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Titanium dioxide-based DGT for measuring dissolved As(V), V(V), Sb(V), Mo(VI) and W(VI) in water

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ABSTRACT

A titanium dioxide-based DGT method (Metsorb-DGT) was evaluated for the measurement of As(V), V(V), Sb(V), Mo(VI), W(VI) and dissolved reactive phosphorus (DRP) in synthetic waters. Mass vs. time DGT deployments at pH 6.06 (0.01 mol L^{-1} $NaNO_3$) demonstrated linear uptake of all analytes ($R^2 \geq 0.994$). Diffusion coefficients measured using a diffusion cell were in reasonable agreement with diffusion coefficients measured using DGT samplers (D_{Cell}/D_{DGT}=0.82–1.10), although a systematic difference was apparent. The Metsorb-DGT method was independent of ionic strength (0.001–0.7 mol L^{-1} $NaNO_3$ at pH 7.1) for the measurement of all analytes (C_{DGT}/C_{Sol}=0.88–1.11) and, with the exception of V(V), the method was independent of pH (3.98–8.24, 0.01 mol L^{-1} $NaNO_3$), indicated by C_{DGT}/C_{Sol} values in the range 0.88–1.13 for short-term deployments (up to 10 h). For V(V) at pH 3.98, Metsorb-DGT underestimated the solution concentration by 17%, presumably due to weak binding of the VO_2^+ species. The Metsorb-DGT and ferrihydrite-DGT (in situ precipitated ferrihydrite) methods were compared by deploying samplers in synthetic freshwater (pH 7.20, conductivity 223 μS cm^{-1}) and synthetic seawater (pH 8.3. salinity 34.6) for up to four days. For synthetic freshwater, C_{DGT}/C_{Sol} values between 0.87–1.17 were obtained for all analytes measured by the Metsorb-DGT method over the deployment period. For ferrihydrite-DGT, C_{DGT}/C_{Sol} values between 0.97–1.23 were obtained for As(V), V(V), W(VI) and DRP. However, Mo and Sb(V) showed reduced uptake and C_{DGT}/C_{Sol} values were in the range 0.18–1.14 and 0.39–0.98, respectively. In synthetic seawater deployments, Metsorb-DGT was capable of measuring As(V), V(V), Sb(V), W(VI) and DRP for up to 4 days (C_{DGT}/C_{Sol}=0.89–1.26), however, this method was not capable of measuring Mo for deployment times >4 h (C_{DGT}=0.27–0.72). For ferrihydrite-DGT, C_{DGT}/C_{Sol} values in the range 0.92–1.16 were obtained for As(V), V(V) and DRP, however, Mo(VI), Sb(V) and W(VI) could not be measured to within 15% of the solution concentration (C_{DGT}/C_{Sol} 0.02–0.83).

1. Introduction

The oxyanions of arsenic (As), vanadium (V), antimony (Sb), molybdenum (Mo), tungsten (W) and phosphorus (P) are all elements of significant environmental interest that can cause deleterious environmental and/or human health effects [1–6]. In addition, Mo and P are essential elements that are required by plants and animals [4,7]. In well-oxygenated environments, As, V, and Sb are frequently found in the +5 oxidation state [8–10] and Mo and W in the +6 oxidation state [4,5]. Reliable, robust and economical techniques for the measurement of oxyanion species are essential for understanding their behavior and impact within the environment.

The diffusive gradients in thin films (DGT) technique has been used to measure a wide variety of anionic species in water, sediment and soil [11–26]. Ferrihydrite, an iron oxide mineral phase, has been used extensively as a DGT binding agent for the measurement of As, W, Se, V, Mo, Sb and dissolved reactive phosphorus (DRP) [11,13,15,16,18–20]. Originally, the ferrihydrite binding phase was prepared and cast within a polyacrylamide hyrodgel (slurry ferrihydrite) [11,15]. Recently, a new approach has been reported in which the ferrihydrite is precipitated within a pre-cast polyacrylamide gel (*in situ* precipitated ferrihydrite) [19,21]. Precipitating the ferrihydrite *in situ* results in a more even distribution of the binding phase, which is especially important for high resolution sediment measurements. More recently, a DGT technique using a titanium dioxide-based adsorbent (Metsorb-DGT) has also been used to measure a variety of anionic species: As, Se, P, Al and U [17,22,24–28]. Metsorb-DGT has been systematically compared to the slurry ferrihydrite-DGT method and was shown to be advantageous for the measurement of As and P in

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seawater over long-term deployments (up to 4 days) [22,23,25]. The capacity and selectivity of the ferrihydrite binding phase were suggested as reasons why the ferrihydrite performed poorly in comparison to Metsorb [22,25]. Metsorb-DGT has never been compared with the *in situ* precipitated ferrihydrite-DGT method. The precipitated ferrihydrite-DGT has been reported to have a capacity which is three times higher than slurry ferrihydrite-DGT and, hence, may work as well as the Metsorb-DGT method for the measurement of As, DRP and other anions.

