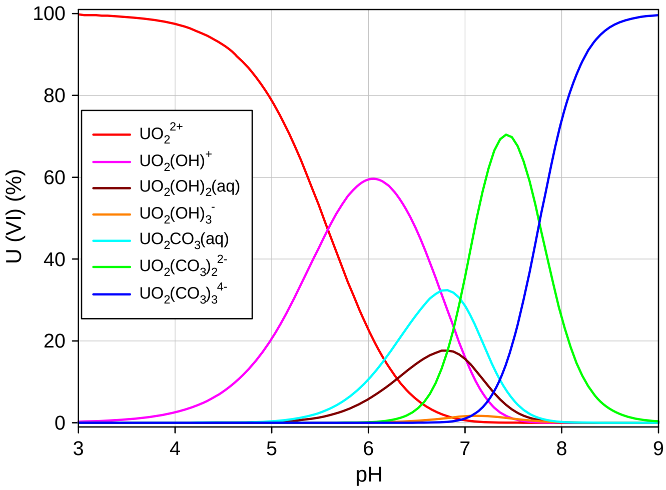

Fig. 2. U(VI) speciation in aqueous solution modelled using MINEQL. [U(VI)]=20 µg L^{-1}; p(CO_2)=3.8 × 10^{-4} atm; ionic strength=0.1 mol L^{-1}; temperature=25 °C.

Table 1
Uranium diffusion coefficients measured at 25.9 ± 0.5 °C using DGT samplers at pH 3.0–8.1 and the corresponding final 0.45 µm-filterable U solution concentration (which was equal to the total U concentration). All solutions were spiked with 20.0 µg U L^{-1} initially before equilibrating with atmospheric CO_2 for over 24 h before the DGT measurements were undertaken. At most of the pH values the measured U concentrations had decreased by the time the DGT measurements were made. The U concentrations reported here were used to determine the diffusion coefficients (Eq. (2)).

pH	**Diffusion coefficient ($\times 10^{-6}$ cm^2 s^{-1})**[a]	**Measured U concentration (µg U L^{-1})**
3.0	2.74 ± 0.14	19.9
3.5	3.22 ± 0.13	16.1
4.9	4.65 ± 0.27	12.4
6.0	3.71 ± 0.11	1.54
6.5	3.72 ± 0.27	1.86
7.0	3.11 ± 0.27	8.30
7.7	4.81 ± 0.54	16.1
8.1	4.44 ± 0.21	20.0

[a] Uncertainties associated with each diffusion coefficient value are a combination of the uncertainty of the slope of the mass vs. time plots (Fig. 1) and the standard deviation of replicate measurements of the solution U concentration measured by ICP-MS.

3.3. Effect of pH on effective diffusion coefficients

The slopes of the linear regressions in Fig. 1 were used to determine effective diffusion coefficients using Eq. (2) (Table 1) using the measured solution concentrations. The effective diffusion coefficients calculated in this study are in general agreement with those previously reported [9,26]. For example, at pH 4.9 and pH 6.0 the measured diffusion coefficients were 4.65 ± 0.27 × 10^{-6} cm^2 s^{-1} and 3.71 ± 0.11 × 10^{-6} cm^2 s^{-1} which agree well with those reported by both Garmo et al. [26] (4.7 × 10^{-6} cm^2 s^{-1} and 3.4 × 10^{-6} cm^2 s^{-1} at pH 5.0 and 5.9, respectively) and Li et al. [9](4.7 × 10^{-6} cm^2 s^{-1} and 3.1 × 10^{-6} cm^2 s^{-1} at pH 4.9 and 6.0, respectively), despite the fact that the previous D values were obtained using diffusion cell measurements, not using DGT time-series measurements as we have done. Clearly D is highly dependent on the exact solution composition.

