

**Evaluation of diffusive gradients in thin-films using a Diphonix[®] resin for
monitoring dissolved uranium in natural waters**

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Abstract

Commercially available Diphonix[®] resin (TrisKem International) was evaluated as a receiving phase for use with the diffusive gradients in thin-films (DGT) passive sampler for measuring uranium. This resin has a high partition coefficient for actinides and is used in the nuclear industry. Other resins used as receiving phases with DGT for measuring uranium have been prone to saturation and significant chemical interferences. The performance of the device was evaluated in the laboratory and in field trials. In laboratory experiments uptake of uranium (all 100% efficiency) by the resin was unaffected by varying pH (4-9), ionic strength (0.01-1.00 M, as NaNO₃) and varying aqueous concentrations of Ca²⁺ (100-500 mg L⁻¹) and HCO₃⁻ (100-500 mg L⁻¹). Due to the high partition coefficient of Diphonex[®], several elution techniques for uranium were evaluated. The optimal eluent mixture was 1 M NaOH/1 M H₂O₂, eluting 90% of the uranium from the resin. Uptake of uranium was linear ($R^2 = 0.99$) over time (5 days) in laboratory experiments using artificial freshwater showing no saturation effects of the resin. In field deployments (River Lambourn, UK) the devices quantitatively accumulated uranium for up to 7 days. In both studies uptake of uranium matched that theoretically predicted for the DGT. Similar experiments in seawater did not follow the DGT theoretical uptake and the Diphonix[®] appeared to be capacity limited and also affected by matrix interferences. Isotopes of uranium (U²³⁵/U²³⁸) were measured in both environments with a precision and accuracy of 1.6-2.2% and 1.2-1.4% respectively. This initial study shows the potential of using Diphonix[®]-DGT for monitoring of uranium in the aquatic environment.

Keywords: Diffusive gradients in thin films, Actinides, Uranium, Diphonix[®] resin, Natural waters, Water monitoring

1. Introduction

Monitoring of pollutants in the aquatic environment is necessary to maintain and protect water quality and this is mandated within legislation e.g. the European Union's Water Framework Directive (WFD, 2000/60/EC) and the European Union's Marine Strategy Framework Directive (MSFD, 2008/56/EC). These activities include monitoring the discharge of radionuclides. Due to both their chemical and radiological properties, radionuclides are highly toxic [1]. Most of the substances enter the aquatic environment through discharges associated with the generation of nuclear power as well from contaminated waste products [2]. The monitoring of radionuclides water usually relies on the collection of spot (bottle or grab) samples of water with subsequent analysis in the laboratory. This can be time consuming and costly and often episodic fluctuations in the concentration of a pollutant can be missed. A number of alternative monitoring strategies have been proposed, including the use of passive sampling devices [3]. Several designs of passive sampler exist for different classes (e.g. non-polar and polar organics, organometallics and metals) of chemicals and these have been reviewed [3-5]. For monitoring inorganic substances, metals and radionuclides the diffusive gradients in thin-films (DGT) sampler has been used extensively [6-9]. The device consists of a binding layer, which contains a specific resin with functional groups selective to the target ions; a layer of hydrogel of known thickness, which serves as the diffusive layer; and a protective outer membrane with a known pore size. DGT measures the labile, dissolved fraction of analytes [10] and pre-concentrates them *in situ* which reduces the risk of introducing contamination and chemical transformation of the sample [3].

Several workers have used DGT with different resin sorbents (copper ferrocyanide [11] and ammonium molybdophosphate [8] for ^{133}Cs , ^{134}Cs and ^{137}Cs ; TEVA[®] resin for ^{99}Tc

[12]; MnO₂ for Ra [13, 14]) to measure radionuclides in natural waters. For the measurement of total U, DGT sorbent phases include Chelex-100 [9, 15-17], Whatman DE 81 [15], MetsorbTM (TiO₂) [9, 18-20] and Dowex resin [21].

To our knowledge a resin with a strong affinity for the actinides has not been used with the DGT technique to monitor environmentally relevant concentrations of these chemicals. Resins with actinide specificity used to pre-concentrate U include the Actinide ResinTM, TRansUranium (TRU) and UTEVA[®], all available from TrisKem International (Bruz, France). However, TRU and UTEVA[®] have a higher partition coefficient for U in acidic media (1-10 M) [22], and it is difficult to back extract the U from the Actinide ResinTM due to its high partition coefficient and acid resistance [23]. We assessed the uptake of U using a DGT containing a Diphonix[®] chelating resin (100-200 mesh, TrisKem International) as it has a strong affinity for tetra- and hexa-valent actinides [24]. Diphonix[®] resin comprises a polymeric support containing geminally substituted diphosphonic acid groups and strongly hydrophilic sulfonic groups on a polymer backbone [24] (Figure S1 in supplementary data). The presence of two functional groups means the resin is a dual-mechanism polymer and can be characterised as a chelating ion-exchange resin [24]. The sulfonic acid cation exchange group allows for the rapid access of non-specific ions into the polymeric network, while the diphosphonic acid group is selective for a number of metal cations. Diphosphonic acid is strongly acidic and chelates the U through either ionised or neutral diphosphonic acid ligands due to the coordination properties of the P=O groups [24]. Diphonix[®] resin has been characterised by Chiariza et al. [24] (see Figures S2 and S3 in supplementary data). This resin has been used previously to remove U from groundwater. Using Diphonix[®], Phillips et al. [25] showed that U could be removed successfully from solutions with a pH > 5, and showed it was less sensitive to interferences by carbonates and nitrates, sulphates, iron, calcium and

sodium than the Chelex-100 resin. Diphonix[®] was therefore a good candidate resin for use in the DGT for the measurement of U in natural waters, due to its high affinity for actinides in weakly (< 0.1 M) acidic environments [25].

As other ions in solution can interfere with the uptake of U, the performance of the Diphonix[®] resin in the presence of some complexing agents was investigated [26]. Diphonix[®] has a high affinity for common environmental interferences such as Ca²⁺ [24, 25], so the uptake of uranium-calcium complexes and the competition of Ca²⁺ with UO₂²⁺ uptake were measured. Carbonate interferences were assessed as the resin is a cation-exchanger and the uranium-carbonate complexes are anionic to neutral (UO₂(CO₃)₂²⁻, UO₂(CO₃)₃⁴⁻) and so may not be accumulated on the resin. The measurement of the accumulation of U over time in both artificial seawater and low-ionic strength water was undertaken. Finally, DGT samplers containing Diphonix[®] resin were tested at two field sites: calcium carbonate-rich river water and a marine harbour, and the uptake of U measured over time.

2. Experimental

2.1. Chemical and standards

Chemicals were of analytical grade or better and supplied by Fisher Scientific Ltd. (Loughborough, UK), unless otherwise specified. Milli-Q (ultra-pure) water (> 18.2 MΩ cm, Millipore, Watford, UK) was used as the laboratory water. All U inductively coupled plasma-mass spectrometer (ICP-MS) standards and experimental working solutions were prepared in low density polyethylene (LDPE) or polystyrene (PS) containers with polypropylene lids (PP) from a 1000 mg L⁻¹ in 2% HNO₃ (Spex Certiprep, Fisher Scientific Ltd.) U stock solution unless otherwise stated. The ICP-MS internal standard was prepared from a 1000 mg

L^{-1} in 2% HNO_3 (Spex Certiprep) bismuth stock solution. These solutions were adjusted to a given pH by addition of either 1.0 M HNO_3 or 1.0 M NaOH , and to a given ionic strength by addition of NaNO_3 , with the pH monitored throughout experiments. Solutions were equilibrated with atmospheric CO_2 for 24 h before use unless otherwise specified. All measurements were undertaken in triplicate with containers open to the atmosphere to ensure continuing equilibration with the atmospheric $p\text{CO}_2$ (i.e. to ensure a constant inorganic carbon concentration throughout the experiments). All plastic apparatus was soaked for 24 h in 10% HNO_3 and rinsed three times in Milli-Q water prior to use.