The present study focuses on the development of Metsorb-DGT for the simultaneous measurement of DRP, As(V), V(V), Sb(V), Mo(VI) and W(VI) in freshwater and seawater, with the last four species being described for the first time with Metsorb-DGT. The following series of laboratory experiments were conducted to validate the Metsorb-DGT technique, some of which involved comparison of Metsorb-DGT with the precipitated ferrihydrite-DGT method (herein referred to as ferrihydrite-DGT): testing several elution procedures and determining elution factors; measuring diffusion coefficients using diffusion cells and time-series DGT deployments; evaluating the performance in solutions of various ionic strength and pH; and measuring mass vs. time kinetics over 4 days in synthetic freshwater and seawater. This study has extended the range of elements able to be determined using Metsorb-DGT in surface waters and confirmed its superior performance compared to the ferrihydrite-DGT technique.

2. Experimental

2.1. General experimental

Deionised water (Milli-Q Element) was used to prepare all solutions. 1000 mg L^{-1} solutions of Mo(VI), V(V), Sb(V) and W(VI) were prepared fresh using $Na_2MoO_4.2H_2O$, NH_4VO_3, $KSb(OH)_6$ and $Na_2WO_4 \cdot 2H_2O$ (all AR grade), respectively. 1000 mg L^{-1} As(V) and P standard solutions were obtained from High Purity Standards and Merck, respectively. All plastic containers and DGT components were acid-cleaned in 10% (v/v) HNO_3 (AR grade, Merck) for at least 24 h and rinsed thoroughly with deionised water prior to use. All salts used to prepare experimental solutions were AR grade or higher.

2.2. DGT procedures

2.2.1. Gel preparation

Diffusive gels were prepared according to Zhang and Davison [29] and Metsorb (Graver Technologies, DE, USA) binding gels were prepared according to Bennett et al.[17]. Precipitated ferrihydrite binding gels were prepared according to Luo et al. [19] and were stored in water prior to use.

2.2.2. DGT deployment

DGT samplers were supplied by DGT Research Ltd. and were assembled as described previously using a 0.45 μm cellulose nitrate membrane filter (Millipore).[29] DGT samplers were deployed in plastic containers in 2–7 L of well-mixed solution. The pH, temperature and conductivity/salinity of the deployment solutions were monitored regularly throughout each experiment. Dilute HNO_3 and NaOH were used to adjust pH as required. Samples of the experimental solution were removed at the beginning of each experiment and whenever DGT samplers were retrieved, filtered (0.45 μm), acidified to 2% (v/v) HNO_3 and stored at <4 °C in the dark until analyzed.

2.2.3. Elution

Metsorb binding gels were eluted in 1 mL of either 1 mol L^{-1} NaOH or a mixture of 1 mol L^{-1} NaOH and 1 mol L^{-1} H_2O_2, for 24 h. Ferrihydrite binding gels were eluted in 1 mL of 1 mol L^{-1} HNO_3 for 24 h and the following elution efficiencies were used: As(V) (78.0 ± 4.8%) [19]; Sb(V) (85.1 ± 3.5%) [19]; Mo(VI) (79.3 ± 5.4%) [12] and P (100 ± 5.4%) [21]. Reported elution efficiencies for V(V) and W(VI) from ferrihydrite are limited and potentially unreliable, therefore, a value of 85% (average of the elution efficiencies reported above) was assumed. For synthetic seawater and freshwater experiments, the Metsorb binding gels were rinsed in 5 mL of deionized water for 1 h (to remove salts associated with the binding gel) prior to elution [22].

2.2.4. Calculation of the DGT concentration

The DGT-measured concentration (C_{DGT}, ng mL^{-1}) was calculated using the DGT equation [29] along with the diffusion coefficients (D) measured in the current study corrected to 25 °C: As(V) $(6.78 \pm 0.24) \times 10^{-6}$ cm^2 s^{-1}; V(V) $(8.02 \pm 0.35) \times 10^{-6}$ cm^2 s^{-1}; Sb(V) $(6.86 \pm 0.30) \times 10^{-6}$ cm^2 s^{-1}; W(VI) $(6.26 \pm 0.08) \times 10^{-6}$ cm^2 s^{-1}; and Mo(VI) $(6.81 \pm 0.28) \times 10^{-6}$ cm^2 s^{-1}. A D value of 6.05×10^{-6} cm^2 s^{-1} was used for P [11]. For seawater and high ionic strength (0.7 mol L^{-1} $NaNO_3$) deployments a value of $0.9 \times D$ was used [30].

2.3. Sample analysis

Measurements were performed using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500a). All ICP-MS samples and standards were prepared in a 2% (v/v) HNO_3 matrix. Quality control standards at 10 μg L^{-1} were analyzed every 20–30 samples. Sc, Y and In were added to all samples (final concentration of 10 μg L^{-1}) as an internal standard to account for instrument drift. Phosphorus measurements were performed using a Merck phosphate test kit (US Standard Methods 4500-P E).

2.4. Laboratory evaluation

2.4.1. Uptake and elution efficiencies

Uptake and elution efficiencies were measured by immersing five Metsorb binding gel discs (4.91 cm^2) in 4.5 mL of 100 μg L^{-1} of a mixed analyte solution (prepared in 0.01 mol L^{-1} $NaNO_3$/0.005 mol L^{-1} sodium acetate at pH 5). After 24 h the gels were removed, eluted and analyzed. Samples of the uptake solutions were also analyzed (after acidification) to determine the mass of analyte remaining in solution. The mass of adsorbed analyte, and thereby the uptake and elution efficiencies of the analyte, were calculated by difference.