The calculated effective diffusion coefficients of U varied significantly with pH. This type of behaviour has been observed previously [9]. Solution pH may affect the uptake of U on the Metsorb resin by altering both the surface charge on the TiO_2 particles (the point of zero charge occurs at pH 5.5–6.5 [31,32]) and the speciation of U ions in the deployment solution. However, the results in Fig. 1 indicate that the uptake efficiencies at each pH were high enough for linear mass uptake over time and therefore the DGT equation was valid. The U species predicted to be present in the deployment solutions are shown in Fig. 2, as calculated by the MINEQL speciation programme. Between pH 7.7–8.1 U species were dominated by the anionic forms of carbonate species ($UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) for which diffusion coefficients were between $4.4–4.8 \times 10^{-6}$ cm^2 s^{-1}. However, at pH 7 the diffusion coefficient decreased to 3.1×10^{-6} cm^2 s^{-1} corresponding to a prevalence of neutral U species (i.e. UO_2CO_3 and $UO_2(OH)_2$). Below pH 7, carbonate species become less dominant with the smaller cationic forms of U (UO_2OH^+ and UO_2^{2+}) the prevalent species. The change in D with pH is very complex indicating that there are several competing processes occurring. While it is anticipated that molecular weight will have an effect, as it changes considerably with pH, no clear trend is apparent. There is a clear decreasing trend in D for pH 4.9, 3.5 and 3.0. The U species do not substantially change in average charge (+1.98, +1.98, +1.73, respectively) over these pH values and the average molecular molar mass of species also does not change substantially with pH. Electrostatic interactions operate over very short distances, so this trend in D cannot be explained by any change in surface charge of the binding surface. These results suggest that there may be changes in the polyacrylamide diffusion gel over this pH range that is retarding the diffusion of positively charged ions as pH decreases. This observation needs to be investigated more in future studies as electrostatic effects have been observed in polyacrylamide hydrogels previously [33]. This effect was used, in a much more controlled manner, by Panther et al. [34] to speciate inorganic As using a Nafion diffusive layer that repelled the negatively charged species. Similar effects have been noted at pH <5 for DGT determination of U using chelex, DE 81 and Dowex resin binding phases [5,9], which all used polyacrylamide hydrogel as the diffusive layer. The diffusion coefficients determined for each pH (Table 1) will be used for each of the subsequent experiments, with the D value for pH nearest to that of the solution pH used, except for between pH 7 and 7.7, in which case there was assumed to be straight line relationship between 3.11 and 4.81×10^{-6}.

3.4. Effect of Ionic strength on DGT measurement

The ability of the Metsorb method to determine the U concentration of a solution (C_{DGT}) was assessed for a range of ionic strengths. The efficacy of the technique was evaluated by calculating the ratio of the DGT measured concentration (C_{DGT}) to the concentration of U in the deployment solution determined by ICP-MS directly; a ratio of 1 indicates that the Metsorb technique was accurate. Metsorb-DGTs were deployed in exposure solutions with ionic strength ranging from 0.0001–0.7 mol L^{-1} $NaNO_3$ at pH 8.0. The Metsorb DGTs accurately (100 ± 4%) determined the concentration of U in solution for ionic strengths ≤ 0.01 mol L^{-1}, with significant underestimations at higher ionic strengths (i.e. 82% and 76% accurate for 0.1 mol L^{-1} and 0.7 mol L^{-1} $NaNO_3$, respectively). A diminished U uptake with greater ionic strength, regulated by $NaNO_3$ concentration, has been similarly observed when employing other binding phases (Chelex, DE 81 and Dowex) [5,9]. Li et al. [5] reported a 5-fold decrease in U binding at 1.0 mol L^{-1} $NaNO_3$ using a Dowex resin and suggested that this was a consequence of competition of anions with the anionic forms of U, which are predominant in alkaline waters.

Our results suggest that there is not likely to be an effect on diffusion coefficients at ionic strengths below 0.01 mol L^{-1}, however this should be investigated for deployments in natural waters in which DGT-labile uranium concentrations differ substantially from measured solution concentrations. In high ionic strength solutions it is likely that multiple effects are responsible for the DGT underestimation, so for all future experiments we have continued to use 0.9 × D, as reported previously [9].

3.5. Comparison of Metsorb- and Chelex-DGT measurements in synthetic freshwater and seawater

The applicability of the Metsorb-DGT technique to determine U concentration in differing ionic strength solutions was further evaluated in synthetic freshwater and natural seawater solutions. Mass-accumulation over time using Metsorb-DGT was assessed relative to the performance of a Chelex-DGT measurement described previously, [8] but with the diffusion coefficients determined in this study. DGT samplers with Metsorb or Chelex binding gels were deployed for up to four days in synthetic freshwater and a coastal seawater (salinity=36.2 ± 1.0) solutions at pH of 8.25 and 7.86, respectively. Uranium concentrations in both test solutions remained relatively stable during the deployment period (see Fig. 3 caption).

For the synthetic freshwater solution, there was good agreement between the mass of accumulated U by Metsorb-DGT and the predicted mass of U accumulated using the DGT equation (dashed line Fig. 3a). The determination of the DGT concentration employed the previously calculated D for pH 8.1, which may explain the slight overestimation with the Metsorb DGT technique at all time points ($C_{DGT\text{-}Metsorb}/C_{sol}$ was between 1.00 and 1.11) if D at pH 8.25 is a little lower. Overall, the average Metsorb-DGT concentration measured over the deployment time (15.5 ± 1.4 μg L^{-1}) was in excellent agreement with the average filtered grab sample concentrations (14.7 ± 0.1 μg L^{-1}). Comparatively, the accumulated mass of U on the Chelex DGT was significantly less than the predicted mass, and the DGT measured U concentrations were underestimated by 20–30% (i.e. $C_{DGT\text{-}Chelex}/C_{sol}$ was between 0.71 and 0.82). These results indicate that, in freshwaters, the Metsorb-DGT technique is more likely to accurately measure the U concentration than Chelex-DGT. However, this should be further evaluated in any waters to be monitored for uranium.

