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An evaluation of ferrihydrite- and Metsorb™-DGT techniques for measuring oxyanion species (As, Se, V, P): effective capacity, competition and diffusion coefficients

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Abstract

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Keywords

diffusion, competition, capacity, effective, p, v, coefficients, se, evaluation, species, oxyanion, measuring, techniques, dgt, metsorb, ferrihydrite, CMMB

Disciplines

Medicine and Health Sciences | Social and Behavioral Sciences

An evaluation of ferrihydrite- and Metsorb™-DGT techniques for measuring oxyanion species (As, Se, V, P): effective capacity, competition and diffusion coefficients

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Supplementary information appended.

Key words: passive sampler, diffusive gradients in thin films, elution efficiencies, environmental monitoring

Abstract

This study investigated several knowledge gaps with respect to the diffusive gradients in thin films (DGT) technique for measurement of oxyanions (As(III), As(V), Se(IV), Se(VI), PO_4^{3-}, and V(V)) using the ferrihydrite and Metsorb™ binding layers. Elution efficiencies for each binding layer were higher with 1:20 dilutions, as analytical interferences for ICP-MS were minimised. Diffusion coefficients measured by diffusion cell and by DGT time-series experiments were found to agree well and generally agreed with previously reported values, although a range of diffusion coefficients have been reported for inorganic As and Se species. The relative binding affinity for both ferrihydrite and Metsorb™ was $PO_4^{3-} \approx$ As(V) > V(V) ≈ As(III) > Se(IV) >>> Se(VI) and effective binding capacities were measured in single ion solutions, and spiked synthetic freshwater and seawater, advising practical decisions about DGT monitoring. Under the conditions tested the performance of both ferrihydrite and Metsorb™ binding layers was directly comparable for As(V), As(III) Se(IV), V(V) and PO_4^{3-} over a deployment spanning ≤2 days for both freshwater and seawater. In order to return quantitative data for several analytes we recommend that the DGT method using either ferrihydrite or Metsorb™ be deployed for a maximum of 2 days in marine waters likely to contain high levels of the most strongly adsorbing oxyanions contaminants. The high pH, the competitive ions present in seawater and the identity of co-adsorbing ions affect the capacity of each binding layer for the analytes of interest. In freshwaters, longer deployment times can be considered but the concentration and identity of co-adsorbing ions may impact on quantitative uptake of Se(IV). This study found ferrihydrite-DGT outperformed Metsorb-DGT while previous studies have found the opposite, with variation in binding materials masses used being a likely reason. Clearly, preparation of both binding layers should always be optimised to produce the highest capacity possible, especially for seawater deployments.

1. Introduction

In the past few years there has been considerable research into developing new diffusive gradient in a thin film (DGT) techniques for measuring oxyanion species in fresh or marine waters. This research has explored several binding layer materials: ferrihydrite for PO_4^{3-} [1], total inorganic arsenic [2], Se(VI), V(V) [3], and W(VI) [4]; Metsorb™ titanium dioxide for PO_4^{3-},[5] total inorganic arsenic, Se(IV) [6] and uranium [7]; zirconium oxide for PO_4^{3-} [8]; other layers investigated for uranium include Spheron-oxin® [9] and MnO_2 [10]; mercaptopropanol has been studied for uptake of As(III) [11] and Chelex-100 for As(III) in marine waters [12]. This research is a comparative evaluation of simultaneous measurements of labile inorganic As, Se, PO_4^{3-}, and V(V) with ferrihydrite- and Metsorb™ in both simulated freshwater and seawaters.

The DGT technique is used to quantitatively measure labile species *in situ* in freshwater and marine systems [13]. This method calculates a time-integrated concentration of dissolved labile species in the bulk solution, C_{DGT}, using the DGT equation *(Eq. 1)* derived from Fick's First Law of Diffusion [14].

$$C_{DGT} = \frac{M * \Delta g}{D * A * t} \qquad \text{(Eq. 1)}$$

C_{DGT} can be calculated using the measured mass of analyte accumulated on a binding gel, M, the distance diffused through, Δg (combined thickness of diffusive gel and filter membrane), the diffusion coefficient of analyte in diffusive gel and filter membrane, D, deployment time, t, and sampling area exposed to the bulk solution, A. Therefore, an accurately known rate of diffusion through the diffusive layer for each analyte is necessary to derive quantitative measurements. To date, diffusion coefficient values reported for the species As(V), As(III), Se(VI) and Se(IV) have shown wide disparity, as much as 30 - 40% variation in some cases [2-4, 6, 15].

Much of the initial research on resin binding affinities and capacities has used single elements. However, single-element assays are not environmentally relevant, as aquatic systems are complex mixtures of dissolved and colloidal phases. Thus, to evaluate the performance of binding resins under environmentally relevant conditions, simultaneous uptake of analytes requires consideration. Several studies have compared DGT binding layers for one or two analytes [16, 17], with only one recent study describing multi-element uptake for oxyanions over extended deployment times [18].

Ferrihydrite is selective for several oxyanions and competition amongst these ions and their varying adsorption affinities has been investigated [19-21] and found to follow the general order

As(V) > PO_4^{3-} > As(III) > silicate > bicarbonate [22]. However, more complex adsorption interactions have also been observed: As(III) adsorption decreased when concentrations of bicarbonate, silicate and PO_4^{3-} were lower [22]; a moderate negative effect on adsorption of As(V) in the presence of PO_4^{3-} was magnified if bicarbonate and silicate were also present [20]; and, at pH >7, PO_4^{3-} concentrations had a greater effect on As(V) adsorption [19] while CO_3^{2-} and Si affected total arsenic adsorption [23]. For selenium the sequence of anion competitive adsorption on ferrihydrite at pH 7.0 was orthophosphate > silicate > molybdate > fluoride > sulfate > selenite, with Se(IV) adsorption much stronger than Se(VI) [24]. Although adsorption of Se(VI) to ferrihydrite is well documented, the binding affinity of ferrihydrite for selenate is very low [25] and the surface complexation of Se(VI) on iron hydr(oxide) varies with pH and ionic strength [26].

Metsorb™ contains titanium dioxide (anatase) which is selective for a similar range of oxyanions (http://www.gravertech.com) and, although not as well studied as ferrihydrite, similar competition effects have been observed [27]. Knowledge of the competition between analyte ions is therefore critical in order to establish reliable working parameters for passive sampler measurements made using ferrihydrite- or Metsorb™-DGT techniques. For example, several studies have shown how the effective capacity of a binding layer will vary depending on analyte speciation [3, 28] and the deployment conditions [17], and that it is necessary to quantitatively measure analyte species over times relevant to the deployment times [18].

This study aims to address some of the critical knowledge gaps concerning measurement of oxyanion species (As(III), As(V), Se(IV), Se(VI), V(V) and PO_4^{3-} (as DGT-labile P)) by ferrihydrite- and Metsorb™-DGT. The possibility of competition between analytes adversely affecting analytical performance, and the effective capacity of binding gels in complex environments was investigated over extended deployment times. The precipitated ferrihydrite binding layer [3] was used and characterised in detail in this study. Diffusion coefficients for these analyte ions were determined by diffusive cell measurements and controlled DGT deployments, the two methods typically used within the literature, and discussed in light of literature values. We also sought to thoroughly understand the effect of competitive uptake by other ions present in deployment environments.

2 Materials and methods

2.1 General procedures

All chemicals were analytical reagent grade or equivalent. All plasticware (polycarbonate or polyethylene) and glassware was rigorously cleaned before use by soaking in 10% (v/v) HNO_3 (Analytical Reagent grade) for a minimum of 24 h, followed by thorough rinsing with Milli-Q water

(18.2 MΩ/cm; Milli-Q Academic Water System; Millipore). Analyte solutions (typically 25 mM) were freshly prepared to avoid speciation changes: As(V) and As(III) were prepared from $Na_2HAsO_4.7H_2O$ and $NaHAsO_3.7H_2O$, respectively (Ajax Chemicals, Australia); Se(VI) and Se(IV) were prepared from Na_2SeO_4 and $NaHSeO_3$, respectively (Sigma-Aldrich, USA); V(V) was prepared from NH_4VO_3 (Ajax Chemicals, Australia); and a 530 µM PO_4^{3-} solution was prepared from KH_2PO_4 (Ajax Finechem).

Deployments were made in both natural seawater and synthetic freshwater solutions. Seawater was collected from Towradgi Beach, NSW, Australia, filtered (0.2 µm, MiniSart, Sartorius) and stored at room temperature (21±1°C). Where necessary, salinity of filtered seawater was adjusted to test salinity of 35 using Milli-Q water and pH 8.1 ± 0.1 with HCl. Synthetic freshwater was prepared using 0.01 M $NaNO_3$ in Milli-Q water at pH 6.0 ± 0.2. DGT deployments were conducted at 21°C. Salinity, temperature and pH measurements were performed using a pH probe, Duraprobe and multiparameter meter (Thermo Scientific 5-Star Plus, Orion Pacific Pty Ltd).