2.4.2. Time-series accumulation

The time-series accumulation of As(V), V(V), W(VI), Sb(V), and Mo(VI) by Metsorb-DGT (from a mixed analyte solution) was evaluated at pH 6.06 (0.01 mol L^{-1} $NaNO_3$/0.0005 mol L^{-1} sodium acetate) for up to 24 h in a solution containing between 13–25 μg L^{-1} of analyte. Effective diffusion coefficients were calculated using the slope of the linear regression of the mass of analyte accumulated in the binding gel over time, as detailed by Bennett et al. [17].

2.4.3. Diffusion coefficient measurement using a diffusion cell

A diaphragm diffusion cell custom-made from Perspex was used to measure the diffusion coefficients of As(V), V(V), W(VI), Sb(V) and Mo(VI) [31]. The cell consisted of two 100 mL compartments connected by a 1.58 cm diameter opening. A disc of polyacrylamide hydrogel (0.08 cm thickness; 2.5 cm diameter) and a 0.45 μm cellulose nitrate filter membrane (0.01 cm thickness) were placed between the two compartments. A 0.05 cm thick plastic spacer was also used to prevent excess compression of the gel. The cell was then clamped using screws. Diffusion coefficients were determined in 0.01 M $NaNO_3$, pH 7.15 ± 0.1 at 21 °C with a mixed analyte solution containing As(V), V(V), W(VI), Sb(V) and Mo(VI) (all at 5 mg L^{-1}). The solutions in both cell compartments were stirred continuously using magnetic stirrers. Samples (1 mL) were taken from both sides every 10 min for 2 h and preserved for analysis. Diffusion coefficients were calculated as described by Zhang and Davison [31].

2.4.4. pH and ionic strength

To examine the efficacy of the Metsorb-DGT method across a wide pH and ionic strength range, samplers were deployed in mixed analyte solutions (50 μg L^{-1} of each analyte) of varying pH (5.0–8.3; 0.01 mol L^{-1} $NaNO_3$) or ionic strength (0.001–0.7 mol L^{-1} $NaNO_3$; pH 7.0) for 8–10 h.

2.4.5. Synthetic freshwater and synthetic seawater

Metsorb-DGT and ferrihydrite-DGT were deployed in a synthetic freshwater (pH=7.20 ± 0.10; conductivity=223 μS cm^{-1}) and a synthetic seawater (pH 8.30 ± 0.15; salinity=34.6) for 8–97 h to evaluate the performance of the binding gels. The composition of the synthetic freshwater and synthetic seawater is given in the supporting information of Panther et al. [22]. The synthetic waters were spiked with 3–80 μg L^{-1} of each analyte. For the seawater deployment, the concentration of As in solution could not be measured by ICP-MS due to the polyatomic ArCl (m/z 75) interference. The Metsorb gels were first eluted with 1 mol L^{-1} NaOH to elute As, V, Mo, W and P, followed by elution with 1 mol L^{-1} NaOH/1 mol L^{-1} H_2O_2 to elute Sb.

3. Results and discussion

3.1. Uptake and elution

Metsorb uptake efficiencies for As(V), V(V), Mo (V), W(VI), DRP and Sb(V) were >98% (n=6). Metsorb binding gels were eluted with 1 mol L^{-1} NaOH or a mixed eluent of 1 mol L^{-1} NaOH/1 mol L^{-1} H_2O_2. Both eluents have previously been used in Metsorb-DGT applications; NaOH for As, Se, P and Al [17,22,28] and NaOH/H_2O_2 for U [27]. When eluting with 1 mol L^{-1} NaOH, elution efficiencies >86% were obtained for all analytes investigated (Table S1), with the exception of Sb(V) (20.2 ± 3.7%). Elution with 1 mol L^{-1} NaOH/1 mol L^{-1} H_2O_2 resulted in elution efficiencies >88% for all analytes including Sb(V) (Table 1), with the exception of P. The elution efficiency with 1 mol $L^{-1}H_2O_2$ added was actually higher for each of the species in Table 1 than with just NaOH. The elution efficiency of P from the Metsorb binding gel could not be determined for NaOH/H_2O_2. Addition of acid (necessary for P spectrophotometric measurements) to the eluted sample produced an orange colouration, probably as a result of a titanium-peroxide complex forming at low pH [32], which interfered with the spectrophotometric measurement of the blue phosphomolybdate complex. However, a single Metsorb-DGT sampler can still be used to measure DRP and Sb(V) simultaneously if a two step elution is employed. For example, eluting the gel with NaOH to elute P (and other oxyanions), followed by elution with NaOH/H_2O_2 (to elute Sb(V)) would allow both analytes to be measured simultaneously. This approach was utilized for the synthetic freshwater and synthetic seawater measurements. Alternatively, ICP-MS could be used to measure P and this would only require a single elution with H_2O_2/NaOH.