2.2. Preparation of DGT devices

Polyacrylamide (PAM) diffusive gels (thickness 0.4, 0.8, 1.2 and 1.6 mm) were prepared according to Zhang and Davison [27]. The gels contained 15% v/v acrylamide solution (Acros Organics, ThermoFisher, Loughborough, UK) and 0.3% v/v of patented agarose cross-linker (DGT Research Ltd., Lancaster, UK). N,N,N',N' -tetramethylethylenediamine (TEMED, Acros Organics) was used as the catalyst and a freshly prepared solution of 10% ammonium persulfate (Acros Organics) was used as the initiator for polymerisation. The diffusive gels were stored in either 0.01 M NaNO_3 or 0.4 M NaCl prior to either freshwater or seawater deployments, respectively.

The 0.4 mm thick PAM binding gels were prepared with Diphonix[®] resin (product number DP-B-500-M-H, TrisKem International) using 1 g in 10 mL gel solution prior to polymerisation, according to [27]. Diphonix[®] resin is supplied with a high moisture content and was left to air dry in a laminar flow hood for 2 h prior to fixation in the acrylamide. In

order to ensure homogeneity of the resin gel mixture, it was continuously agitated using a magnetic stirrer (whilst ensuring that no air bubbles were introduced) prior to casting.

DGT mouldings were from DGT Research Ltd. (Lancaster, UK) and washed for 24 h in 10% HNO₃, and then rinsed three times in Milli-Q water prior to use. The devices were assembled according to [10] and stored at 4°C in zip lock plastic bags, containing 1-2 mL of water (matrix matched to deployment site) to ensure the diffusion properties of the gels were not altered, and to prevent the gels drying out. A disk of (0.2 µm pore size) Supor[®] polyethylene sulfone (Pall Corporation, Portsmouth, UK) was used as the outer membrane.

2.3. Analysis of DGT devices

After exposure, the Diphonix[®] resin binding gel was removed from the DGT device and eluted (48 h) with 1 M NaOH/1 M H₂O₂ (2 mL) solution (100 mL made by combining 90 mL 1.1 M NaOH and 10 mL H₂O₂ [30% w/v]). After seawater deployments, the resin gels were immersed in Milli-Q water (5 mL) for 1 h in a polypropylene container (30 mL) to remove excess unbound salts as detailed in [28]. Not including a washing step has been shown to reduce elution efficiency for some analytes [9] and was therefore employed here as a precaution. During this step it was unlikely that any U would be lost due to its high binding affinity for the resin. The eluents were then diluted 20 fold with Milli-Q water prior to instrumental analysis due to interference from the total dissolved solids, which are required to be < 2%. U was determined in all solutions by ICP-MS using an Agilent 7500ce series instrument (Agilent Technologies Inc., Japan). Total U was measured under normal plasma conditions in 'no gas mode' (no gas [He/H₂] in the reaction cell – only Ar), with the sample introduction system fitted with a micromist nebuliser. The analytical limit of detection

(calculated by the Agilent Chemstation software) for U was 1 ng L^{-1} , with a measurement relative standard deviation better than 7%. Laboratory blanks for each experiment were measured in triplicate using Diphonix[®] gel disks that had not been exposed to U. The average mass of U found was $0.79 \pm 0.08 \text{ ng}$ and $0.50 \pm 0.18 \text{ ng}$ for ^{238}U and ^{235}U respectively. Bismuth ($m/z = 209$; $25 \text{ } \mu\text{g L}^{-1}$) was used as an internal standard to compensate for any potential instrument drift. Certified reference materials SLRS-5 (river water reference material for trace metals, National Research Council Canada, Canada) and NASS-4 (seawater reference material for trace elements, National Research Council Canada, Canada) were analysed directly for SLRS-5 and after a 20-fold dilution for NASS-4 and were found to be within 1% of their stated values.

$^{235/238}\text{U}$ isotopic ratios were measured using an Agilent microflow ($100 \text{ } \mu\text{L min}^{-1}$) PTFE self-aspirating nebuliser, to eliminate any signal pulses caused by the peristaltic pump using the micromist concentric nebuliser. Isotopic ratios were determined with 3% standard deviation as low as $0.1 \text{ } \mu\text{g L}^{-1}$ total U ($0.000725 \text{ } \mu\text{g L}^{-1} \text{ } ^{235}\text{U}$). The certified reference material U005a (New Brunswick Laboratories, DoE, Washington, USA) was analysed and was found to be within 99.5% of the isotopic value ($0.00509 \text{ } ^{235/238}\text{U}$).

2.4. Calculation of time-weighted average concentrations of uranium

The concentration of U measured by the ICP-MS in $\mu\text{g L}^{-1}$ from the eluent was multiplied by the dilution factor ($\times 20$) to give the U concentration (C_e). The absolute mass (M) of the U in the resin gel was then calculated using equation 1, where M is calculated taking into account the gel volume ($V_g, \text{ cm}^3$), the eluent volume ($V_e, \text{ mL}$), the measured concentration of U in the eluent ($C_e, \text{ ng mL}^{-1}$) and the elution factor (f_e) [27].

$$M = \frac{Ce(Vg+Ve)}{fe} \quad (1)$$

M from equation 1 was then used to calculate the (time-weighted average) TWA concentrations (equation 2) where the concentration (C_{DGT} , ng mL⁻¹) was calculated using the mass of the analyte in the binding gel (M , ng), the thickness of the diffusive path length (diffusive gel and filter membrane) (Δg , cm), the diffusion coefficient of the analyte (D , cm² s⁻¹) (as determined at different pHs for U by [9]), deployment time (t , s) and the area of the sample exposure window (A , cm²).

$$C_{DGT} = \frac{M\Delta g}{DtA} \quad (2)$$

The diffusion coefficients (D) were corrected for temperature (T , °C) using the Stokes-Einstein equation (equation 3) [29] and the viscosity of water (η , mPa s) [30]. Diffusion coefficients used for seawater were 10% lower than freshwater [10], due to increased viscosity of higher ionic strength solutions.

$$\frac{D_1\eta_1}{T_1} = \frac{D_2\eta_2}{T_2} \quad (3)$$

The diffusive boundary layer (DBL) thickness (δ) was calculated using equation 4 after Warnken et al. [31]. A straight-line plot of $1/M$ versus Δg has a slope (m) of $1/(DC_{DGT}At)$ and an intercept (b) of $\delta/(DC_{DGT}At)$. The intercept (b) divided by the slope (m) of this plot gives δ , also accounting for the discrepancies in diffusion coefficients of uranyl in the gel (equation 5).

$$\frac{1}{M} = \frac{\Delta g}{DC_{DGT}At} + \frac{\delta}{DC_{DGT}At} \quad (4)$$

$$\delta = \frac{b}{m} \left(\frac{D_M^W}{D_M^{gel}} \right) \quad (5)$$

The thickness of the DBL was included in the C_{DGT} calculations for the field trials using equation 2. The effective sampling area (A_e) was 3.8 cm² instead of the 3.14 cm² used in the laboratory trials, as described by Warnken et al. [31].

The predominant uranyl species in the freshwater site ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$) had a similar diffusion coefficient in water [32] as the diffusive gel (so $D_M^W : D_M^{gel} = 1$) and was, therefore, not considered here. The predominant uranyl species in seawater is $\text{UO}_2(\text{CO}_3)_2^{2-}$ and has a higher diffusion coefficient in water ($D_M^W : D_M^{gel} = 1.18$) [32] and was therefore accounted for when calculating the thickness of the DBL (equation 5).

2.5. Performance of Diphonix[®] resin

2.5.1. Uptake and elution efficiencies of uranium

The uptake and elution efficiencies of the resin gel for U were determined using a batch method. Disks (0.16 cm³) of the resin gel were placed in PS vials (30 mL) and a solution (10 mL, 0.01 M NaNO₃ at pH 7 ± 0.2) containing 100 µg L⁻¹ of U(VI) added. Vials were shaken (48 h) on a rotating table (IKA[®] KS 130 Basil, Sigma-Aldrich Ltd., Gillingham, UK) at 240 revolutions min⁻¹. Aliquots (1 mL) were taken and acidified (using 20 µL, 6 M HCl) before and after resin gel exposure to determine the mass balance and percentage uptake of U. To determine the elution efficiencies (the quantity of U eluted from the resin as a ratio of the U taken up by the resin), the resin gels were removed from the solutions and placed into new PS vials containing a trial eluent detailed in Table 1. The tubes were then agitated (48 h) on the rotating table and the resin gel removed. Control experiments containing 10 mL

of $100 \mu\text{g L}^{-1}$ of U, 0.01 M NaNO_3 at $\text{pH } 7 \pm 0.2$ with no resin gels showed no sorption of U to the vessel.