2.2 DGT preparation and assembly

DGT samplers and agarose-based cross-linker for preparing DGT gel stock solution were purchased from DGT Research Pty (UK). Standard gel stock solution used in the synthesis of binding and diffusive gels was prepared as described by Zhang *et al.* [1]. Preparations of gel materials and DGT devices were as described [1] and were performed in an AURA SD4 Laminar Flow Cabinet. Prior to assembly, diffusive gels were immersed for at least 24 h in an appropriate conditioning solution, 0.01 M $NaNO_3$ for freshwater deployments and 0.12 M NaCl for seawaters. Cellulose nitrate filter membranes (0.45 µm pore-size, 0.11 mm thickness, Whatman) were used.

The precipitated ferrihydrite binding layers were prepared as previously described [3, 29]. In brief, a 0.64 mm diffusive gel layer was immersed in 0.15 M $Fe(III)(NO_3)_3$ for >2 h with regular gentle agitation. The layer was rinsed with Milli-Q water then immersed in 0.05 M 2-(*N*-morpholino)ethanesulfonic acid buffer (MES, ≥ 99%, Sigma-Aldrich), pre-adjusted to pH 6.3 with 1 M NaOH (Merck, Germany) for 1 h. Gels were rinsed thoroughly, stored in Milli-Q water at 4°C and deployed within two weeks of synthesis. Metsorb™ binding layers were prepared using a method described by Bennett *et al*. [6].

2.3 Binding gel blanks and DGT detection limits

For each batch of binding layers synthesised and used in the DGTs, a blank measurement was made for the entire process. This monitored for contamination during synthesis and handling, in

addition to identifying variations between batches. Blank measurements were conducted in triplicate (Table 2) and calculated from the measured mass of analyte on gel binding layers (*Eq. 1*). The blank masses were subtracted from the measured mass on deployed DGT devices. Gel blanks were also used to calculate method detection limits (MDL, 3 times the standard deviation of the blank) on a per experiment basis using all the DGT deployment conditions. The required time to reach the MDL was calculated for a DGT piston, fitted with a diffusive gel and filter membrane of combined thickness 0.091 cm, deployed in a freshwater solution at 25^{o}C and containing 150 nM of As, Se, V and 1500 nM of P. Calculations were performed using the appropriate sample dilution, elution efficiency and diffusion coefficient for each analyte.

2.4 Elution efficiency

Elution efficiency, expressed as a percentage, is the ratio of mass recovered through elution from the binding gel compared to mass adsorbed from solution [14]. The elution efficiency was determined for inorganic As, Se, V(V) and PO_4^{3-} from ferrihydrite and Metsorb™ binding layers. A single binding disc was immersed in up to five solutions (5 mL) ranging in concentration from 0.3 to 13 μM of analyte. Elution efficiencies were conducted in triplicate at each concentration and for ferrihydrite and Metsorb™ were measured in spiked solutions of both synthetic freshwater and filtered seawater at pH 8.1.

The ferrihydrite binding gels were eluted in 1 mL of 3.2 M HNO_3 for 24 h. The iron in the ferrihydrite binding layers completely dissolved in the acid solution leaving a clear gel disc therefore the eluant could be diluted directly to 0.32 M HNO_3 for analysis. The Metsorb™ binding gels were eluted in 1 mL of 1 M NaOH for 24 h then an aliquot of the eluant was neutralised and matrix matched to 0.32 M HNO_3 prior to analysis. To identify the effects of matrix on the instrumental analysis of the analytes, elution samples were prepared to dilution factors equivalent to 1 mL of eluant diluted to a final volume of 10, 20 and 30 mL and analysed in triplicate.

To evaluate the performance of DGT binding layers, a comparison of the DGT derived concentration, C_{DGT}, was made to the directly measured solution concentration, C_s, and a ratio value of 1 ± 0.1 for C_{DGT}/C_s indicated a quantitative measurement.

2.5 Comparison of diffusion coefficient measurements

Measurements of diffusion coefficients through the polyacrylamide gel and filter membrane were conducted using both a diffusion cell, D_{cell} [30] and DGT devices, D_{DGT} [2, 3]. The diffusion coefficient, D, was calculated using the slope of the linear regression of the measured mass of

analyte as a function of time (*Eq. 2*), the concentration of the bulk solution, C_s, measured directly and the known Δg and A values.

$$D = \frac{Slope * \Delta g}{Cs * A} \qquad \text{(Eq. 2)}$$

*Method 1***.** The diffusion cell compartments were connected by a 1.5 cm diameter window, which contained a diffusive gel, 0.080 cm, and cellulose nitrate filter membrane, 0.011 cm (0.45 μm, Whatman GmbH, Germany) with the filter membrane exposed to the analyte source compartment, giving a diffusive path length of 0.091 cm. Both compartments were filled with 90 mL of either synthetic freshwater or filtered seawater, equilibrated (2 h) and stirred constantly. 1 mL of solution was removed from the source compartment and replaced with spike solution for a final concentration of between 50 and 140 μM. The solution was equilibrated for 10 - 15 min prior to removing 500 μL aliquots from each compartment every 5 - 15 min for up to 2.5 h. Temperature and pH were monitored throughout the experiment. Aliquots were diluted and acidified to 0.32 M HNO_3 for ICP-MS analysis. *Eq. 2* is used, when the source compartment concentration does not change over the measurement period, to calculate $D_{cell.}$

Method 2. Mass accumulated over time experiments were also used to determine DGT derived diffusion coefficients, D_{DGT}. Triplicate DGT devices were deployed in: single analyte solutions of As(V), As(III), Se(VI) and Se(IV); dual analyte solutions (As(V) and Se(VI); As(III) and Se(IV)); and multiple analyte solutions (As (as either V or III), Se (as either VI or IV), VO_4^{3-}, and PO_4^{3-}). Bulk solutions consisted of either synthetic freshwater or filtered seawater, pH 8.1 ± 0.1. DGT devices were removed at measured time intervals, concurrently with grab samples of bulk solution.

2.6 The effects of pH and ionic strength on uptake on DGT measurements

Analyte solutions of ~0.6 - 1.3 μM were prepared, adjusted to the required pH (using 0.1 M NaOH or HNO_3) and continuously stirred for 2 h to equilibrate prior to deployments. Ferrihydrite DGTs (containing 0.091 cm diffusive path lengths) were deployed in triplicate for 4 h. Deployments for As(III) and Se(IV) were conducted under N_2. Ionic strength experiments ranged from 0.001 to 0.2 M $NaNO_3$ at pH 6.0 ± 0.2 and pH experiments from pH 4.0 to 8.0 ± 0.3. Calculations of C_{DGT}, using *Eq. 1*, were made using diffusion coefficients obtained at pH 6.0 ± 0.2 in 0.01 M $NaNO_3$ for freshwater experiments, and for seawater diffusion coefficients were either obtained in seawater at pH 8.1 ± 0.1 or calculated as 8% lower than that obtained at pH 6.0 ± 0.2 in 0.01 M $NaNO_3$ [30,

31].

2.7 Quantitative uptake and effective capacity in the presence of competing ions

Ferrihydrite DGT pistons were deployed in triplicate in well-stirred synthetic freshwater or filtered seawater at pH 8.1 ± 0.1 for 3 - 72 h. Single element solutions contained As(V), As(III), Se(IV) or Se(VI). The effective capacity of the binding gel was determined during these experiments, and was performed individually for As and Se at high concentrations.

Competition uptake effects were studied in synthetic freshwater with As and Se species, or in synthetic freshwater or seawater with various combinations of As and Se species with V(V) and PO_4^{3-} (Table 1). Solution compositions were selected to represent different water conditions, while the concentrations were selected for analytical and experimental convenience. The selection considered that trace element concentrations and speciation can be difficult to maintain in laboratory experiments, due to adsorption losses and microbial processes, as was observed for solution As and Se Red (Table 1). If competition effects were not observed at these concentrations they would not be likely to occur at lower concentrations. Sample aliquots of bulk solution were taken during extended deployments and processed through anion exchanger phase cartridges (SAX) to monitor for speciation changes of As and Se [32, 33].

2.8 Sample analysis

Analytes were quantified by Octopole Reaction Cell – Inductively Coupled Plasma – Mass Spectrometer (ORC-ICP-MS, Agilent 7500ce) utilising standard and collision/reaction gas modes where applicable. Selected measurements of ^{31}P conducted by OCR-ICP-MS in helium collision gas mode and standard mode compared well with measurements taken using a spectrophotometer (Shimadzu, UV-1700) using a modified molybdenum-blue method previously described [1]. Analytical standards for ICP-MS analysis were prepared in 0.32 M Baseline® HNO_3 (Seastar™ Chemicals Inc., Canada) using a multi-element standard (IV-ICPMS-71D, Inorganic Ventures, USA). Additional quality control standards of known concentration were analysed at regular intervals to monitor for signal drift, and spike recoveries were used for quality assurance purposes.