Table 1
Elution efficiencies (mean ± S.D.; n=10), gel blanks and DGT method detection limits (MDL)

	Metsorb elution efficiency (%)[a]	Metsorb gel blank (ng)[a]	Metsorb-DGT MDL (μg L^{-1})[b]	Ferrihydrite gel blank (ng)[c]	Ferrihydrite-DGT MDL (μg L^{-1})[b]
As	92.1 ± 2.5	0.58 ± 0.18	0.02	0.98 ± 0.23	0.03
Mo	94.8 ± 3.6	3.25 ± 0.43	0.06	1.99 ± 0.39	0.05
V	90.8 ± 2.3	14.1 ± 2.5	0.28	0.41 ± 0.18	0.02
Sb	90.3 ± 4.6	0.51 ± 0.11	0.01	0.46 ± 0.17	0.02
W	97.9 ± 1.6	2.64 ± 1.21	0.16	0.67 ± 0.34	0.04
DRP	92 ± 5.0[d]	14.3 ± 4.6	0.75[e]	17.1 ± 3.8	0.63[e]

[a] Eluted with 1 mol L^{-1} NaOH/1 mol L^{-1} H_2O_2.

[b] MDL=3σ blank and using D_{DGT} values reported in Table 2, t=24 h, A=3.14 cm^2 and Δg=0.08 cm. Temperature=25 °C.

[c] Eluted with 1 mol L^{-1} HNO_3.

[d] Elution efficiency reported by Panther et al. [22] using 1 mol L^{-1} NaOH.

[e] Calculated using D value reported in Panther et al. [22].

3.2. Gel blanks and method detection limits

Metsorb and ferrihydrite binding gel blanks and DGT method detection limits (MDLs) are presented in Table 1. For As(V), Sb(V) and DRP the ferrihydrite and Metsorb gel blanks were comparable, whereas, for Mo, V(V) and W(VI) the ferrihydrite gel blanks were significantly lower than the Metsorb gel blanks. For V(V), the Metsorb gel blank was ~34 times higher than the corresponding value for ferrihydrite indicating contamination of the Metsorb binding agent. If required, the Metsorb blank values may be lowered by cleaning the binding agent with NaOH prior to use; a similar approach has been used to significantly lower the Al blank value for Metsorb [28]. The ferrihydrite and Metsorb-DGT MDLs (Table 1) for As(V), Mo(VI), Sb(V) and DRP were all similar. For W(VI) and V(V), the DGT MDLs for Metsorb were four and 14 times higher, respectively, than the ferrihydrite-DGT MDLs, due to greater variability in the blank values. With the exception of V(V), all measured DGT MDLs for Metsorb and ferrihydrite were comparable or better than those reported by other workers [12,17,19]. The DGT MDLs can easily be lowered by increasing the deployment time or decreasing the thickness of the diffusive layer.

3.3. Time-series accumulation

When evaluating new DGT adsorbents, or applying pre-existing DGT methods to new analytes, the assumption that there is a linear relationship between the mass of analyte accumulated and time needs to be confirmed. Experiments were conducted to investigate the uptake of As(V), Mo(VI), V(V), Sb(V) and W(VI) by Metsorb-DGT over a 24 h period. Good linearity was observed for all analytes investigated ($R^2 \geq 0.994$) and the relative standard deviations (RSD) of triplicate DGT samplers were generally less than 10% (Fig. S1). These results confirm rapid uptake of the analytes by the Metsorb adsorbent, ensuring that the concentration of analyte at the interface between the Metsorb binding gel and diffusive gel is effectively zero. These results confirm that Metsorb is an appropriate DGT adsorbent for the new analytes investigated (Mo(VI), V(V), Sb(V) and W(VI)) over the time period employed (24 h) and conditions used in this experiment (0.01 mol L^{-1} $NaNO_3$ at pH 6.06).

3.4. Diffusion coefficients

The diffusion coefficients of As(V), Mo(VI), V(V), Sb(V) and W(VI) were measured using two methods: a diaphragm diffusion cell (D_{Cell}) and DGT deployments (D_{DGT}). The regression lines from Fig. S1 were used to calculate effective diffusion coefficients for

DGT deployments. The D_{Cell} and D_{DGT} values are given in Table 2. With the exception of W(VI), all D_{Cell} values were 8–18% less than the D_{DGT} values. A similar discrepancy between D_{Cell} and D_{DGT} has been reported by Bennett et al. [17] and was purported to be due to the presence of a small diffusive boundary layer (DBL) associated with the diffusion cell experiments, effectively increasing the diffusive path length which results in calculation of a lower *D* value. However, an improved diffusion cell design, in which DBL formation was much less likely, was used for this study. An alternative explanation may be due to lateral diffusion that occurs within the DGT sampler diffusive layer, as first reported by Warnken and co-workers [33], which results in a 20% increase in the actual area of the sampler compared to the geometrical area. Lateral diffusion would contribute to the mass of analyte accumulated by the DGT sampler but would not contribute to the mass of analyte diffused from one compartment of the diffusion cell to the other, hence, D_{DGT} may be greater than D_{Cell}, as observed in the current study. However, it is important to note that overall there is reasonable agreement between the two measurement methods used in this study.

Table 2 also compares the *D* values measured in the current study with literature values that have been measured using a diffusion cell or DGT samplers with other binding layers. Generally, reasonable agreement (within 20%) between the *D* values measured in the current study and those reported in the literature is observed. However, due to differences in the diffusion coefficients reported in the literature for both anions and cations, we recommend that researchers measure their own diffusion coefficients to ensure accurate DGT concentration measurements.