Two further elution procedures were tested to extract the U from the resin; microwave digestion using reverse *aqua regia* (3:1 v/v mixture of HNO_3 and HCl) at a frequency of 2.45 GHz for 35 min and digestion using lithium metaborate fusion as described by Croudace et al. [23]. In the later procedure the resin gels were heated in a graphite crucible (9 mL, SCP Science, Courtaboeuf, France) with lithium metaborate flux (2 g) at 1100°C for 15 min. The clear flux was then poured directly into 8.0 M HNO_3 (5 mL) and stirred vigorously until dissolved. The dissolved flux was then diluted 20 times (due to high lithium salt content) prior to analysis using ICP-MS.

2.5.2. *Effect of pH and ionic strength on uptake of uranium*

A batch method was used as per section 2.5.1. A 0.16 cm^3 disk of Diphonix[®] resin gel was placed in a PS vial (30 mL) and exposed to solutions (10 mL) containing $100 \mu\text{g L}^{-1}$ of U (VI) in 0.01 M NaNO_3 at pH 4, 5, 6, 7, 8 and 9 (to test the effect of pH) or $100 \mu\text{g L}^{-1}$ of U (VI) in 0.01, 0.05, 0.1, 0.4, 0.7 and 1.0 M NaNO_3 at pH 7 (to test the effect of ionic strength). The solutions used to investigate the effect of pH on the uptake of U were sealed immediately upon reaching the desired pH to prevent any ingress of atmospheric carbon dioxide. Vials were shaken (48 h) on a rotating table. One mL aliquots of the solution were taken and acidified (using $20 \mu\text{L}$, 6 M HCl) before and after resin gel exposure to determine the mass balance and percentage uptake of the U. Solutions were made up in the PS vials in triplicate for each pH value tested here with no addition of resin gels, to assess the sorption of U to the PS vials.

2.5.3. *Effect of interferences and ligands on uptake of uranium*

Effect of the presence of calcium (Ca^{2+}) and bicarbonate (HCO_3^-), as a potential interferences to U uptake by the device were tested. Table S1 (supplementary data) details the concentrations used, which exceeded typical environmental values to ensure any effect from an episodic event (e.g. heavy rain or flooding) could be seen. The high concentrations of HCO_3^- are double those seen in some fluvial systems [33] but similar to that found in seawater, with Ca^{2+} five times that found in some alkaline fluvial systems [34] and approximately that found in seawater. An acid washed PP container (3 L) containing a 0.01 M NaNO_3 , $100 \mu\text{g L}^{-1}$ U solution (3 L) plus either Ca^{2+} or HCO_3^- was equilibrated for 24 h at $\text{pH } 7.0 \pm 0.4$ for the Ca^{2+} additions and $\text{pH } 7.8 \pm 0.2$ for the HCO_3^- additions. DGT devices were then deployed (24 h) in triplicate, then removed and eluted as per section 2.3. Two aliquots (1 mL) of the solution were taken daily from the exposure tank. One was filtered through a $0.2 \mu\text{m}$ filter and acidified (20 μL , 6.0 M HCl), the other was acidified (20 μL , 6.0 M HCl) to measure the concentration of U. Equation 2 was used to calculate the C_{DGT} , and this was compared to concentration of U in the spot water samples.

2.5.4. *Mass accumulation of uranium over time*

To measure the uptake of U over time, DGT devices containing Diphonix[®] resin were exposed (5 days) in square PP tanks (5 L) to 0.01 M NaNO_3 (low ionic strength water) plus 0.983 mM L^{-1} NaHCO_3^- to buffer the solution to $\text{pH } 7.7$ (a similar pH to that at the freshwater field test site) or an artificial seawater solution (prepared using the major salts detailed in [35]: NaCl , Na_2SO_4 , KCl , NaHCO_3 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) containing $100 \mu\text{g L}^{-1}$ U). Devices were removed in triplicate at the time intervals of 4, 8, 24, 48, 72, 96 and 120 h, and

the resin gels eluted as per section 2.3. Two aliquots (1 mL) of the solution were taken daily from the exposure tank. One was filtered through a 0.2 μm filter and acidified (20 μL , 6.0 M HCl), the other was acidified (20 μL , 6.0 M HCl) with no filtration to ensure no precipitates were formed in the solution that may affect DGT uptake.

2.5.5. Field deployments

Two field sites (freshwater and marine) were used. The freshwater site (51.446933 N, -1.3838275 W) was located on the River Lambourn near Boxford, Berkshire, UK. The river has a chalk-fed aquifer catchment and an average pH of 7.8-8 [34]. DGT devices were deployed between Perspex plates (15 x 7 cm, 8 devices per plate) and attached to a rope and float and weighted to the river bed. The marine site was located adjacent to the National Oceanography Centre, Southampton, UK (50.891313 N, -1.3938260 W). This is a well-mixed estuary with a salinity of 29 to 33, dependent upon tidal fluctuations and freshwater inputs. The deployment site, was located by an enclosed pontoon, and was therefore a low flow site with only the tidal fluctuations agitating the water. Devices were deployed as above 1 m below the water surface. Ropes were used to attach the exposure plate to the dock pontoon.

Three DGT devices containing the Diphonix[®] resin gel were removed on days 1, 2, 3, 5, 7 and 10 of the trial. To assess the influence of the DBL, DGTs were deployed for 3 days with diffusive layer PAM gel thicknesses (including 0.015 cm to account for the Supor[®] filter membrane) of 0.015, 0.055, 0.095 and 0.135 cm as per Warnken et al. [31]. Diffusion coefficients from Hutchins et al. [9] were used to calculate the TWA concentrations of U over the different deployments. Spot samples of water (20 mL), collected each time a DGT device

was retrieved, were filtered (0.2 μm pore size Supor[®] filter membranes) and acidified *in situ* with 6 M HCl (40 μL). Water temperature and pH were recorded on each occasion so that diffusion coefficients could be corrected for variations in environmental conditions.

Triplicate procedural DGT blanks were exposed to the field environment during deployment and retrieval of the samplers. Blanks were eluted and analysed with the samples as above.

3. Results and discussion

3.1. Uptake and elution efficiencies and the effect of pH and ionic strength

Uptake and elution efficiencies were measured by exposing the Diphonix[®] gels to a known mass of U and then eluting the bound element. Uptake of U by the Diphonix[®] resin was 100% ($1,008 \pm 3$ ng), which has a very high affinity for the tetra- and hexa-valent actinides even in acidic environments with reported distribution ratios D_R , mg L^{-1} (see equation S1 in supplementary data for explanation) of $\sim 20,000$ for 10.0 M HNO_3 , 500 for 4.0 M HF and 700 for 4.0 M H_2SO_4 [24]. This made extraction of U difficult to achieve using conventional acidic extractants. Elution techniques presented by other workers were trialled, such as a lithium metaborate fusion described by Croudace et al. [23]. This technique successfully extracted Pu and U from an ActinideTM resin with a higher partition coefficient for the actinides than Diphonix[®]. Using a version of this procedure in our laboratory, difficulties were experienced in ensuring all the flux products were transferred from the graphite crucible to the acid solution due to the small quantities of resin used in each gel disk. The use of a different crucible material (e.g. platinum-gold used by Croudace et al. [23]) may help to increase the recovery for this complex multi-step handling procedure.

Microwave digestion of the Diphonix[®] resin using reverse *aqua regia* was also trialled, however, due to the design of these closed vessels the gas evolved during the digestion of the gels could not be vented. Due to these difficulties both these alternative elution techniques were not proceeded with further.