Analysis of P, As and Se by ICP-MS is problematic due to both interferences caused by polyatomic ions as well as signal suppression due to the presence of easily ionised elements such as Na^+ [34, 35]. Use of collision or reaction gases with ORC-ICP-MS under optimised conditions has been shown to remove some or all polyatomic interferences on ^{31}P, ^{75}As [35], ^{78}Se and ^{82}Se [35, 36]. In a complex sample matrix the analysis of ^{31}P remains problematic as the presence of high

concentrations of Fe is the likely cause of signal suppression which results in lower elution efficiency values at lower sample dilutions (Table 3) but washing ferrihydrite binding layers in Milli-Q water to remove seawater, and dilution of elution samples to 1:20 (≤0.005 M $NaNO_3$) markedly counters signal suppression due to high Fe concentrations or signal suppression due to Na^+ content.

3 Results and discussion

3.1 Binding gel blanks and DGT method detection limits

As DGT is an accumulation technique the MDL varies with deployment time and solution concentration. For this study, all MDLs were extremely low (Table 2). For As, Se, and V in a 150 nM mixed solution, the mass of analyte required to provide a DGT-labile concentration above the detection limit was accumulated within 1 h of deployment for both ferrihydrite- and Metsorb™ DGTs. For PO_4^{3-} at the higher concentration of 1500 nM, it took 4.0 and 4.4 h of deployment for ferrihydrite- and Metsorb™, respectively, as the blank mass was higher due to interferences experienced during ^{31}P analysis using an ICP-MS [37]. The mass of analyte required to exceed the limit of quantification (LOQ) was obtained for As, Se, and V within 30 min of deployment, whilst for PO_4^{3-} it was achieved in 5.6 h. This data shows that the DGT methods described here are very suitable for ultra-trace analysis of As, Se and V ions and trace analysis of P.

3.2 Elution efficiencies

The elution efficiencies (E_f) were clearly influenced by the analytical procedure (Table 3) where the 1:10 dilution of the eluant for both ferrihydrite and Metsorb™ produced lower E_f than more dilute eluants. For the ferrihydrite binding gel, elution of analytes in acid resulted in complete dissolution of the ferrihydrite, hence 100% elution could be assumed. Therefore E_f <100% were attributed to signal suppression during ICP-MS analysis due to the high concentration of Fe^{3+} in solution. The Metsorb™ gel elution process (1 M NaOH) in Bennett *et al*. [6] used a 1:10 dilution resulting in a final concentration of 0.1 M Na^+, which was prohibitive for simultaneous analysis of P by OCR-ICP-MS used in this study. Signal suppression by ionisation is due to concomitant salts in the sample matrix that are easily ionised in comparison to the analyte of interest (first ionisation potential, P 10.486 eV, Na 5.139 eV) [34]. The ICP-MS signal suppression in both cases was confirmed by the sequential increase in E_f with increasing dilution of eluted samples, with eluents <0.05 M NaOH producing E_f that were similar to those determined by Panther *et al*. [2] and Osterlund *et al*. [4].

Table 1. Concentration (μM) of analytes in multi-analyte deployments. Values in parentheses denote concentrations at the end of a deployment due to change in speciation, and Ox and Red denote oxidised and reduced species, respectively.

Experiment	Total μM	As(V)	As(III)	Se(VI)	Se(IV)	V(V)	PO_4^{3-}
As and Se (Ox)[a]	2.4	1.3		1.1			
As and Se (Red)[a]		(0.3)	0.9	(0.06)	1.0		
Fresh (Ox)[a]	25	1.3		1.0		20	2.1
Fresh (Red)[a]	8.2		1.2		1.0	3.9	2.1
Marine A	6.1	1.3			0.6	3.1	1.1
Marine B	3.2	0.5			0.5	1.2	1.0

[a] Matrix ions are detailed in section 2.1.

Table 2. DGT ferrihydrite and Metsorb™ binding gel blanks and limit of quantification (LOQ). Method detection limits (MDL) were calculated for a 24 h deployment using a diffusive thickness of 0.091cm (diffusive gel and filter membrane), sampling area 3.14 cm^2 and diffusion coefficient at 25°C. The LOQ for As, Se, V(V) and PO_4^{3-} were measured during the same analysis as gel blanks.

	Ferrihydrite		Metsorb™		LOQ nM
Analyte	gel blank nmol	MDL nM ([b]time to reach MDL, h)	gel blank nmol	[a]MDL nM ([b]time to reach MDL, h)	([c] time to reach LOQ, h)
As(V)	0.010 ± 0.001	0.23 (0.04)	0.009 ± 0.001	0.19 (0.04)	0.69 (≤ 0.5)
As(III)	0.006 ± 0.001	0.18 (0.03)	0.004 ± 0.001	0.16 (0.02)	0.87 (≤ 0.5)
Se(IV)	0.016 ± 0.005	1.3 (0.17)	0.016 ± 0.006	1.3 (0.17)	1.0 (≤ 0.5)
Se(VI)	0.028 ± 0.001	0.25 (0.04)	0.025 ± 0.004	1.0 (0.16)	1.5 (≤ 0.5)
V(V)	0.021 ± 0.006	1.5 (0.25)	0.021 ± 0.005	1.3 (0.21)	2.1 (≤ 0.5)
PO_4^{3-}	4.5 ± 0.3	97 (2.2)	5.0 ± 0.4	100 (3.0)	261 (5.6)

[a] calculated using 3σ x standard deviation of the handling blank (n=3)

[b] The MDL in solution corresponds to required time to reach the MDL when a DGT piston is deployed in a freshwater solution at 25°C containing 150 nM of As, Se, V and 1500nM of P.

[c] 10 times the standard deviation of the ICP-MS solution blank concentration (10σ).

Table 3 presents the E_f values for the synthetic freshwater study, however, E_f values obtained from seawaters were consistent with freshwaters for As(V), As(III), Se(IV) and V(V) eluted from both ferrihydrite and Metsorb™ (*SI Table S1*). When binding layers are well-washed prior to elution, the matrix of a deployment solution did not affect the E_f values. Seawater E_f values were not obtained for PO_4^{3-} and Se(VI) but are assumed to be the same as in freshwater due to the uniform results for the other analytes.

As the 1:20 or 1:30 final dilution factor for both ferrihydrite and Metsorb™ were similar and suitable for simultaneous analysis of all analytes, a 1:20 dilution was adopted for the binding gels from both fresh and marine waters for subsequent work.

3.3 Determination of oxyanion diffusion coefficients

Diffusion coefficients are reported at 25°C, converted from *D* at the measured temperature using the Stokes Einstein equation [31]. The diffusion coefficients were determined by two techniques (section 2.5) with <3% variation between D_{DGT}, and D_{cell} (Table 4) for both spiked seawater and synthetic freshwater measurements. The greatest variation between D_{cell} and D_{DGT} was for As(III) and is most likely the error associated with measuring speciation change (oxidation to As(V)) during the experimental procedures.

The D_{cell} in synthetic freshwater ranged from 60 to 76% the value in water, D_w, for As(V), Se(VI), PO_4^{3-} [31], As(III) [38] and V(V) [39]. The corresponding measured diffusion coefficients for diffusive gels in seawater ranged from 53 to 69% of the value in water. This lower range of diffusion coefficients in seawater diffusive gels is consistent with predictions made by Li and Gregory [31], who observed a 5 and 8% decrease of the water D_w value in seawaters between 0 and 25°C, respectively.

The measured diffusion coefficient, D_{cell}, for PO_4^{3-} and VO_4^{3-} (Table 4) is in excellent agreement with previous studies (PO_4^{3-}: 6.05×10^{-6} cm^{-2} s^{-1} [1]; VO_4^{3-}: 6.72×10^{-6} cm^{-2} s^{-1} [4] and 6.5×10^{-6} cm^{-2} s^{-1} [3]), differing by ≤3%. However, the diffusion coefficients published thus far for As(V), As(III), Se(VI) and Se(IV) are quite disparate. Our diffusion coefficients for As(V) shows some agreement with Fitz *et al*. [15] (6.01×10^{-6} cm^{-2} s^{-1}) but is 15 to 20% higher than values from Luo *et al.* [3], Osterlund *et al*. [4] and Panther *et al.* [2] (5.18, 5.21 and 4.85×10^{-6} cm^{-2} s^{-1}, respectively), and 11% lower than Bennett *et al*. [6] (6.83×10^{-6} cm^{-2} s^{-1}). The diffusion coefficient for As(III) in this study, 7.65×10^{-6} cm^{-2} s^{-1}, lies between two previously reported results, Panther *et al.* [2] with 6.40×10^{-6} cm^{-2} s^{-1} measured in a buffered solution, and Bennett *et al*. [6] at 10.5×10^{-6} cm^{-2} s^{-1}. For Se(VI) the diffusion coefficient obtained in this study, 7.22×10^{-6} cm^{-2} s^{-1}, is 16% higher than the value obtained by Luo *et al*. 6.1×10^{-6} cm^{-2} s^{-1} [3].

Table 3. Elution efficiencies (E_f) for precipitated ferrihydrite and Metsorb™ binding gels, expressed as a ratio of eluted to bound analyte (mean ± SE, n=9), deployed in spiked (ranging from 0.3 to 13 μM) synthetic freshwaters (pH 6.0 ± 0.2 and 0.01 M $NaNO_3$).