The D_{DGT} values are a combined measurement of the rate of diffusion of analyte through the DGT diffusive layer and the binding ability of the Metsorb binding agent for the analyte, hence, D_{DGT} values were used for all subsequent calculations.

3.5. *pH and ionic strength*

The effect of pH (3.98–8.24) and ionic strength (0.001–0.7 mol L^{-1}) on the utility of Metsorb-DGT for measuring As(V), Mo(VI), V(V), Sb(V) and W(VI) was investigated. Generally, over the pH (Table 3) and ionic strength (Table 4) range investigated, good agreement between C_{DGT} and C_{Sol} was obtained as indicated by $C_{\mathrm{DGT}}/C_{\mathrm{Sol}}$ ratios between 0.88 and 1.13. These results indicate that the analyte uptake efficiency by Metsorb is independent of ionic strength and pH, demonstrating that the charge of the analyte or Metsorb binding agent does not significantly affect uptake efficiency across the pH and ionic strength range studied. A clear exception was observed for V(V) at pH 3.99, for which $C_{\mathrm{DGT}}/C_{\mathrm{Sol}}$ was 0.83. Similar results for V(V) have been observed by Luo et. al. [19] who reported that the ferrihydrite-DGT method underestimated the dissolved V(V) concentration by ~40% at pH 3.13 and ~20% at pH 4.42. Luo et al. [19] explained this underestimation as weak binding between the positively charged VO_2^+ species (dominant V(V) species at pH <5.5) and the positively charged ferrihydrite surface. Similar interactions are most likely occurring between VO_2^+ and the titanium dioxide surface of Metsorb ($pH_{\mathrm{pzc}}=5.9$ for anatase mineral form of TiO_2) [34], resulting in a 17% underestimation at pH 3.99. Overall, the pH and ionic strength results obtained in the current study are in good agreement with the work of Bennett et. al. [17], Luo et. al. [19], and Mason et. al. [12] and confirm that the Metsorb-DGT is capable of measuring the oxyanions of As(V), Mo(VI), V(V), Sb(V) and W(VI) over the pH and ionic strength ranges typically encountered in most natural waters.

Table 3
Effect of pH on the measurement of As(V), Mo(VI), Sb(V), V(V) and W(VI) by Metsorb-DGT at 0.01 mol L^{-1} $NaNO_3$.

pH	**$C_{\mathrm{DGT}}/C_{\mathrm{Sol}}$**				
	As	Mo	Sb	V	W
3.98	0.90 ± 0.07	1.04 ± 0.15	0.98 ± 0.02	0.83 ± 0.03	1.11 ± 0.13
5.07	0.95 ± 0.12	0.88 ± 0.11	0.92 ± 0.12	0.90 ± 0.08	0.89 ± 0.07
6.02	1.05 ± 0.10	0.93 ± 0.04	0.96 ± 0.11	0.91 ± 0..15	0.88 ± 0.10
7.23	0.98 ± 0.06	1.13 ± 0.05	0.96 ± 0.07	0.97 ± 0..5	0.96 ± 0.11
8.24	0.97 ± 0.09	1.04 ± 0.12	0.89 ± 0.07	1.11 ± 0.10	0.98 ± 0.04

Uncertainties associated with $C_{\mathrm{DGT}}/C_{\mathrm{Sol}}$ values are derived from replicate DGT and grab sample measurements.

Table 4
Effect of ionic strength (mol L^{-1} $NaNO_3$) on the measurement of As(V), Mo(VI), Sb(V), V(V) and W(V) by Metsorb-DGT at pH 7.1.

Ionic strength	**$C_{\mathrm{DGT}}/C_{\mathrm{Sol}}$**				
	As	Mo	Sb	V	W
0.001	0.90 ± 0.07	1.04 ± 0.15	0.98 ± 0.02	0.89 ± 0.03	1.11 ± 0.13
0.01	0.95 ± 0.12	0.88 ± 0.11	0.92 ± 0.12	0.94 ± 0.08	0.89 ± 0.07
0.7	0.97 ± 0.09	1.04 ± 0.12	0.89 ± 0.07	1.11 ± 0.10	0.98 ± 0.04

Uncertainties associated with $C_{\mathrm{DGT}}/C_{\mathrm{Sol}}$ values are derived from replicate DGT and grab sample measurements.

Table 2
Measured diffusion coefficients ($\times 10^{-6}$ cm^2 s^{-1}) using a diffusion cell (D_{Cell}) and DGT samplers (D_{DGT}) at 25 °C[a]

	As	Mo	V	Sb	W
Diffusion cell (D_{Cell})[b]	5.54 ± 0.17	6.28 ± 0.13	7.14 ± 0.04	6.04 ± 0.12	6.89 ± 0.08
DGT deployments (D_{DGT})[c]	6.78 ± 0.24	6.81 ± 0.28	8.02 ± 0.35	6.86 ± 0.30	6.26 ± 0.37
$D_{\mathrm{Cell}}/D_{\mathrm{DGT}}$	0.82	0.92	0.89	0.88	1.10
Literature D_{Cell} values	4.85, [15] 5.18, [19] 5.21, [18] 5.57, [17]	6.48, [12] 5.96, [18]	6.48, [19] 6.72, [18]	5.40, [19] 5.55, [18]	5.45[18]
Literature D_{DGT} values	4.90, [15] 5.25, [19] 6.83, [17] 5.26, [18]	5.42, [18] 6.48, [12]	6.26, [19] 6.66, [18]	5.46, [19] 5.38, [18]	5.56[18]

[a] Uncertainty with *D* values are derived from the S.D. of the mass vs. time plots and the uncertainty associated with the analyte concentration.