Other eluents and techniques were evaluated, (Table 2), including an ethylenediaminetetraacetic acid eluent described by Maxwell et al. [36] for the extraction of Be from Diphonix[®], citric acid (on the recommendation of Triskem International), HNO₃ (a commonly used eluent for DGT) and NaOH (successfully used to extract U from a TiO₂-based resin [9]).

A solution of 1 M NaOH/1 M H₂O₂ (2 mL) was used to elute the U from the Diphonix[®] resin-gels, as the recovery was the highest (average of 90% across pH 4-9), as shown in Figure 2. The major drawback to this eluent is the necessity for sample dilution to ensure that the total dissolved salt content is < 2% for the ICP-MS analysis. This avoids signal suppression by the Na⁺ ions. Another reason for the 20-fold dilution is to ensure that there is no corrosion of the glass introduction system and torch in the ICP-MS by the NaOH. This 20-fold dilution could be avoided through the addition of a clean-up step to eliminate the Na⁺ ions and convert to a mildly acidic solution as described by Zheng & Yamada [37]. Sample clean-up in conjunction with this methodology is an area for further research.

There are a number of reasons NaOH may have eluted the U from Diphonix[®]. Firstly, NaOH could have been effective because at pH 14 the affinity of U for the –OH groups in the resin and the formation constant of UO₂(OH)₄⁻² is higher than phosphorus containing ligands (such as the phosphonic acid functional groups in the Diphonix[®] resin). Similar elution efficiencies (95.2 ± 0.4%) for U using 1.0 M NaOH/1.0 M H₂O₂ with a TiO₂-based resin were found by [9]. Chiarizia et al. [38] described the removal of Cr from Diphonix[®] using

0.33 M H₂O₂ in 1.0 M NaOH solution, which alters the oxidation state due to the sodium peroxide formed by the H₂O₂/NaOH mixture being strongly oxidizing. It is possible that the stripping mechanism for U is similar to that displayed for Cr. NaOH solutions are not normally used in the radiochemical extraction and separation of actinides due to the precipitates formed by the tri- and tetra-valent actinides. Alternative elution schemes for use with Diphonix[®] resin include a diphosphonic acid or 1-hydroxyethylidene-1,1-diphosphonic acid based eluent with oxidation using Fenton's reagent, followed by radiochemical separation using TRU resin (available from TrisKem International) [39]. This scheme extracts very tightly bound actinides and separates those thus avoiding isobaric or spectral interferences during the analysis phase. This method cannot be used with ICP-MS analysis undertaken in this study without further purification steps as phosphoric acid is highly corrosive to the nickel sampling and skimmer cones and the lens stack of the instrument.

There was consistent uptake (100%) of U across all pHs and ionic strengths tested (Figures 1 and 2) and was in agreement with previous studies showing phosphoric acid ligands take up U over a wide pH range [40, 41].

The limit of detection (LoD) for the method was calculated using the Diphonix[®] gel disk blank. This had 0.79 ± 0.08 ng U; by taking the LoD as 3 times the standard deviation of the blank plus the blank (to ensure that any U detected was significantly greater than the blank measurement). Hence the lowest detectable mass of U sequestered on the Diphonix[®] resin was 1.03 ng. Accounting for the elution volume (2 mL), the dilution factor required for ICP-MS analysis (x 20), and the elution factor (0.9), this gave a LoD of $0.046 \mu\text{g L}^{-1}$ for U.

3.2. Effect of interferences and ligands on uptake of uranium under laboratory conditions

Speciation distributions for each ligand tested were calculated using Visual Minteq, version 3, beta (© 2010 [KTH, Department of Land and Water Resources Engineering, Stockholm, Sweden](#)) (formation constants are shown in Table S2 of the supplementary data) [42]. This was undertaken in order to support the experimental work outlined in section 2.5.3. The DGT U concentration of the deployment solution in each tank over the deployment period was calculated using equation 2, and compared as a ratio to the concentration of U measured in spot water samples. A ratio of 1:1 shows that the DGT device was measuring the same labile U inorganic species as were present in the spot water samples.

Increasing the concentration of Ca in the exposure tanks did not affect the uptake of U by the Diphonix[®] resin (Figure S4a in supplementary data). Ca²⁺ ions formed complexes with UO₂²⁺ in the presence of atmospheric carbon dioxide at pH > 6.5. Ca forms soluble CaUO₂(CO₃)₃²⁻ and Ca₂UO₂(CO₃)₃ complexes [43, 44] (Figure S4b in supplementary data). The resin was either capable of dissociating and out-competing the anionic species or took up the U-Ca complexes directly.

Carbonate speciation with the uranyl ion accounts for 90–100% of U in the oceans [45]. The complexation of U with carbonate may affect uptake by the devices used in this study. Other studies showed increasing the anionic strength of a solution, by adding HCO₃⁻, can severely affect uptake [7]. Here both Chelex-100 and Spheron-Oxin[®] resins showed a decrease in the uptake of U with increasing carbonate concentrations, probably as a result of the increasingly anionic species formed. There was no decrease in the uptake of U observed in our study (Figure S5 in supplementary data) as a result of carbonate complexation, due to the higher affinity of U for phosphonic acid. It is likely that uptake kinetics of U in the presence of strongly anionic ligands will be lower, but the di-phosphonic groups in the

Diphonix[®] resin should dissociate the uranyl anion [40, 41]. Even in the presence of high concentrations of anionic ligands, such as NO₃⁻, Diphonix[®] was still capable of removing U from solution [24].

3.3. Accumulation of uranium over time

In the low ionic strength water, the amount of U accumulated by the Diphonix[®] resin was in agreement with the theoretically predicted value (using equation 2) (Figure 3a). The predominant U species present at pH 7.7 was UO₂(CO₃)₂²⁻ with no precipitates formed. The device did not appear to be capacity limited under the experimental conditions used. Using equation 2, the observed ratio of the DGT uptake of U/solution concentration of U was 1:1 for the entire deployment period. Deployments in artificial seawater (Figure 3b) showed devices have a linear uptake of U, but not as predicted by equation 3 after 4 h. This is similar to Chelex-100 in this medium [9]. Whilst Diphonix[®] has the capability to take up U from complex media in the presence of high concentrations of CO₃²⁻, uptake kinetics may be compromised by competition with other commonly occurring cations. We have shown in the laboratory that changing the concentration of Ca²⁺ did not affect the accumulation of U by the device. The effects of other major cations (e.g. Mg²⁺) present in a complex environmental matrix, whilst not investigated in this study, may have an impact on the overall uptake efficiency of the DGT device.

3.4. Field deployments

Over the deployment period at the freshwater site the average concentration of U in spot water samples, taken each time a DGT sampler was retrieved, was 0.2 µg L⁻¹. At this site

100% of the U predicted (using equation 2) was taken up for the first 7-days of the trial, after which the accumulation decreases to 70% of the predicted value by day 10 (Figure 4a). As U was not capacity limited under laboratory conditions in artificial freshwater and accumulated 4.4 $\mu\text{g U}$ (Figure 3a), the field limitation (reached at 4.3 ng U accumulated) is most likely as a result of biofouling of the diffusional surface area. Previous studies have shown that U can be effectively removed from water using microbial mats [46] or the binding sites on the resin being filled by other compounds.

At the marine site over the deployment period, the average concentration of U measured in spot water samples taken each time a DGT sampler was retrieved, was 3.3 $\mu\text{g L}^{-1}$. This was similar to concentrations of U found previously at this site [19]. The predominant U species in the marine environment are $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, with diffusion coefficients of $5.52 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25°C [32]. This gives a $D_M^W : D_M^{gel}$ ratio of 1.18 which was considered when calculating the DBL (equation 5). The DGT accumulated (within error range) U linearly for 3 days and was in agreement with equation 2, thereafter uptake departed from the predicted values (Figure 4b). U in seawater exists predominantly as soluble uranyl carbonate anions, which were taken up under laboratory conditions, it can be reasoned that the high carbonate concentrations would not be responsible for the departure of the DGT values from the predicted values. This departure could be due to a synergistic effect of the different cations present in this complex matrix competing with the U for available binding sites on the resin. The deviation from the modelled uptake as per the C_{DGT} equation (equation 2) occurred in the laboratory after 0.06 $\mu\text{g U}$ had been accumulated by the device. In the field, departure from the modelled uptake occurred when 0.02 $\mu\text{g U}$ had been accumulated. The discrepancy in the deployment time could be as a result of the concentration of the U solution used (100 $\mu\text{g L}^{-1}$ in the laboratory; 3.3 $\mu\text{g L}^{-1}$ in the field) and the lower U

accumulation in the field as a result of the highly complex matrix (only major ions were included in the laboratory trial solutions) resulting in ionic competition for binding sites on the resin.