In seawater solutions (0.45 μm filtered) spiked with 26.3 ± 1.0 μg U L^{-1}, the mass of U accumulated by Metsorb-DGT was significantly less than the predicted accumulated U mass for deployment times >8 h (Fig. 3b). Further experiments carried out at U concentrations of about10 and 125 μg L^{-1} showed similar behaviour, with only 8 h deployments being accurate (Fig. S1). These 8 h results suggest that the assumed 0.9 × D was appropriate for seawater deployments. However, the results for longer deployments suggest that anions and/or cations in the seawater solution are competing for binding sites with the uranium species present, leading to saturation effects with the Metsorb adsorbent. No single binding capacity was suggested between the three concentrations; higher U masses were accumulated in the higher concentration solutions, so this effect clearly varies with U concentration. Metsorb-DGT may function better in estuarine waters of lower salinity but this has not been evaluated in this study.

Deployment of Chelex-DGT in a synthetic seawater (see SI for details) containing 10 μg L^{-1} U (Fig. S2) resulted in much lower masses of U being accumulated relative to the predicted mass. The mass of U accumulated by Chelex-DGT actually decreased

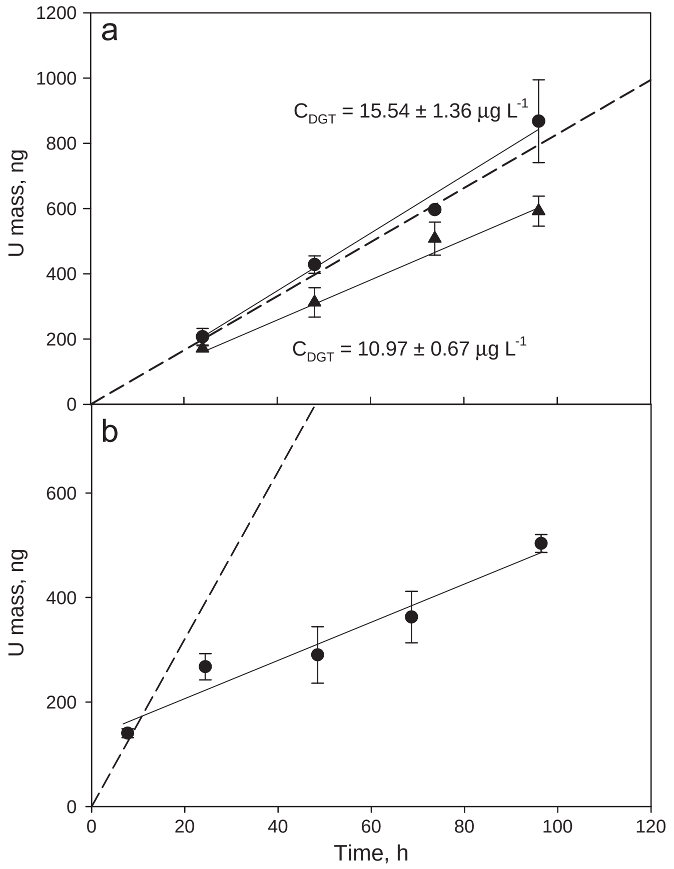

Fig. 3. Mass of U accumulated by Metsorb-DGT (●) and Chelex-DGT (▲) for (a) synthetic freshwater and by Metsorb-DGT (●) for (b) coastal seawater (0.45 μm filtered) deployments. Experimental conditions: (a) $[U]_{start}=14.8\ \mu g\ L^{-1}$ and $[U]_{End}=14.6\ \mu g\ L^{-1}$, pH 8.25 ± 0.02; (b) $[U]_{start}=27.2\ \mu g\ L^{-1}$ and $[U]_{End}=25.4\ \mu g\ L^{-1}$, pH 7.86 ± 0.02, salinity$=36.2\pm1.0$. The dashed line represents the predicted mass of accumulated uranium based calculated using the DGT equation.