	Ferrihydrite			Metsorb™		
	Dilution factor[a]					
Analyte	1:10	1:20	1:30	1:10	1:20	1:30
As(V)	0.89 ± 0.05	1.00 ± 0.02	0.98 ± 0.02	0.81 ± 0.09	1.00 ± 0.02	1.00 ± 0.02
As(III)	0.88 ± 0.03	0.99 ± 0.01	0.94 ± 0.03	0.86 ± 0.09	0.99 ± 0.13	1.01 ± 0.10
Se(VI)	0.80 ± 0.07	0.94 ± 0.03	0.94 ± 0.03	0.83 ± 0.06	0.93 ± 0.05	Not obtained
Se(IV)	0.81 ± 0.07	0.94 ± 0.03	0.94 ± 0.03	0.81 ± 0.05	0.94 ± 0.03	0.95 ± 0.03
V(V)	0.90± 0.04	0.99 ± 0.02	0.99 ± 0.02	0.90 ± 0.05	0.99 ± 0.02	0.99 ± 0.03
PO_4^{3-}	Not obtained[b]	0.81 ± 0.07	0.80 ± 0.09	Not obtained[b]	0.61 ± 0.09	0.69 ± 0.09

[a] Dilution of 1 mL of binding layer eluant for OCR-ICP-MS analysis
[b] Not obtained for P due to ICP-MS interferences at this dilution (see section 2.8)

Table 4. Diffusion coefficients (x 10^{-6} cm^{-2} s^{-1}, at 25°C) in diffusive gels and filter membrane using a diffusion cell (D_{cell}) and ferrihydrite DGT devices (D_{DGT}), mean ± standard error.

	0.01 M $NaNO_3$, at pH 6.0 ± 0.2		Seawater at pH 8.1 ± 0.1		Literature values in 0.01 M $NaNO_3$	
	D_{cell}	D_{DGT}	D_{cell}	D_{DGT}	D_{water}	D_{cell} or D_{DGT}
As(V)	6.10 ± 0.06	6.05 ± 0.05	5.50 ± 0.13	5.51 ± 0.08	[a]9.05	[c]5.2, [d]6.01, [e]5.21, [f]6.83, [g]4.85
Se(VI)	7.22 ± 0.08	7.10 ± 0.05	6.55 ± 0.14	Not obtainable	[a] 9.46	[c]6.1, [f]7.44
V(V)	6.70 ± 0.06	6.73 ± 0.08	6.01 ± 0.09	6.05 ± 0.10	[i]11.3	[c]6.5, [e]6.72/6.66
PO_4^{3-}	6.09 ± 0.12	6.01 ± 0.07	Not obtainable		[a] 8.46	[h]6.05
As(III)	7.65 ± 0.09	7.45 ± 0.04	6.99 ± 0.10	6.90 ± 0.09	[b]11.1	[f]10.5, [g]6.40
Se(IV)	7.30 ± 0.08	7.05 ± 0.07	6.40 ± 0.12	6.49 ± 0.09		[f]8.91

[a] Li and Gregory [31], [b] Leaist [38], [c] Luo et al., [3], [d] Fitz et al. [15], [e] Osterlund et al. [4], [f] Bennett et al. [6], [g] Panther et al. [2],[h] Zhang et al. [1], [i] Ribeiro et al. [39].

In previous studies, diffusion coefficients of metal ions through diffusive gels were ~85% of the value of diffusion coefficients in water [40] whilst the oxyanion PO_4^{3-} was found to be ~71% [1]. In this study the diffusion coefficients of the oxyanions measured in synthetic freshwater are between 67-76% the value of that in water, D_w. The reason for this decrease eludes us. It is not likely to be charge effects, as Luo *et al*. [3] found no measurable charge effect of analytes binding to the diffusive layer. Also, in a study of cation diffusion, Zhang and Davison [30] demonstrated the relatively free diffusion of cations through the diffusive gels. It is possible that the decrease in diffusion coefficient is a result of pore size restricting the free diffusion of the larger molecules [40]. The variation in diffusion coefficient values between laboratories (Table 4) suggests that oxyanion species are more susceptible to variations in diffusive layer preparation and storage conditions than cations. This warrants further investigation.

3.4 The effects of pH and ionic strength

Between pH 4 and 8 As(V), As(III) and Se(IV) showed quantitative uptake onto ferrihydrite, returning 100 ± 10% of the directly measured concentration. Results in synthetic freshwater concur with previous work for As(V) [2-4], As(III) [2] and Se(IV) Metsorb™ [6]. For Se(VI) at the higher pHs of 7.0 and 8.0, uptake was not quantitative, falling below 90% of the directly measured concentration. Low uptake of Se(VI) on ferrihydrite at higher pH has previously been documented [26], and is likely to be due to the decrease in the number of available surface binding sites, as the number of fully protonated sites decreases with increasing pH [25, 26]. The uptake at pH 4 - 8 indicates that diffusion coefficients do not differ greatly from those experimentally derived at pH 6.0 (*SI Table S2*). Similar results have been seen in other studies [2, 4].

When deployed in solutions across a range of ionic strengths of $NaNO_3$, the uptake of As(V), As(III) and Se(IV) was quantitative onto ferrihydrite at 4 h. However, increasing ionic strengths decreased Se(VI) adsorption, with C_{DGT} <90 and <60 % of the directly measured solution value, C_{soln}, at 0.1 and 0.2 M $NaNO_3$, respectively. In spiked seawaters, uptake of Se(VI) was negligible, with almost complete suppression of uptake. The mass adsorbed to the binding gel did not increase between 4 and 8 h, with C_{DGT} at 5 and 3% of theoretical values, respectively (*SI Table S3*). This uptake suppression is a result of both high pH and high ionic strength (competing ions). As ferrihydrite is able to adsorb a range of cations and anions in the complex seawater matrix, primarily sulfate, carbonates, silicate and metal ions [22, 41], the uptake of competitive ions will reduce the binding sites available for analytes of interest. As sulfate and selenate have identical pH sorption envelopes [42] it is likely that sulfate is the major competitive ion for selenate in seawater. Therefore, as uptake of Se(VI) onto ferrihydrite in seawater was <5% at 4 h, thus uptake of selenium onto ferrihydrite in seawater deployments is assumed to be Se(IV) with <5% error margin.

3.5 Quantitative uptake and effective capacity in single element solutions

The binding gels are deemed to be within effective capacity if analyte uptake increases linearly over time and is in agreement with the predicted DGT response (determined by the directly measured concentration in solution and DGT *Eq.* 2), which indicates that the principles of DGT are adhered to [1, 14]. Deviation of uptake from linearity indicates that the effective capacity of a binding gel was exceeded. Effective capacity in freshwaters was determined (Table 5) by measuring uptake from 1.5 to 48 h using single analyte solutions (*SI Figures S2-S4,* solid line ± 10%) of approximately 50 and 130 µM for As(V), 50 µM for As(III) and Se(IV), and approximately 15 µM for Se(VI). Although the effective capacity of Metsorb™ was not studied here, Panther *et al*. [17] demonstrated that Metsorb™ had an effective capacity for PO_4^{3-} of approximately 1200 nmol. When deployed in solutions of the same concentration the effective capacity for As(V) onto ferrihydrite was ~290 nmol in seawater, which is 56% of the As(V) synthetic freshwater capacity of 520 nmol (Table 5; and *SI Figure S4*). Lower effective capacity in seawater can be attributed to both the higher concentrations of competing major ions and a decrease in adsorption capacity due to increased pH. The adsorption capacity of ferrihydrite for As(V) has been shown to decrease as pH increased above 7.5 [25, 43]. These factors mean that longer deployment times in solutions containing high concentrations of competing ions (e.g. seawater) will in effect lower the number of available binding sites for As(V) over time due to continual uptake of competitive ions. In freshwaters, As(III) on the ferrihydrite binding layer was still within capacity at 460 nmol (*SI Figure S3*), however, an effective capacity in seawater for both reduced species As(III) and Se(IV) was difficult to obtain. Despite running experiments under nitrogen, there was still appreciable oxidation of As(III) to As(V) and to a lesser extent, Se(IV) to Se(VI).

The effective capacity for Se(VI) in freshwater was 30 nmol (Table 5) and was reached in only 3.5 h. This was more than one order of magnitude lower than for As(V), As(III) and Se(IV), Se(VI). It was also lower than the Se(VI) effective capacity reached by Luo *et al*. [3], which may be attributable to variations in experimental conditions. The lower affinity of Se(VI) for ferrihydrite compared to Se(IV) and arsenic is well documented [24, 25, 44]. No effective capacity was obtained for Se(VI) in seawater, as uptake is negligible (Figure 1b and *SI Table S3*).

3.6 Quantitative uptake in the presence of competing ions

The performance of ferrihydrite- and Metsorb™-DGT was evaluated using multi-element solutions (Table 1). Competition effects were observed for oxyanions on both binding layers when the DGT were deployed in multi-element freshwater solutions and in multi-element seawaters (Figs 1 and 2). The results are described below.

Table 5. Effective capacity for precipitated ferrihydrite binding gels.