At each site the average thickness of the DBL for the DGT was calculated according to equation 5; being 0.062 ± 0.004 cm at the freshwater site and 0.107 ± 0.013 cm at the marine site (Figures S6 and S7 respectively, in supplementary data). This was in agreement (DBL = 0.046 ± 0.006 cm) with previous work at the freshwater site, but higher (DBL = 0.042 ± 0.019 cm) at the marine site. The concentration of U calculated using equation 2 was reduced by up to 40% at the freshwater site and 50% at the marine site if the effect of the DBL was not accounted for. The difference in DBL at the two sites could be attributed to differences in water turbulence. At the marine site the water flow rate was low due to the enclosed nature of the dock the pontoon, only being agitated by tidal fluctuations.

Isotopic ratios ($^{235/238}\text{U}$) of U were measured for the DGT and in spot water samples (Table 3). Both field sites were found to have a natural $^{235/238}\text{U}$ ratio of 0.00725. This ratio could be determined accurately (within 1.5%) after 1 day of deployment at the marine site and after 2 days at the freshwater site. The longer accumulation time needed at the freshwater site was a result of the lower concentrations of U being present. The average concentration of U in the River Lambourn was $0.2 \mu\text{g L}^{-1}$ and $3.3 \mu\text{g L}^{-1}$ at the marine site throughout the deployment period. The limiting factor in the measurement of isotopic ratios using ICP-MS is the low abundance of ^{235}U , which can be overcome through longer ICP-MS counting times for this isotope. This means that the isotopic ratios were distinguishable in the spot water samples at both deployment sites. The freshwater samples required no dilution and could be analysed directly with the ICP-MS; the seawater samples required a 20-fold dilution due to high matrix interferences. Diphonix[®] outperformed other resins used to measure isotopic

ratios of U in these environments. The accuracy of the isotopic ratio measurements in this study were 0.25% and 1.2 % for marine and freshwater sites respectively. Values for the accuracy of these measurements in a previous study for Chelex-100, MetsorbTM and MnO₂ resins ranged from 5-8 %, 1-2 % and 0.1-4.0 % respectively [19]. These data support the potential use of the DGT in long-term environmental monitoring programmes for actinides.

4. Conclusions

The performance of the Diphonix[®] resin used with DGT technique was assessed in the laboratory and under freshwater and marine field conditions. Field trials showed that the accumulation of U predicted using the DGT equation was 7 days in freshwater and 3 days in seawater. These are thus considered the maximum permitted field deployment times for this technique when undertaking any environmental monitoring. This deployment time is longer than other resins (e.g. Chelex-100, MetsorbTM and MnO₂) tested for the sequestration of U [19]. The measurement of isotopic ratios of U was possible using the Diphonix[®] resin with a higher precision (1-2%) and accuracy (within 1.3%) than found in previous studies [19, 20]. The Diphonix[®] resin was found to be not capacity limited in freshwater systems; the time limit of 7 days was due to potential biofouling of the membrane [20]. However, in marine systems due to potential ionic interferences its usefulness as a monitoring tool is potentially limited. The resin outperformed most other sorbents used previously with DGT both in terms of isotopic measurements and linearity of the accumulation of U over time, especially for freshwater environments. Future research should be focused on extending the capabilities of this method to examine other actinides. A clean-up step, or further development of the HEDPA elution scheme, in conjunction with radiochemical separations may provide a

method that is capable of measuring a wider range of actinides such as Am, Pu and Th [40, 41].

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Table 1. Eluents trialled to extract uranium complexed onto the Diphonix[®] resin. Eluent strength and volumes are also listed. The elution trials used 30 mL polystyrene tubes which were shaken with the resin gel (48 h) on a rotating table (IKA[®] KS 130 Basil, Sigma-Aldrich Ltd., Gillingham, UK) at a set speed of 240 revolutions min⁻¹.

Eluent	Volume (mL)
1.0 M NaOH + 1 M H ₂ O ₂ *	2
0.5 M NaOH + 1 M H ₂ O ₂ **	2
0.2 M Na ₄ EDTA	10
0.2 M citric acid	1
8.0 M HNO ₃	2
1.0 M HNO ₃ + 1 M H ₂ O ₂ ***	2

*100 mL made by combining 90 mL 1.0 M NaOH and 10 mL H₂O₂

**100 mL made by combining 90 mL 0.5 M NaOH and 10 mL H₂O₂

***100 mL made by combining 90 mL 1.1 M HNO₃ and 10 mL H₂O₂

Table 2. Elution efficiency of the eluents trialled to extract uranium complexed onto the Diphonix[®] resin. Eluent strength and volumes are also listed. The elution trials used polystyrene tubes (30 mL) which were shaken with the resin gel (48 h) on a rotating table (IKA[®] KS 130 Basil, Sigma-Aldrich Ltd., Gillingham, UK) at a set speed of 240 revolutions min⁻¹. The standard deviation is based on triplicate experiments.

Eluent	Volume (mL)	Elution efficiency (%)	Standard deviation
1.0 M NaOH + 1.0 M H ₂ O ₂	2	90	4.4
0.5 M NaOH + 1.0 M H ₂ O ₂	2	77	19.4
0.2 M Na ₄ EDTA	10	2.5	5.6
0.2 M citric acid	1	0.1	0.05
8.0 M HNO ₃	2	1.78	0.4
1.0 M HNO ₃ + 1.0 M H ₂ O ₂	2	0.05	0.005

Table 3. Isotopic ratios ($^{235/238}\text{U}$) of uranium found in DGT-Diphonix[®] resin devices and spot water samples taken at the marine and freshwater field sites (the natural isotopic ratio for $^{235/238}\text{U}$ is 0.00725).

	Average isotopic ratio	Marine		Freshwater		
		RSD* (%)	Accuracy** (%)	Average isotopic ratio	RSD* (%)	Accuracy** (%)
DGT-Diphonix [®] resin device	0.00730	1.60	-1.38	0.00734	2.19	-1.20
Spot water sample	0.00735	2.55	-0.59	0.00723	1.51	0.25

*Standard deviation calculated as a % of the mean (precision).

**Calculated as (actual reading – measured/actual) x 100.

Figure captions

Fig. 1. Uptake and elution efficiency of Diphonix[®] resin gel for uranium across a range of ionic strengths. Where ▲ are the uptake efficiencies and ◆ are the elution efficiencies for uranium. Each replicate was 20 mL of solution at pH 7, with an ionic strength of 0.01 M (as NaNO₃) and a uranium concentration of 100 µg L⁻¹. Error bars are the standard deviation of triplicate measurements.

Fig. 2. Uptake and elution efficiency of Diphonix[®] resin gel for uranium across a range pHs. Where ▲ are the uptake efficiencies and ◆ are the elution efficiencies for uranium. Uptake conditions were 0.01 M NaNO₃, 20 mL of 100 µg L⁻¹ uranium. Error bars are the standard error of triplicate measurements.

Fig. 3 (a). Mass of uranium accumulated with time for 120 h deployment in a 0.01 M NaNO₃ solution (pH 7.7 ± 0.05, buffered using 0.983 mM HCO₃). Average concentration of uranium in the exposure tank was 106 µg L⁻¹, average temperature was 20°C and the calculated diffusion coefficient was 3.14 x 10⁻⁶ cm² s⁻¹; (b). Mass of uranium accumulated with time for 120 h deployment in artificial seawater. Solution pH 8.1 ± 0.05, average concentration of uranium the exposure tank was 104 µg L⁻¹, average temperature was 20°C and the calculated diffusion coefficient 3.35 x 10⁻⁶ cm² s⁻¹. Dashed lines represent model uptake of uranium as calculated from equation 2, using the average solution concentration of uranium; and the solid line represents the linear regression for the uptake of uranium during the linear uptake phase. Error bars are the standard error of triplicate measurements.