[b] pH=7.1, ionic strength=0.01 mol L^{-1} $NaNO_3$.

[c] pH=6.06 ± 0.02, ionic strength=0.01 mol L^{-1} $NaNO_3$.

It is important to note that outside of the pH range studied (3.98–8.24) the uptake efficiency of the anionic species may be lower due to the charge on the analyte and/or adsorbent varying with pH; the authors suggest further investigation if this DGT technique is to be used outside of the pH range stated.

3.6. Synthetic freshwater

DGT samplers containing Metsorb or precipitated ferrihydrite binding gels were deployed in synthetic freshwater spiked with As(V), Mo(VI), V(V), Sb(V), W(VI) and DRP (between 4 and 80 $\mu g\,L^{-1}$) for up to four days. Deployment times of 4–5 days in the laboratory will often be adequate to reveal possible interferences, especially in seawater, and four days is a typical deployment time for in situ determinations. Mass vs. time plots for Metsorb-DGT showed good agreement between the mass of analyte accumulated by the DGT sampler and the predicted mass of analyte for all oxyanions investigated (Fig. 1, closed squares). Furthermore, $C_{\text{DGT-Metsorb}}/C_{\text{Sol}}$ values between 0.89 and 1.17 were obtained for all analytes (Table S2), indicating that Metsorb-DGT quantitatively measures the analyte concentration in freshwater over the 4 day deployment.

Linear mass vs. time plots were obtained using ferrihydrite-DGT for As(V), V(V) and W(VI) and $C_{\text{DGT-Ferr}}/C_{\text{Sol}}$ values between 0.97–1.23 were obtained across the sampling periods (Table S3). The good agreement between $C_{\text{DGT-Ferr}}$ and C_{sol} validates the use of the assumed 85% elution efficiency for V(V) and W(VI). For Mo(VI) and Sb(V), poor agreement was obtained between the accumulated mass and the predicted mass for deployment times >5.9 h, indicating competition between Mo/Sb(V) and other ions in solution for binding sites on the ferrihydrite adsorbent. Over short deployment times (5.9 h), the ferrihydrite-DGT method accurately measured the dissolved concentration of Mo(VI) ($C_{\text{DGT-Ferr}}/C_{\text{Sol}}=1.14$) and Sb(V) ($C_{\text{DGT-Ferr}}/C_{\text{Sol}}=0.98$), however for deployment times ≥ 25.7 h the $C_{\text{DGT}}/C_{\text{Sol}}$ values ranged from 0.18 to 0.61 and from 0.38 to 0.69 for Mo(VI) and Sb(V), respectively, indicating considerable underestimation of the dissolved concentration by ferrihydrite-DGT. To our knowledge, this is the first time that the ferrihydrite-DGT method has been evaluated for Mo(VI), V(V), Sb(V) and W(VI) in synthetic freshwater for up to four days. Luo and co-workers [19] used similar deployment times (up to 72 h) and found good agreement between the predicted and accumulated mass of Sb(V), however their deployments were carried out in 0.01 mol L^{-1} $NaNO_3$ at pH 5.01. It is possible that the presence of major ions from the synthetic freshwater used in our experiments (Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}), which are not present in the simple $NaNO_3$ matrix, may be affecting uptake of Sb(V) and Mo(VI) by the ferrihydrite-DGT method. This effect has been observed experimentally for the measurement of Al by Chelex-DGT [28].

Mass vs. time experiments were not carried out for DRP. Metsorb- and ferrihydrite-DGT samplers were only deployed for 72 and 93 h. For a deployment time of 72 h, $C_{\text{DGT}}/C_{\text{Sol}}$ ratios for the Metsorb and ferrihydrite samplers were 0.98 and 0.95, respectively, and for a deployment time of 93 h, the corresponding ratios were 1.02 and 0.91, respectively. These values are in good agreement with those reported by Panther et. al. [22] who compared the performance of Metsorb-DGT and ferrihydrite-DGT (slurry form) in freshwater over similar deployment times to those carried out in this study.