Analyte	Solution Conc nM	Effective capacity in synthetic freshwater nmol	Time to effective capacity h	Effective capacity in seawater nmol	Time to effective capacity h
As(V)	130	530	8		
As(V)	50	520	16	290	10
As(III)	55	>460	>10	Not obtained	
Se(IV)	50	>400	>10	Not obtained	
Se(VI)	15	30	3.5	Not obtained	

Arsenic (V), Arsenic (III) and orthophosphate. Both ferrihydrite- and Metsorb™-DGT produced quantitative measurements for As(V) (Fig 1a and 2a) and PO_4^{3-} (Figure 1f and 2f) in fresh and marine waters. The uptake of As(III) was only measured in freshwater over 41 h (under N_2) due to the difficulty in maintaining arsenite for long deployments, especially in seawater. The uptake of As(III) was quantitative for both ferrihydrite and Metsorb™, with a change of oxidation state from As(III) to As(V) of <15%. Competition effects for all three of these elements were negligible.

Vanadate (V). The freshwaters (high and low concentrations) showed quantitative adsorption of V(V) onto both ferrihydrite and Metsorb™. However, the seawater solutions showed the effects of competitive ion uptake on adsorption of V(V) towards the end of the deployments for both binding layers. In the 'Marine A' solution, V(V) uptake was quantitative at 31 h but at 43 h fell to 0.88 and 0.83 of the theoretical adsorbed value for ferrihydrite and Metsorb™, respectively. The 'Marine B' solution, which had a lower concentration, was quantitative at 60 h for both binding layers but at 72 h fell to 0.89 and 0.88 of the theoretical value for ferrihydrite and Metsorb™-DGT, respectively. Hence at marine pH, V(V) has a marginally lower affinity for ferrihydrite and Metsorb™ compared to As(V) and PO_4^{3-}.

Selenium (VI). The freshwater deployments showed a significant amount of Se(VI) was adsorbed to ferrihydrite, however measured concentrations were not in the quantitative range (1.0±0.1), confirming the lower affinity of Se(VI) for ferrihydrite, especially in the presence of

several competing ions (Figure 1b). For the low concentration freshwater solutions ('As and Se Ox', Table 1), the uptake of Se(VI) was quantitative at 4 h but fell to 0.89 and 0.71 of theoretical values at 8 and 44 h, respectively. This is concerning as most DGT deployments would be much longer than 4 h. At higher Se(VI) concentrations (Fresh (Ox)), adsorption of Se(VI) decreased from 0.41 of theoretical at 4 h down to <0.07 at 24 h, indicating capacity effects, even with minimal competition (data not shown).

The Metsorb™ binding layer is not selective for Se(VI) (Figure 2b) which agrees with previous results. For the 'As and Se Ox' solutions, after 4 h the Metsorb™-C_{DGT} value for Se(VI) was <0.40 of the directly measured solution concentration and fell to <0.20 after this time. In the presence of a greater total concentration of competitive ions Metsorb™-C_{DGT} results were below 0.10 (Figure 2b). Relative to DGT-ferrihydrite in freshwater, the error margin introduced by non-quantitative uptake of Se(VI) onto DGT-Metsorb™ is much lower, and over deployment times >24 h would be less than 5%.

Selenite. Se(IV) has a lower adsorption affinity for ferrihydrite and Metsorb™ compared to arsenic, V(V) and PO_4^{3-}. For the 'Fresh Red' low concentration solutions (Table 1), after 41 h quantitative uptake of Se(IV) was maintained for ferrihydrite but uptake onto Metsorb™ dropped to 0.82 of theoretical adsorbed value. The change of oxidation state from Se(IV) to Se(VI) in 'Fresh Red' was approximately 0.05 at 41 h, so although uptake of Se(VI) onto Metsorb™ is much lower than onto ferrihydrite in freshwater conditions, the impact of the change in species could account in part for the low uptake value onto Metsorb™, and a truer value would be between 0.82-0.85 at 41 h.

For the 'Marine A' high concentration solutions, ferrihydrite maintained quantitative uptake of Se(IV) for 43 h, but Metsorb™ dropped to 0.84 and 0.71 of theoretical at 31 and 43 h, respectively. In 'Marine B' low concentration solutions, ferrihydrite was quantitative for Se(IV) at 60 h but at 72 h fell to 0.87 of theoretical. For Metsorb™ Se(IV) was only quantitative up to 36 h and dropped to 0.88 and 0.73 of theoretical at 48 and 72 h, respectively.

Summary and discussion. These results indicate that the relative binding layer affinity order for both ferrihydrite and Metsorb™ is $PO_4^{3-} \approx$ As(V) > V(V) ≈ As(III) > Se(IV) >>> Se(VI). As maintaining speciation of As(III) throughout long deployments was problematic, further testing in multi-element solutions would be required to produce more comprehensive data for As(III). Analyte uptake onto ferrihydrite and Metsorb™ binding layers produced very similar results for the freshwater deployments under the conditions tested. For ferrihydrite, in the freshwater deployments the total nmol of all analytes adsorbed onto the binding layer was 240 nmol at 41 h for Fresh Red and 400 nmol at 24 h for Fresh Ox. The total mol uptake was within the effective capacity totals determined for As(V), As(III) and Se(IV) in single element solutions in the synthetic freshwater

(Table 5). As the results are quantitative for all analytes except Se(VI) there are no indications of passivation of the binding layer due to co-binding solutes under these conditions. For Metsorb™ under the same conditions a total of 230 nmol of all analytes had adsorbed on the binding layers at 41 h and 410 nmol at 24 h for Fresh Red and Fresh Ox, respectively.

The effect of the competitive ions in seawaters was shown to increase as the length of deployment increased. The total nmol of all analytes adsorbed onto the ferrihydrite binding layer was 170 nmol at 43 h for Marine A, with slightly higher concentrations, and uptake was quantitative for As(V), Se(IV) and PO_4^{3-}, whilst just outside quantitative for V(V) at 0.89. For Marine B, the measurements of all four analytes were quantitative on ferrihydrite with a total of 120 nmol adsorbed at 60 h, however, at 72 h, uptake of both V(V) and Se(IV) had fallen just outside the quantitative range. For Metsorb™ Marine A deployments, the effective capacity for Se(IV) was reached at 31 h, a total of 120 nmol of measured analytes on binding layer, whilst for V(V) effective capacity was reached at 43 h, adsorbing a total of 160 nmol of analytes. In the 'Marine A', Metsorb™ effective capacity for Se(IV) was exceeded at 61 h, with a total of 115 nmol adsorbed. However, for the lower concentrations in Marine B, at 72 h 132 nmol of total measured analytes had adsorbed with uptake still quantitative for As(V) and PO_4^{3-} , with V(V) adsorption at 0.89 of theoretical and Se(IV) at only 0.73.

Work by Panther *et al*. [17] indicated the effective capacity of their Metsorb™ binding layer to be ~1200 nmol of P and quantitative uptake of As(V), V(V) and PO_4^{3-} was possible in a multi-element solution of seawater for up to 4 days [18]. The results presented here indicate that the effective capacity was reached much sooner. It is likely that incorporation of different masses of material within the binding gels may be behind these different observations, with an increase mass producing an increased measurement capacity. Panther *et al.* [17] has optimised Metsorb™-DGT more thoroughly and this study has optimised ferrihydrite-DGT more thoroughly, so these DGTs performed better in the respective seawater measurements. Clearly both binding layers should be optimised to produce the highest capacity possible especially for seawater deployments.

4. Conclusion

Our work has demonstrated the importance of evaluating binding layers in multi-element deployments to ensure quantitative uptake and to determine the analyte specific limitations on deployment times. Under the conditions tested the performance of both ferrihydrite and Metsorb™ binding layers was directly comparable for As(V), As(III) Se(IV), V(V) and PO_4^{3-} over a deployment spanning ≤2 days for both freshwater and seawater. This work has demonstrated that in multi-element seawater solutions, Se(IV) has a lower affinity for the Metsorb™ and ferrihydrite binding layers compared to As(V), V(V) and orthophosphate. For As(V), V(V) and orthophosphate both ferrihydrite and Metsorb™ binding layers produced very similar results over the duration of both the fresh and seawater deployments with As(V) and PO_4^{3-} remaining quantitative throughout.

In order to return quantitative data for several analytes we recommend that DGT method using either ferrihydrite or Metsorb™ be deployed for a maximum of 2 days in marine waters likely to contain high levels of the most strongly adsorbing oxyanions contaminants. The high pH, the competitive ions present in seawater and the identity of co-adsorbing ions affect the capacity of each binding layer for the analytes of interest. In freshwaters, longer deployment times can be considered but the concentration and identity of co-adsorbing ions may impact on quantitative uptake of Se(IV). In marine environments, high concentrations of analytes that bind with high affinity to ferrihydrite and Metsorb™, such as arsenic, V(V) and PO_4^{3-}, will have a detrimental effect on the quantitative uptake of Se(IV) over deployment times over 2 days. In marine waters containing very high concentrations of As and PO_4^{3-} the 2 day deployment recommendation should be shortened. There is a greater effect on adsorbent effective capacity in marine waters, therefore, marine deployments are limited to a far greater extent than in freshwater.