Fig. 4. Mass of uranium accumulated with time for Diphonix[®]-DGT devices in 10-day field trials (a). Freshwater deployment, average water pH 7.9, average water temperature 12°C, average concentration of uranium in spot water samples 0.2 µg L⁻¹, calculated diffusion coefficient for uranium 1.59 x 10⁻⁶ cm² s⁻¹; thickness of DBL 0.062 ± 0.004 cm; (b) marine deployment, average water pH 8.2, average water temperature 13°C, average concentration of uranium in spot water samples 3.3 µg L⁻¹, calculated diffusion coefficient for uranium 1.43 x 10⁻⁶ cm² s⁻¹, thickness of DBL 0.091 ± 0.011 cm. Dashed lines represent model uptake of uranium as calculated from equation 2, using the average water concentration of uranium; and the solid line represents the linear regression for the uptake of uranium during the linear uptake phase. Error bars are the standard error of triplicate measurements.

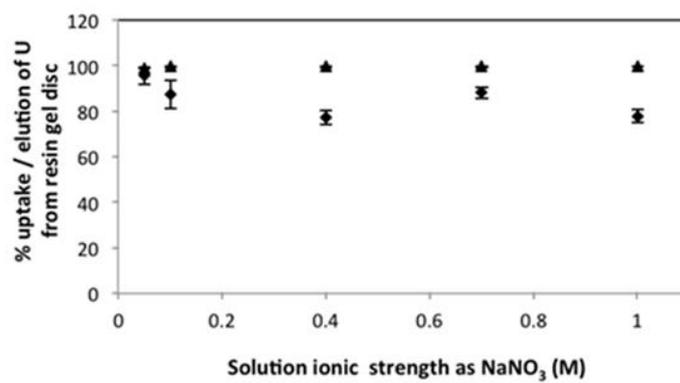


FIGURE 1

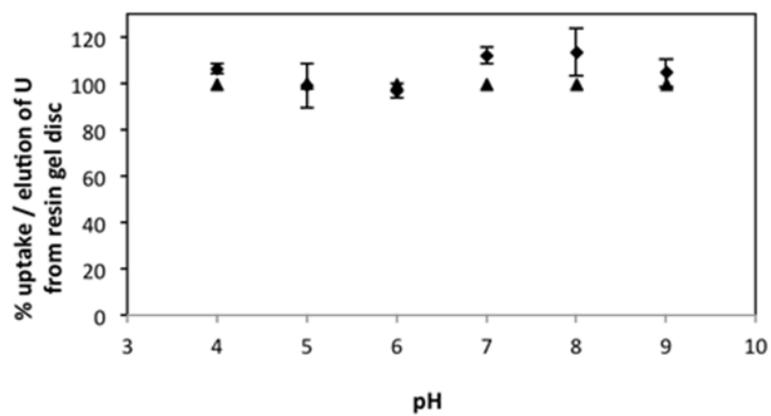


FIGURE 2

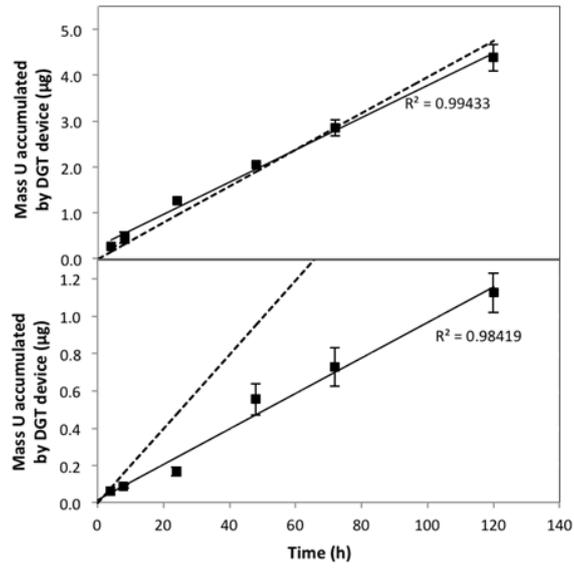


FIGURE 3

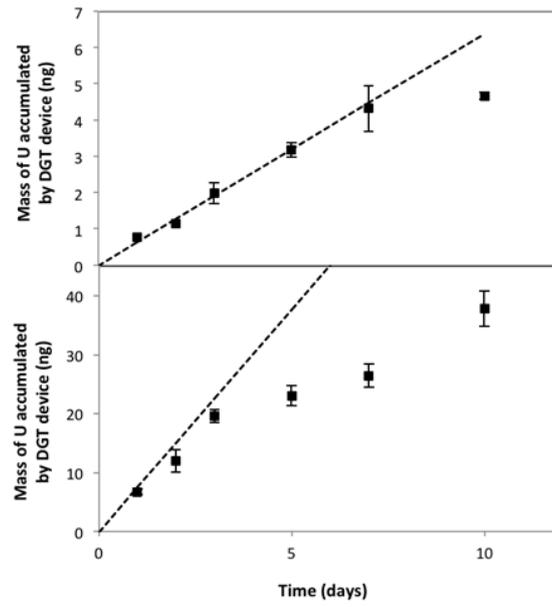


FIGURE 4

SUPPLEMENTARY DATA

Evaluation of diffusive gradients in thin-films DGT using a Diphonix[®] resin for monitoring dissolved uranium in natural waters

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Structure of Diphonix[®] resin

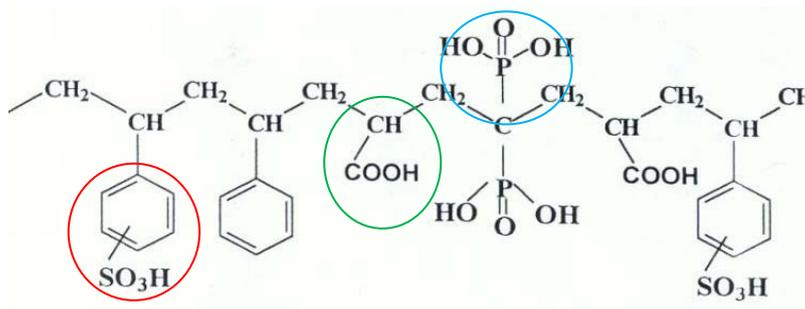


Figure S1. Structure of Diphonix[®] resin showing the hydrophilic sulfonic functional groups (highlighted in red), the phosphonic acid groups (highlighted in blue) and carboxylic acid (highlighted in green) all of which are active in binding metal ions from solution (from TrisKem International Diphonix[®] fact sheet, http://www.triskem-international.com/iso_album/ft_resine_diphonix_en.pdf).

Diphonix[®] was a candidate resin for the measurement of U in natural waters in conjunction with DGT due to its high affinity for the actinides in weakly (< 0.1 M) acidic environments [1]. Figure S2 shows the retention of the actinides americium, plutonium, uranium, thorium and neptunium with increasing acid concentrations. The retention is shown as a dry weight distribution ratio (D , mg L⁻¹), which is the ratio between the metal concentrations in the resin phase and in the solution in equilibrium with the resin, as shown in equation S1 below [2]:

$$D = \left(\frac{A_o - A_f}{W} \right) / \left(\frac{A_f}{V} \right) \quad (S1)$$

where A_o and A_f are the aqueous phase activities (counts per minute) before and after equilibration, respectively; W is the dry weight of the resin (g) and V is the volume of the aqueous phase (mL).