3.7. Synthetic seawater

DGT samplers containing Metsorb or precipitated ferrihydrite binding gels were deployed in synthetic seawater spiked with As(V), Mo(VI), V(V), Sb(V), W(VI) and P (between 3 and 80 $\mu g\,L^{-1}$) for up to four days. Mass vs. time plots for Metsorb-DGT showed good agreement between the mass of analyte accumulated by the DGT sampler and the predicted mass of analyte for As(V), V(V), Sb(V) and W(VI) (Fig. 2) with $C_{\text{DGT-Metsorb}}/C_{\text{Sol}}$ values between 0.86 and 1.26 over the four day deployment (Table S4). However, for Mo(VI), Metsorb-DGT did not accurately measure Mo(VI) in

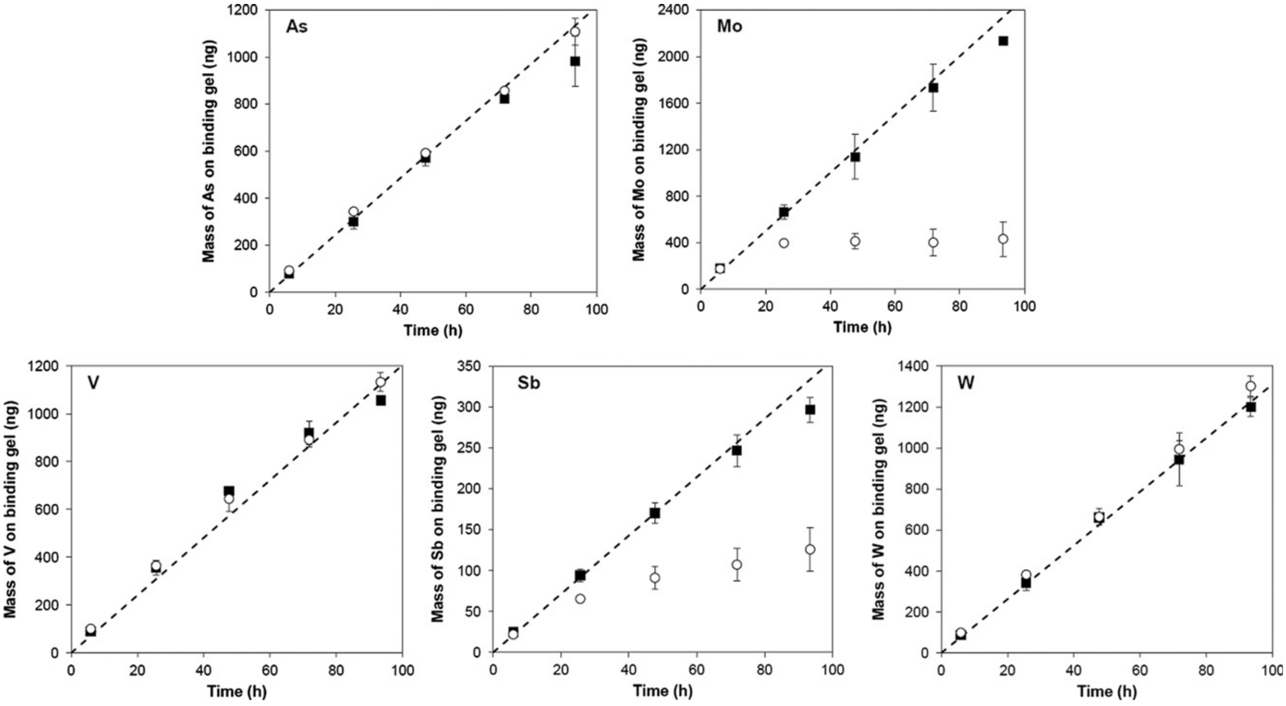

Fig. 1. Average ($n=3$) mass of analyte accumulated by Metsorb-DGT (■) and ferrihydrite-DGT (○) for synthetic freshwater deployments. Error bars represent the standard deviation of triplicate measurements. Dotted line is the predicted uptake calculated using the DGT equation. Experimental conditions: pH $=7.20 \pm 0.08$; conductivity $=230\ \mu S\,cm^{-1}$; temperature $=24.8\ ^\circ C$. Analyte concentrations were: As(V) 15 $\mu g\,L^{-1}$, Mo(VI) 30 $\mu g\,L^{-1}$, V(V) 12 $\mu g\,L^{-1}$, Sb(V) 4 $\mu g\,L^{-1}$ and W(VI) 17 $\mu g\,L^{-1}$.