As both ferrihydrite and Metsorb™ binding layers are selective for a greater range of ions than were considered in this study, future research should consider a greater range of selective ions. By increasing the number of selective oxyanions in competitive binding tests and conducting test over timeframes more representative of the requirements of environmental monitoring it will be possible to set an effective field deployment time for a more comprehensive list of analytes. In addition to parameters for competitive uptake of analytes, consideration needs to be paid to the effects of co-adsorbing analytes and their effect on the overall capacity of the layers, for example passivation of binding positions.

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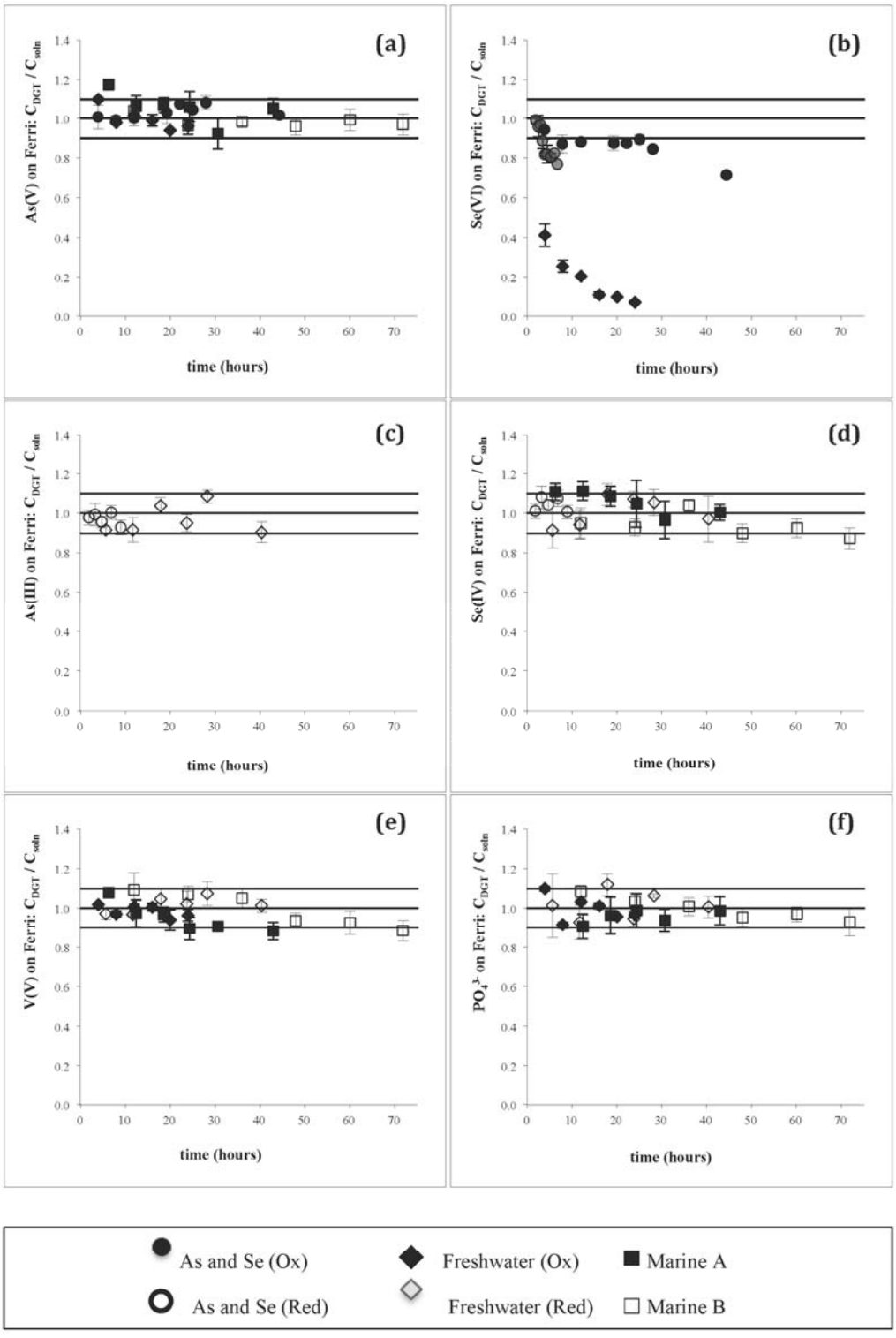
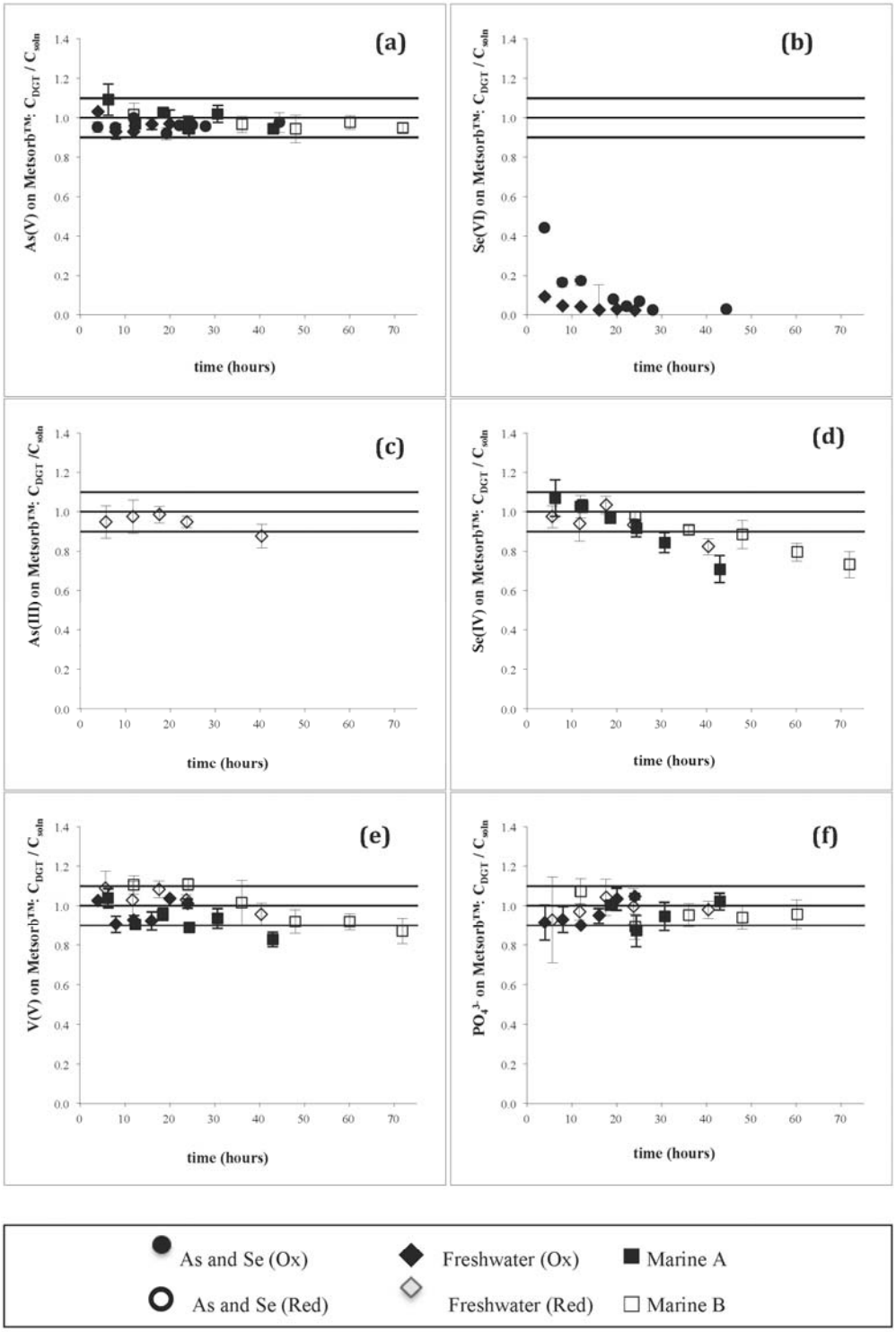


Figure 1. Comparison of measurements of concentration derived from DGT-ferrihydrite, C_{DGT}, versus directly measured concentration, C_{soln} for (a) As(V), (b) Se(VI), (c) As(III), (d) Se(IV), (e) V(V) and (f) PO_4^{3-} for all the solutions in Table 1. The solid line indicates adherence to predicted theoretical uptake and the dotted lines ± 10%.



601 **Figure 2.** Comparison of measurements of concentration derived from DGT- Metsorb™, C_{DGT},
602 versus directly measured concentration, C_{soln} for (a) As(V), (b) Se(VI), (c) As(III), (d) Se(IV),
603 (e) V(V) and (f) PO_4^{3-} for all the solutions in Table 1. The solid line indicates adherence to
604 predicted theoretical uptake and the dotted lines ± 10%.