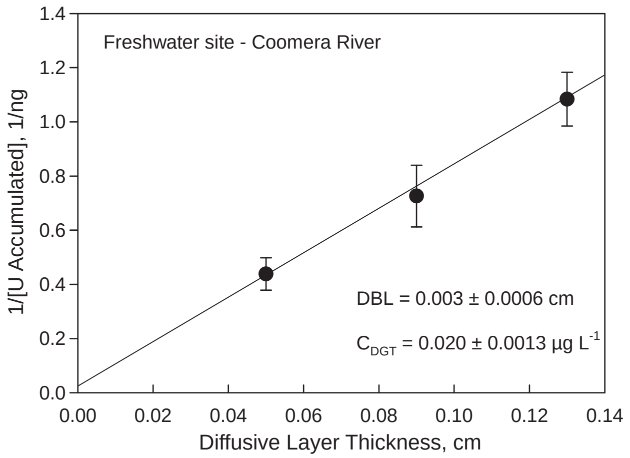

Fig. 4. Plot of reciprocal mass of uranium accumulated by Metsorb-DGT (1/ng) and diffusive layer thickness for Coomera River freshwater site. The linear regression line enables calculation of both the concentration and the diffusive boundary layer thickness. Deployment conditions: $[U]_{start}=0.019\ \mu g\ L^{-1}$ and $[U]_{End}=0.018\ \mu g\ L^{-1}$, pH 7.47 ± 0.13.

from day 1 to day 4. The functional binding group for Chelex-DGT, i.e. the imidoacetate groups, are negatively charged at neutral and alkaline pH probably causing the electrostatic repulsion of anionic uranyl carbonates, the predominant U species in seawater. The fraction of U accumulated on the Chelex resin is therefore a combination of $UO_2^{2+}/UO_2(OH)^+$cations, but the uptake of these species were decreased below that expected probably due to competition with uptake of major cations present in seawater.

3.6. Field measurements of DGT-labile U

The ability of Metsorb-DGT and Chelex-DGT to determine U was assessed in situ, in a natural freshwater (Coomera River; pH 7.47 ± 0.13; conductivity $200\pm4\ \mu S\ cm^{-1}$) by deploying DGT samplers in triplicate for four days (Fig. 4). In situ deployment conditions are given in the Fig. 4 caption. To enable the determination of the diffusive boundary layer thickness (DBL), Metsorb-DGT samplers were deployed with three diffusive layer thicknesses ($\Delta g=0.05$ cm, 0.09 cm, 0.13 cm) at each site, while Chelex-DGT samplers were deployed with a single diffusive layer thickness ($\Delta g=0.09$ cm). Determination of the DBL enables accurate calculation of the analyte concentration and it was assumed that the DBL applied to both Metsorb- and Chelex-DGT devices.

The thickness of the DBL was determined from a plot of the inverse of the accumulated mass against the diffusive layer thickness (cm) (Fig. 4). The DGT-labile concentration of U can be determined from the slope of the regression line of this plot as indicated by Warnken et al.[28] Good linearity for the freshwater deployment ($R^2=0.996$; RSD 6–15%) confirms the applicability of the DGT-Metsorb technique for DBL thickness calculations.

It is often assumed that in fast flowing rivers and tidal flows the effects of the DBL are negligibly small relative to the gel thickness [15]. The thickness of the DBL was 0.003 cm. This value is comparable to published DBL thicknesses observed for both laboratory and field deployments. [19,20,28] Metsorb-DGT U concentrations, employing a D value of $4.25\times10^{-6}\ cm^2\ s^{-1}$, were determined to be $0.020\ \mu g\ L^{-1}$, which agreed well with the average filtered (0.45 μm) grab sample U concentration ($0.019\ \mu g\ U\ L^{-1}$). This excellent agreement suggests that the diffusion coefficients measured here can be used for field deployments with similar pH waters and also supports our conclusion that ionic strength in freshwaters is unlikely to cause problems. These assumptions may need to be investigated further for field deployments under very different conditions however. The Chelex-DGT measurement, corrected for DBL, was $0.029\ \mu g\ U\ L^{-1}$. As D varies a lot between pH 7 and 7.7 our estimate may be inaccurate and responsible for this overestimation. The diffusion coefficient within the range should be characterised in much more detail. This different result between Metsorb- and Chelex-DGTs could signify differences in the DGT-labile uranium measured.

4. Conclusions

The Metsorb-DGT method described in this paper has been shown to accurately measure dissolved U in synthetic and natural freshwaters. This work has confirmed the variation of U diffusion coefficients with pH and speciation changes and illustrates the importance of a thorough study for those analytes whose speciation is highly dependent on pH. This effect is so important for U that we recommend a filtered sample of any water in which DGT measurements are to be made to be used to determine the appropriate diffusion coefficient. The Metsorb-DGT method was more accurate than the Chelex-DGT method when deployed in both a synthetic and natural freshwater, although the techniques should be investigated more for a wider range of freshwaters. The Chelex-DGT was unable to measure U in seawater. Metsorb-DGT was found to give accurate results after 8 h deployments, but experienced competition for longer deployments that lead to an underestimation of the U concentration. These results demonstrate the strong potential for use of Metsorb-DGT to measure inorganic uranium in natural waters but also indicate that further characterisation of the effect of solution conditions on the uranium diffusion coefficients used may be necessary.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.05.012.

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