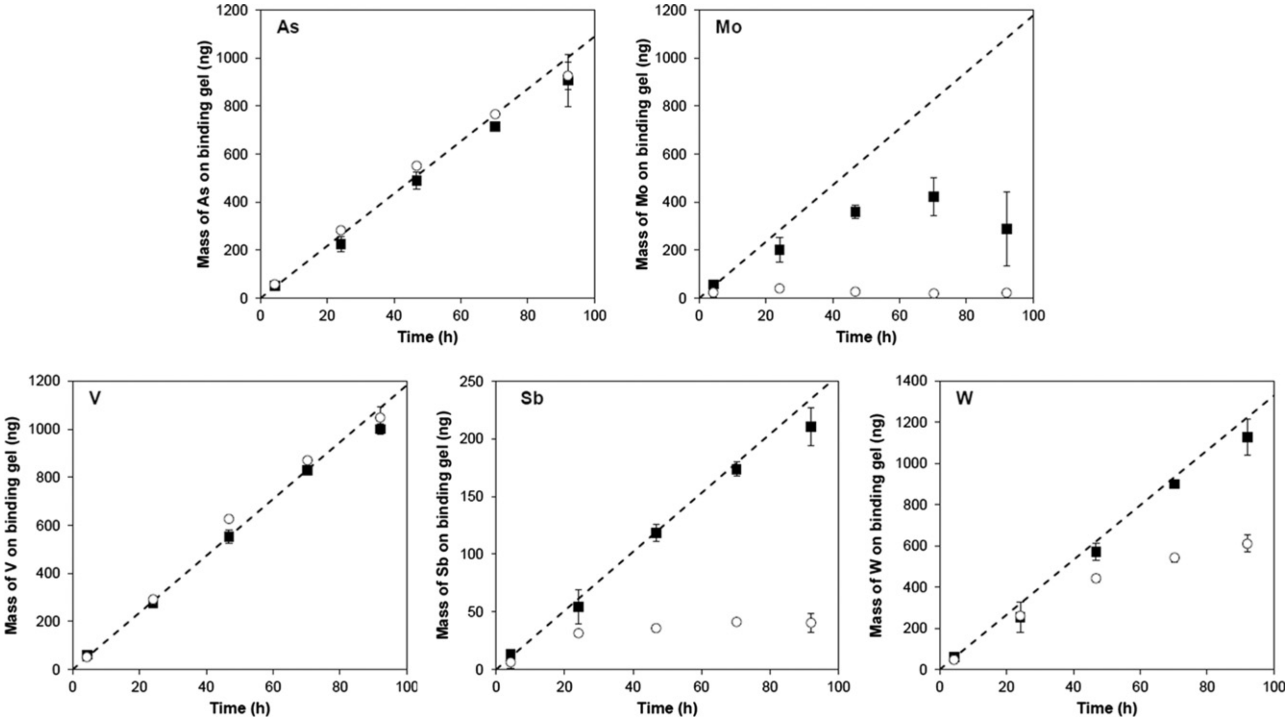

Fig. 2. Average mass (n=3) of analyte accumulated by Metsorb-DGT (■) and ferrihydrite-DGT (○) for synthetic seawater deployments. Error bars represent the standard deviation of triplicate measurements. Dotted line is the predicted uptake calculated using the DGT equation. Experimental conditions: pH=8.30 ± 0.12; salinity=34.6; temperature=24.8 °C. Analyte concentrations were: As(V) 15 μg L^{-1}, Mo(VI) 15 μg L^{-1}, V(V) 13 μg L^{-1}, Sb(V) 3 μg L^{-1} and W(VI) 17 μg L^{-1}.

seawater for deployment times > 4 h; $C_{\text{DGT-Metsorb}}$ /C_{Sol} values ranged from 1.16 at 4 h to 0.27 at 92 h (Table S4). For ferrihydrite-DGT, only As(V) and V(V) showed good agreement between the predicted and measured mass of analyte ($C_{\text{DGT-Ferr}}$ /C_{Sol} in the range 0.92–1.26; Table S5), whereas Mo(VI), Sb(V) and W(VI) all showed large deviations from the predicted uptake, indicating competition between the analyte and other ions in solution for the ferrihydrite adsorbent. Molybdenum was most affected, followed by Sb(V) and then W(VI) (e.g. $C_{\text{DGT}}/C_{\text{Sol}}$ at 92 h for Mo(VI), Sb(V) and W(VI) was 0.02, 0.17 and 0.50, respectively). Panther and co-workers [25] have shown that the presence of bicarbonate in solution affects the uptake of DRP by ferrihydrite-DGT. Metsorb-DGT was not affected by the presence of bicarbonate, presumably due to a higher capacity and/or better selectivity of Metsorb compared to ferrihydrite [22,25].

For DRP, after a deployment time of 70 h, $C_{\text{DGT}}/C_{\text{Sol}}$ ratios for the Metsorb and ferrihydrite samplers were 0.97 and 0.84, respectively, and for a deployment time of 93 h, the corresponding ratios were 0.92 and 0.71, respectively. The DRP results observed in this study are similar to those reported by Panther et. al. [22] and indicate competition between bicarbonate and DRP for binding sites on the ferrihydrite adsorbent.

4. Conclusions

This is the first time that the Metsorb-DGT method has been used to measure V(V), Sb(V), Mo(VI) and W(VI) in freshwater and seawater, and the first application of Metsorb-DGT to simultaneously measure As(V), DRP, V(V), Sb(V), Mo(VI), and W(VI) in water. Furthermore, this is the first time that the ferrihydrite-DGT method has been rigorously tested for a variety of oxyanions in freshwater and seawater for deployment times up to four days.

This study has demonstrated that Metsorb-DGT accurately measures the dissolved concentration of As(V), DRP, V(V), Sb(V), Mo(VI) and W(VI) when deployed in freshwater for up to four days, whereas, for ferrihydrite-DGT, only As(V), DRP, V(V) and W(VI) were measured accurately over the same time scale. For seawater deployments, Metsorb-DGT accurately measured As(V), DRP, V(V), Sb(V) and W(VI) over the four day deployment, whereas, ferrihydrite-DGT was capable of measuring only As(V), DRP and V(V) due to competition for ferrihydrite binding sites by other ions in solution. Neither Metsorb nor ferrihydrite are appropriate adsorbents for measuring Mo(VI) in seawater for deployments > 4 h.

This study has shown the importance of a comprehensive laboratory evaluation of DGT methods prior to being used in the field. This study, and also work by others [22,23,25,28], demonstrates that experiments of similar duration and in similar matrices to the proposed field deployment conditions are essential when evaluating new DGT techniques.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.11.070.

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