605

Appendix A. Supplementary data

An evaluation of ferrihydrite- and Metsorb™-DGT techniques for measuring oxyanion species (As, Se, V, P): effective capacity, competition and diffusion coefficients

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Table S1. Elution Efficiency (E_f) for precipitated ferrihydrite and Metsorb™ binding gels, expressed as a ratio of eluted to bound analyte (mean ± SE, n=9), deployed in spiked filtered seawater (ranging from 1.3 to 13 μ*M*), pH 8.1 ± 0.1.

	Ferrihydrite			Metsorb™	
	Dilution factor+				
Analyte	**1:10**	**1:20**	**1:30**	**1:20**	**1:30**
As(V)	0.90 ± 0.04	0.99 ± 0.03	0.98 ± 0.02	0.98± 0.03	0.98 ± 0.03
As(III)	0.93 ± 0.04	0.99 ± 0.02	0.98 ± 0.03	0.99± 0.03	0.99 ± 0.04
Se(IV)	0.85 ± 0.05	0.95 ± 0.04	0.94 ± 0.05	0.93 ± 0.04	0.95 ± 0.05
V(V)	0.95± 0.03	0.99 ± 0.02	0.99 ± 0.03	0.98 ± 0.03	0.99 ± 0.04

+ Dilution of 1 mL of binding layer eluant for OCR-ICP-MS analysis

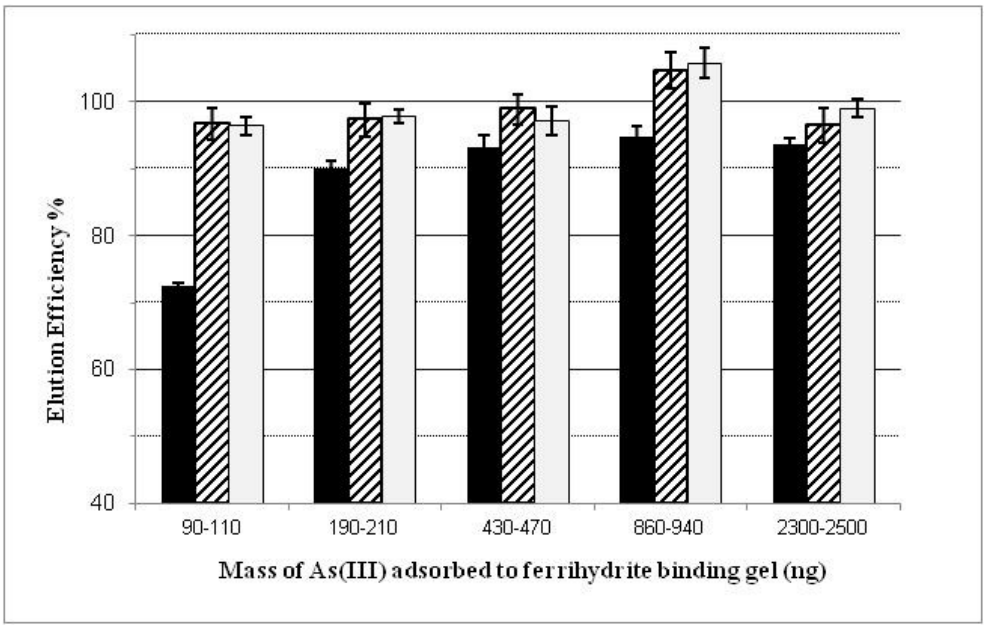
Table S2. The effect of pH on binding of As(V), As(III), Se(VI) and Se(IV) to ferrihydrite, expressed as the ratio of the concentration determined by DGT, C_{DGT}, to concentration measured directly in solution, C_s. Deployment was for 4 h in 0.01M $NaNO_3$ and for As(III) and Se(IV) were conducted under N_2. Mean ± SE (n = 3-12).

pH (±0.5)	As(V)	Se(VI)	As(III)	Se(IV)
4.0	1.02 ± 0.03	0.94 ± 0.03	0.95 ± 0.02	1.02 ± 0.07
5.0	0.96 ± 0.01	1.00 ± 0.02	0.97 ± 0.02	0.98 ± 0.04
6.0	0.97 ± 0.01	0.93 ± 0.02	0.96 ± 0.02	1.00 ± 0.10
7.0	0.94 ± 0.02	0.85 ± 0.04	0.93 ± 0.04	1.05 ± 0.02
8.0	0.96 ± 0.05	0.61± 0.02	0.92 ± 0.01	0.97 ± 0.02

Table S3. The effect of molarity on binding of As(V), As(III), Se(VI) and Se(IV) to ferrihydrite, expressed as the ratio of the concentration determined by DGT, C_{DGT}, to concentration measured directly in solution, C_s. Deployment was for 4 h at pH 6.0 ± 0.2 in $NaNO_3$ or pH 8.1± 0.1 in filtered seawater and for As(III) and Se(IV) were conducted under N_2. Mean ± SE (n = 3-12).

$NaNO_3$ (*M*)	As(V)	Se(VI)	As(III)	Se(IV)
0.001	1.00 ± 0.05	0.96 ± 0.04	0.95 ± 0.02	1.03 ± 0.07
0.01	0.97 ± 0.01	0.93 ± 0.02	0.99 ± 0.01	0.98 ± 0.04
0.1	0.94 ± 0.01	0.86 ± 0.09	0.98 ± 0.09	0.98 ± 0.02
0.2	1.00 ± 0.01	0.51 ± 0.05	0.94 ± 0.06	0.96 ± 0.09
Seawater	0.95 ± 0.02	0.03 ± 0.01	0.93 ± 0.02	0.94 ± 0.03

(A)



(B)

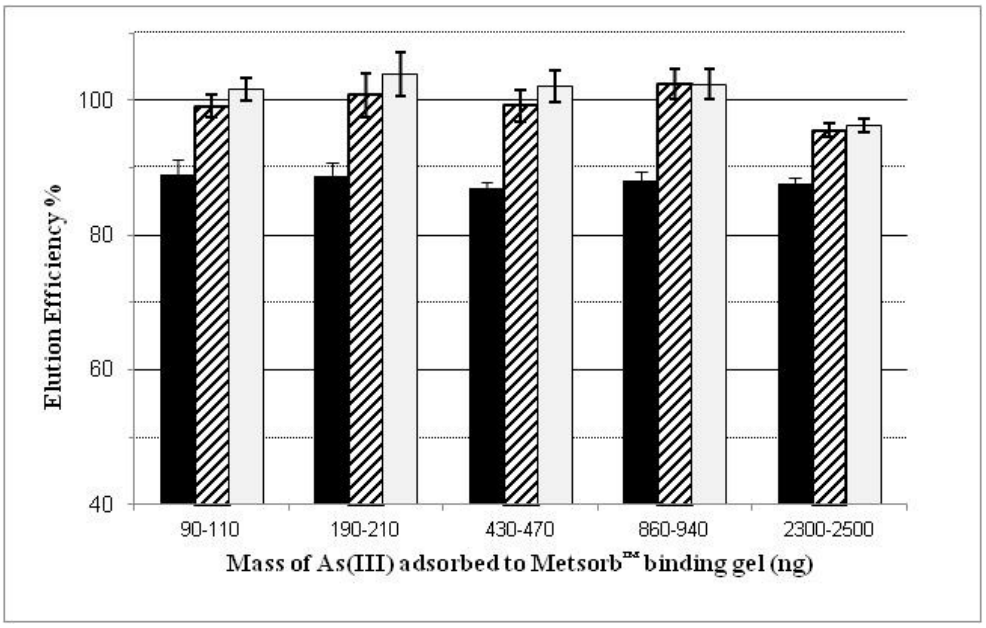
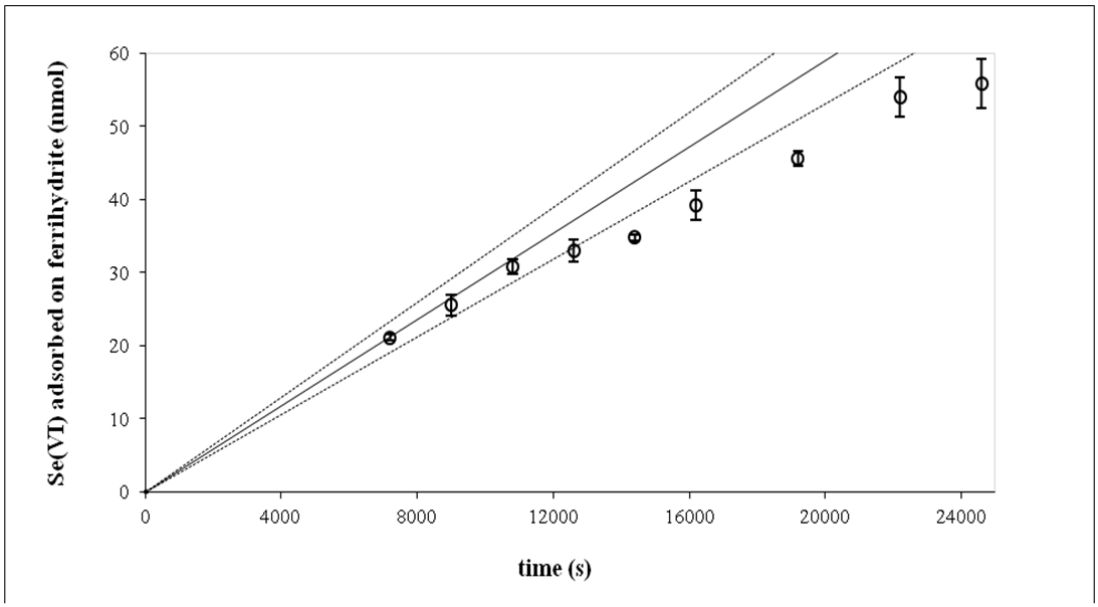


Figure S1. Elution efficiency of As(III) from (A) precipitated ferrihydrite and (B) Metsorb™ binding gel, expressed as a percentage (mean ± SE, n =3), deployed in spiked water (ranging from 0.3 to 13 µM), pH 6.0 ± 0.2 and 0.01 M $NaNO_3$. Comparison of elution efficiency as a function of mass adsorbed to binding gel and final sample volume. One binding gel disc was eluted in 1 ml of 1 M NaOH then diluted to a final volume of 10 mL (■), 20 mL (▨) and 30 mL (□), respectively.