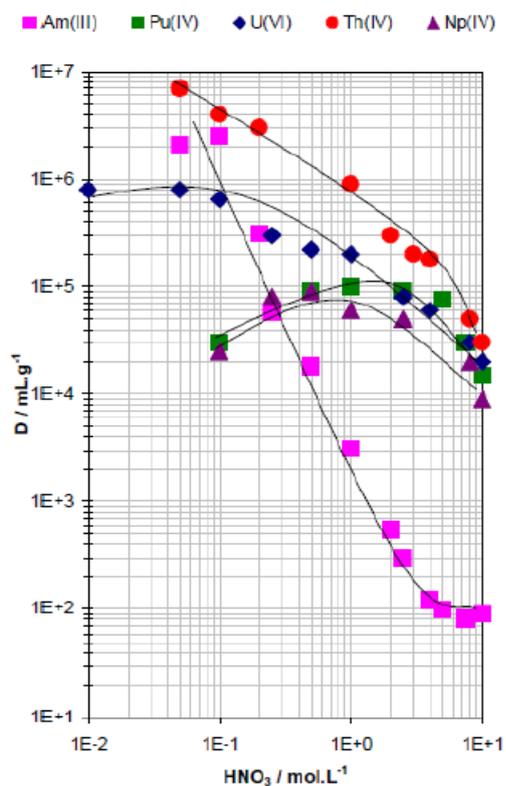


Figure S2. Acid dependency of retention of the actinides americium (Am), plutonium (Pu), uranium (U), thorium (Th) and neptunium (Np) on the Diphonix[®] resin, where D is the dry weight distribution ratio of the metal concentrations in the resin phase and the in the solution in equilibrium with the resin. From Chiarizia et al. [1].

In weakly acidic environments ($\text{HNO}_3 < 0.1 \text{ M}$), it can be seen from Figure S2 that the distribution ratio for U is approximately $1 \times 10^6 \text{ mL g}^{-1}$. Americium and thorium have higher distribution ratios of approximately 2×10^6 and $7 \times 10^6 \text{ mL g}^{-1}$ respectively. Plutonium and neptunium distribution ratios are lower at approximately $2 \times 10^4 \text{ mL g}^{-1}$. These high distribution ratios across a range of actinides demonstrate the potential to extend the use of the Diphonix[®] resin to measure other actinides.

However, the complexation power of the Diphonix[®] resin also extends to other metal cations, such as calcium (Ca^{2+}) aluminium (Al^{3+}) and iron (Fe^{2+}), the uptake of which may inhibit U uptake if they occur in higher concentrations than U [1]. The retention of some commonly occurring cations in natural waters is shown in Figure S3.

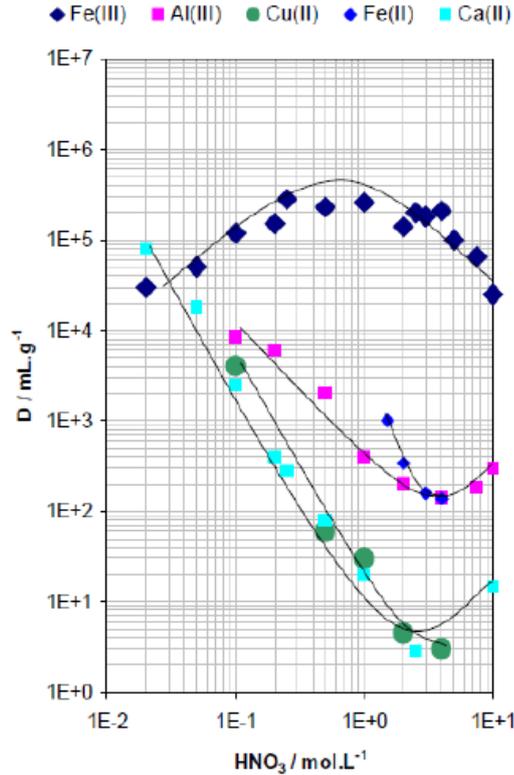


Figure S3. Acid dependency of retention of the commonly occurring cations iron (Fe^{2+} and Fe^{3+}), aluminium (Al^{3+}), copper (Cu^{2+}) and calcium (Ca^{2+}) on the Diphonix[®] resin, where D is the dry weight distribution ratio of the metal concentrations in the resin phase and the in the solution in equilibrium with the resin. From Chiarizia et al. [1].

Diphonix[®] resin has been used in previous studies to remove U from ground water. Phillips et al. [3] showed that U could be successfully removed using Diphonix[®] from solutions with a pH > 5, and was also shown to be less sensitive to interferences by carbonates and nitrates, sulphates, iron, calcium and sodium than the Chelex-100 resin.

Table S1. Salt and concentration of ligands tested in this study.

Ligand (salt used)	Salt concentrations tested in this study		
Ca^{2+} ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)	500 mg L ⁻¹	250 mg L ⁻¹	100 mg L ⁻¹
HCO_3^- (NaHCO_3)	500 mg L ⁻¹	250 mg L ⁻¹	100 mg L ⁻¹

Table S2. Formation constants for U(VI) and U(IV) species in solution used in the Visual Minteq [4] calculation of uranium speciation (I = 0, t = 25°C) (*taken from [5]).

Reaction	log K
$\text{UO}_2^{2+} + \text{H}_2\text{O} \leftrightarrow \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.2
$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{UO}_2(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-12.2
$\text{UO}_2^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$	-20.2
$\text{UO}_2^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{UO}_2(\text{OH})_4^{2-} + 4\text{H}^+$	-33.0
$\text{UO}_2^{2+} + \text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_2\text{OH}_3^+ + \text{H}^+$	-2.7
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	-5.62

Reaction	log K
$3\text{UO}_2^{2+} + 4\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_3(\text{OH})_4^{2+} + 4\text{H}^+$	-11.9
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.55
$3\text{UO}_2^{2+} + 7\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	-31.0
$4\text{UO}_2^{2+} + 7\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	-21.9
$\text{UO}_2^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{UO}_2\text{CO}_3(\text{aq})$	9.67
$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} \leftrightarrow \text{UO}_2(\text{CO}_3)_2^{2-}$	16.94
$\text{UO}_2^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{UO}_2(\text{CO}_3)_3^{4-}$	21.6
$3\text{UO}_2^{2+} + 6\text{CO}_3^{2-} \leftrightarrow (\text{UO}_2)_3(\text{CO}_3)_6^{6-}$	54.0
$2\text{UO}_2^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_2\text{CO}_3(\text{OH})_3^- + 3\text{H}^+$	-0.86
$3\text{UO}_2^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_3\text{CO}_3(\text{OH})_3^+ + 3\text{H}^+$	0.66
$11\text{UO}_2^{2+} + 6\text{CO}_3^{2-} + 12\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-} + 12\text{H}^+$	36.43
$\text{H}^+ + \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^-$	10.329
$2\text{H}^+ + \text{CO}_3^{2-} \leftrightarrow \text{H}_2\text{CO}_3^* (\equiv \text{CO}_{2(\text{aq})} + \text{H}_2\text{O})$	16.683
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3^* (\equiv \text{CO}_{2(\text{aq})} + \text{H}_2\text{O})$	-1.472
$\text{SO}_4^{2-} + \text{H}^+ \leftrightarrow \text{HSO}_4^-$	1.98
$\text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- \leftrightarrow \text{U}^{4+} + 2\text{H}_2\text{O}$	8.89
$\text{U}^{4+} + 5\text{CO}_3^{2-} \leftrightarrow \text{U}(\text{CO}_3)_5^{6-}$	33.9
$\text{U}^{4+} + \text{SO}_4^{2-} \leftrightarrow \text{USO}_4^{2+}$	6.58
$\text{U}^{4+} + 4\text{H}_2\text{O} \leftrightarrow \text{U}(\text{OH})_4 + 4\text{H}^+$	-12.0
$\text{U}^{4+} + \text{H}_2\text{O} \leftrightarrow \text{UOH}^{3+} + \text{H}^+$	-0.65
$\text{UO}_2^{2+} + 2\text{Ca}^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0(\text{aq})$	5.34*
$\text{UO}_2^{2+} + \text{Ca}^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{CaUO}_2(\text{CO}_3)_3^{2-}$	8.86*
$\text{UO}_2^{2+} + \text{PO}_4^{3-} \leftrightarrow \text{UO}_2\text{PO}_4^-$	13.23
$\text{UO}_2^{2+} + \text{PO}_4^{3-} + \text{H}^+ \leftrightarrow \text{UO}_2\text{HPO}_4(\text{aq})$	19.59
$\text{UO}_2^{2+} + \text{PO}_4^{3-} + 2\text{H}^+ \leftrightarrow \text{UO}_2\text{H}_2\text{PO}_4^+$	22.82
$\text{UO}_2^{2+} + \text{PO}_4^{3-} + 3\text{H}^+ \leftrightarrow \text{UO}_2\text{H}_3\text{PO}_4^{2+}$	22.48
$\text{UO}_2^{2+} + 2\text{PO}_4^{3-} + 4\text{H}^+ \leftrightarrow \text{UO}_2(\text{H}_2\text{PO}_4)_2(\text{aq})$	44.04
$\text{UO}_2^{2+} + 2\text{PO}_4^{3-} + 5\text{H}^+ \leftrightarrow \text{UO}_2(\text{H}_2\text{PO}_4)(\text{H}_3\text{PO}_4)^+$	45.05