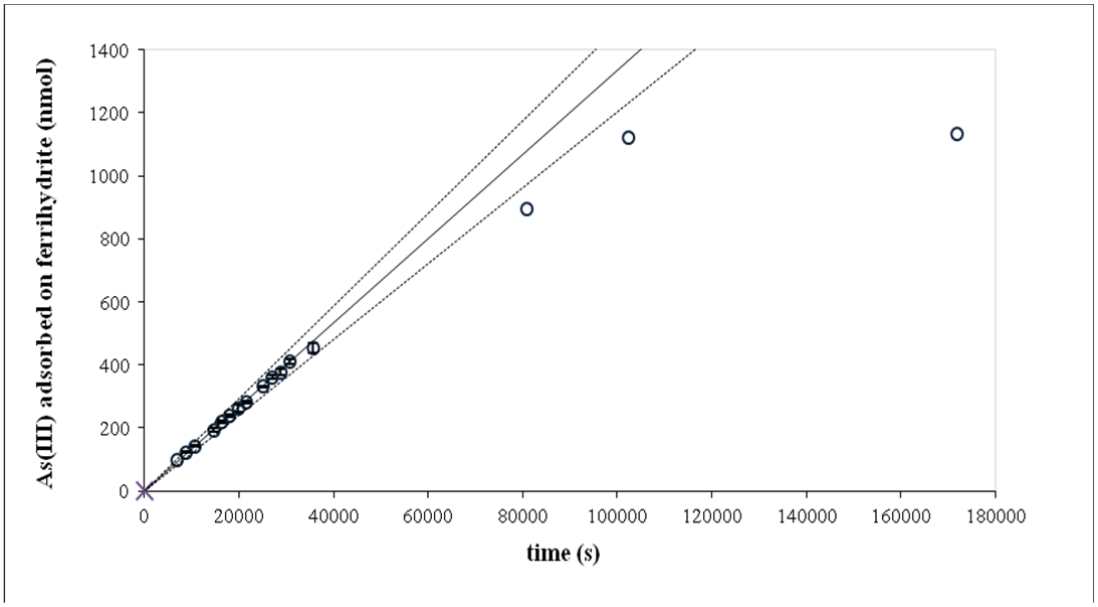


658

659

660 **Figure S2.** Measured mass of Se(VI) adsorbed onto the ferrihydrite (precipitated) gel in the DGT
661 devices plotted against deployment time to determine Se(VI) effective capacity and a D_{DGT} diffusion
662 coefficient in 0.01 M $NaNO_3$, pH 6.0 ± 0.2, Se(VI), (effective capacity for Se(VI) of approximately 30
663 nmol was reached in 3 h in a single element solution of concentration 15 μM Se(VI)).

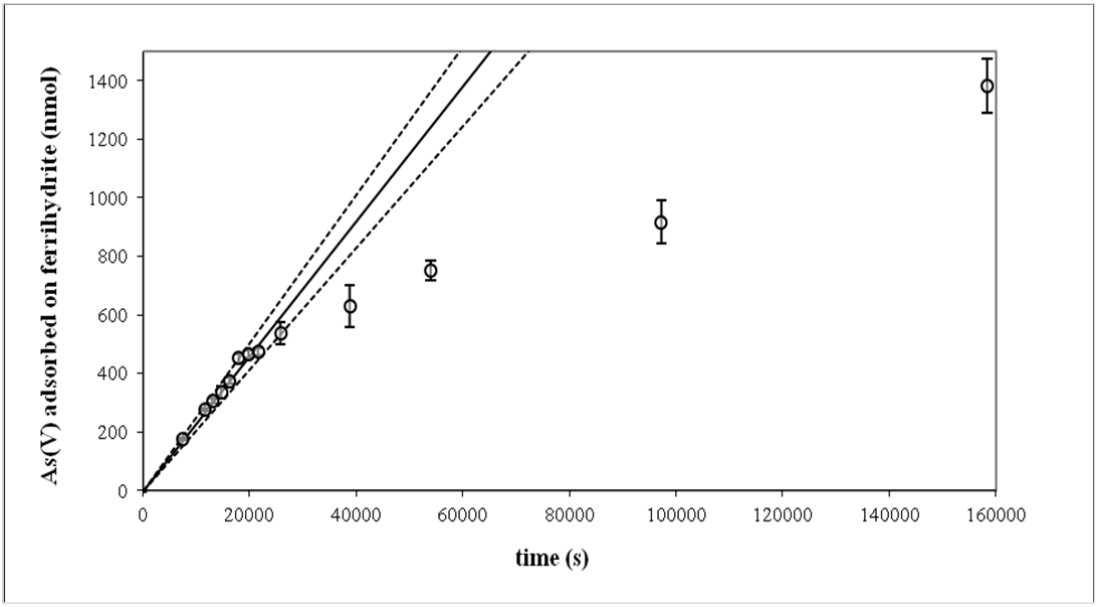
664



665

666 **Figure S3.** Measured mass of As(III) adsorbed onto the ferrihydrite gel in the DGT devices plotted
667 against deployment time to determine As(III) effective capacity and a D_{DGT} diffusion coefficient in 0.01
668 M $NaNO_3$ at pH 6.0 ± 0.2, As(III) concentration 50 μM (ferrihydrite binding layer still within effective
669 capacity for As(III) at 460 nmol, at 10 h under these conditions).

(A)



(B)

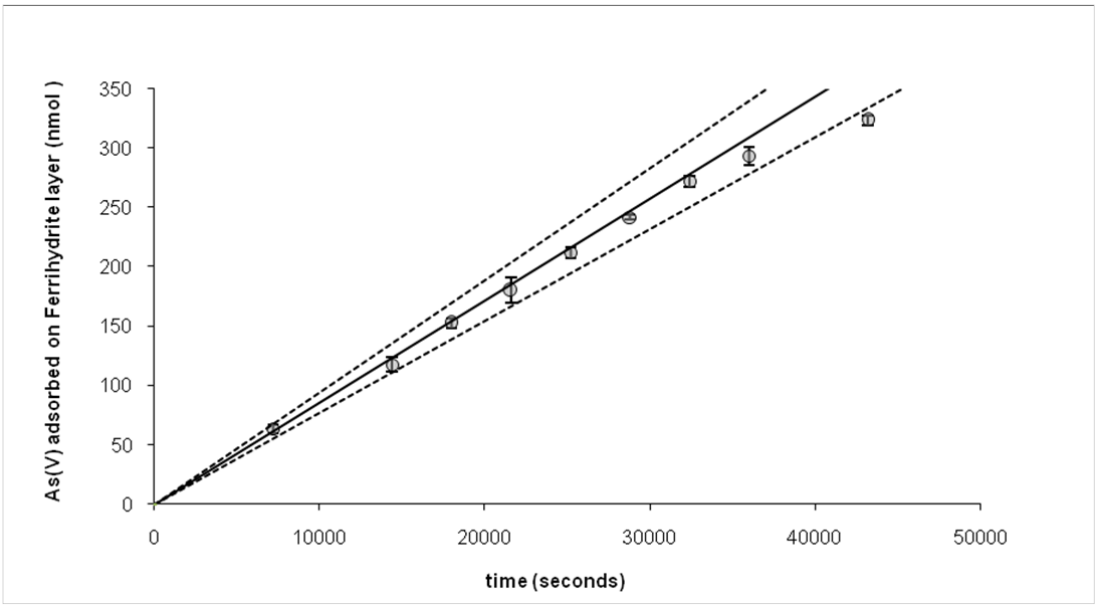


Figure S4. As(V) adsorbed onto the ferrihydrite gel in the DGT devices plotted against deployment time to determine As(V) effective capacity and a D_{DGT} diffusion coefficient in: (a) at 130 µM in synthetic freshwater (0.01 M $NaNO_3$ at pH 6.0 ± 0.2), effective capacity of approximately 530 nmol was reached in 8 h; and (b) at 50 µM in natural seawater at pH 8.1 ± 0.1, effective capacity of approximately 290 nmol was reached in 10 h.