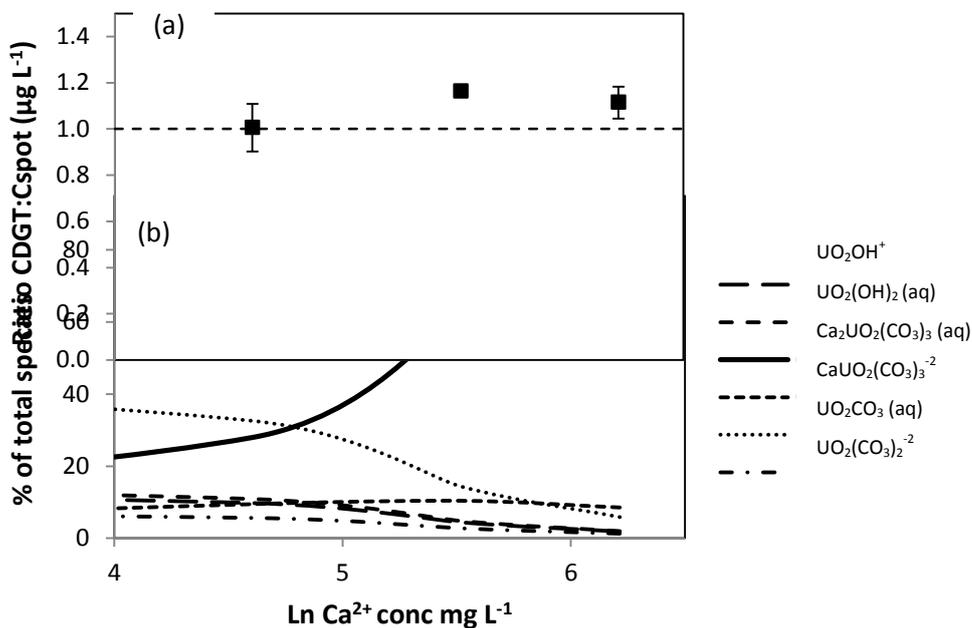


Figure S4. (a) Effect of Ca^{2+} on uptake of uranium by the Diphonix[®] resin gel. Concentration of uranium in DGT (C_{DGT}) is shown as a ratio to the average concentration of the total uranium over the 24 h deployment period measured directly in the solution (C_{total}) across a range of Ca^{2+} concentrations from 100 mg L^{-1} to 500 mg L^{-1} ; average pH 6.5 ± 0.2 , average temperature 20°C , calculated diffusion coefficient $2.47 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Dissolved and total uranium measurements were in close agreement, within error, with 100% of the uranium was predicted to be in solution using Visual Minteq (version 3 beta). Error bars are the standard error of triplicate readings (b) Prediction for uranium species calculated using Visual Minteq (version 3 beta) across Ca^{2+} concentrations from 50 mg L^{-1} to 500 mg L^{-1} , with a pH of 6.5, a U(VI) addition of $100 \mu\text{g L}^{-1}$, calculated ionic strength of 0.01 M, temperature of 20°C an atmospheric partial pressure of dissolved CO_2 . Only the major uranyl species are shown.

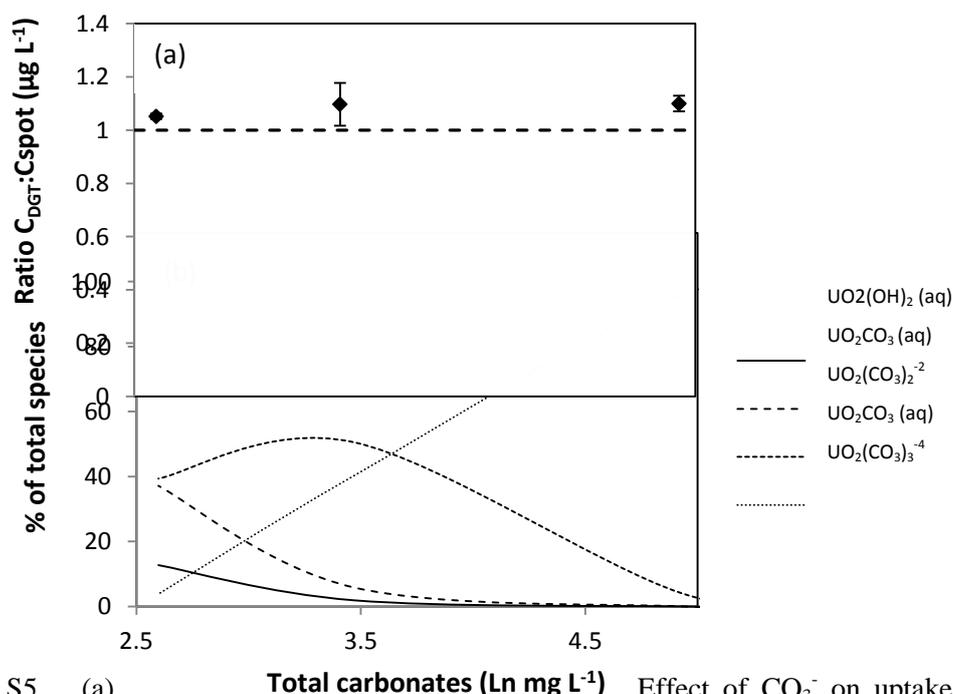


Figure S5. (a) Effect of CO_3^- on uptake of uranium by the Diphonix[®] resin gel. Concentration of uranium in DGT (C_{DGT}) is shown as a ratio to the average concentration of the total uranium over the 24 h deployment period measured directly in the solution (C_{total}) across a range of CO_3^- concentrations shown as total carbonate from 100 mg L^{-1} to 500 mg L^{-1} ; average pH 7.8 ± 0.5 , average temperature 21°C , calculated diffusion coefficient $3.45 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Dissolved and total uranium measurements were in close agreement, within error, with 100% of the uranium predicted to be in solution using Visual Minteq (version 3 beta). Error bars are the standard error of triplicate readings (b) Prediction for uranium species calculated using Visual Minteq (version 3 beta) across CO_3^- concentrations from 100 mg L^{-1} to 500 mg L^{-1} , with a pH of 7.8, a U(VI) addition of $100 \mu\text{g L}^{-1}$, calculated ionic strength of 0.01 M, temperature of 21°C an atmospheric partial pressure of dissolved CO_2 . Only the major uranyl species are shown.

Figure S6. 1/Mass uranium accumulated by the Diphonix[®] resin with Δg to show the diffusive boundary layer (DBL) for the freshwater deployment. Devices were deployed for 3-days. Error bars are the standard error of triplicate measurements. DBL thickness calculated as 0.062 ± 0.004 cm using equation 6.5.

Figure S7. 1/Mass uranium accumulated by the Diphonix[®] resin with Δg to show the diffusive boundary layer (DBL) for the marine deployment. Devices were deployed for 3-days. Error bars are the standard error of triplicate measurements. DBL thickness calculated as 0.107 ± 0.013 cm using equation 6.5.

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