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Extending the functionality of the slurry ferrihydrite-DGT method: Performance evaluation for the measurement of vanadate, arsenate, antimonate and molybdate in water

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Abstract

The monitoring of oxyanions in waters, presents significant challenges due to their relatively low concentrations, and a characteristically changeable/unstable/reactive geochemistry with high spatial and temporal turnover. This results in a very heterogeneous pattern of mobility and bioavailability, which is difficult to capture reliably and in a cost effective manner. The diffusive gradients in thin-films (DGT) technique is a popular analytical tool for testing water quality, primarily because it provides a time-integrated measurement. However, to date, the most widely used DGT configuration for oxyanion sampling, the slurry ferrihydrite binding layer (SF-DGT) has only been fully characterised for phosphate. Confirmatory testing of the functional range of ionic strengths, pH, deployment times and ionic competition effects, that the SF-DGT’s operates within over has not been carried out, but is addressed in this study for V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V}, and Mo\textsuperscript{VI}. In this study SF-DGT Sb\textsuperscript{V} measurements functioned over the largest range of conditions (ionic strength, 0.1–500 mM; pH 3.86 – 9.90), while ionic strengths above 100 and 500 mM were found to be problematic for As\textsuperscript{V} and Mo\textsuperscript{VI}, respectively. Low pH (below 4) caused inferences with V\textsuperscript{V}, conversely As\textsuperscript{V} and Mo\textsuperscript{VI} determination faltered/deviated from predicted responses in pH conditions of ~9. SF-DGT measurements adequately predicted up to weeklong averaged in situ metal oxyanion concentrations in a freshwater river. This study concludes that the SF-DGT configuration is highly suitable for pollution monitoring applications in freshwater systems for key oxyanion species.
1. Introduction

Oxyanions of vanadium(V), arsenic (As), and antimony (Sb) are of significant environmental interest, causing numerous deleterious environmental and/or human health effects. Metal/alloy producers consume around 85% of globally traded V (Moskalyk and Alfantazi, 2003), with an increasing demand/use for V being driven by the voracious growth in iron/steel during the past half-a-century (Yellishetty et al., 2010). The damage to biota inflicted by V generally increases with species valiancy, with inhibition of numerous enzymatic systems; such as ATPases, protein kinases, ribonucleases, and phosphatases, the primary modes of toxicity action (Mukherjee et al., 2004).

Concern relating to As exposure remains high, due to its potency as a group 1 human carcinogen (Straif et al., 2009) coupled with its wide spread prevalence in the environment (Qin et al., 2009). Whereas, the rapid increase in industrial demand for Sb, in alloys, flame retardants and semi-conductors especially, means it’s environmental ‘footprint’ is also escalating fast (Filella and Williams, 2012; Okkenhaug et al., 2012). Antimony is highly toxic, and when ingested in small doses can cause headaches, dizziness and depression. Long-term exposure damages both the liver and kidney (He and Wan, 2004). Molybdenum (Mo) although an essential mineral nutrient for both plants and animals in trace amounts (Pyrzynska, 2007), is emerging as a water quality issue in regions where there are intensive/extensive copper and sulphide ore extractions (Rodriguez-Iruretagoiena et al., 2016). Other
new/important sources of Mo pollution, include waste discharges from the manufacture of electronics (Pichler et al., 2017), catalyst use (Pichler et al., 2017), and geogenic release resulting from over extraction from domestic water wells (Pichler and Mozaffari, 2015).

Although trace element oxyanions can exist as a range of different species, V, As and Sb most commonly occur in aerobic waters in the +5 oxidation state as inorganic ions, with +6 being the prevalent valiancy for Mo. There are a number of oxyanion detection methods, including atomic absorption/fluorescence spectrometry (Liu et al., 2010), inductively coupled plasma mass spectrometry (ICP-MS) (Luo et al., 2010), enzymatic assays (El Khalil et al., 2008), monoclonal antibodies tests (Zhu et al., 2007) and biosensor platforms (Gani et al., 2010). Even though these methods are sensitive and have a good detection limit, their potential use for in situ environmental monitoring has perhaps only been partially realized. This is not a direct criticism of these measurement systems per se, rather a reflection of the sampling collection procedures, which tend to be either field or active sampling based.

The DGT technique has a number of advantages compared with traditional grab sampling approaches, and these benefits are summarized in-depth in a recent review (Davison, 2016). However, DGT’s key merits are to capture the true solution component of freshwater systems, including in this definition, readily labile complexed metal species, which are often not accounted for by other measurement
techniques, while, providing a means to obtain multi-dimensional (temporal/spatial) data in a cost effective manner with minimal disturbance to the sampling environment (Arditsoglou and Voutsa, 2008).

Ferrihydrite, an amorphous iron oxide mineral phase, has been used extensively as a DGT binding agent for the measurement of oxyanions, and can be prepared in one of two ways: i) slurry ferrihydrite (SF) binding phase is added to a polyacrylamide hydrogel during the casting procedure, ii) precipitated ferrihydrite (PF) binding phase is deposited in solid form from solution within a pre-cast/formed polyacrylamide gel. The main advantage of the ferrihydrite SF compared with the PF variant, is the longer sampler storage time, with the latter recommend for use within 38 days of production (Luo et al., 2010). PF-DGT has been used for the measurement of V⁵⁺, As⁵⁺, Sb⁵⁺, Se⁶⁺ and dissolved reactive phosphorus (Zhang et al., 1998; Luo et al., 2010). Another DGT technique using a titanium dioxide-based adsorbent (Metsorb-DGT) has been used to measure a variety of anionic species: V⁵⁺, As⁵⁺, Se⁴⁺, Mo⁶⁺, Sb⁵⁺, P⁵⁺ and W⁶⁺ (Bennett et al., 2010; Panther et al., 2010; Panther et al., 2013). Zirconium oxide (Zr-oxide DGT) as a binding agent in DGT has also been studied for quantification of P⁵⁺, V⁴⁺, As⁵⁺, Se⁶⁺, Mo⁶⁺ and Sb⁵⁺ (Guan et al., 2015). While Amberlite resins have been used as binders in DGT for As⁵⁺ (Rolisola et al., 2014) and V⁴⁺ (Luko et al., 2017). Although SF gels based DGT devices (SF-DGT) have been tested for phosphate in water, the performance characteristics of SF-DGT responding to changing environmental conditions and its field application have not been systematically tested
for V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} and Mo\textsuperscript{VI}.

The overall aim of this study were as follows: to characterize the elution efficiency of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} and Mo\textsuperscript{VI} from the SF binding gels; to ascertain the performance responses of the SF gels-DGT to different ionic strengths, pH, deployment times and ionic competition effects; and to determine detect limit of method. The performance characteristics of the DGT devices containing SF in natural water were tested in field as well.

2. Materials and Methods

2.1. Preparation of solutions and DGT

Chemicals used in this study were of analytical reagent grade. V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} and Mo\textsuperscript{VI} stock solutions were prepared at 1000 mg L\textsuperscript{-1} using sodium orthovanadate, sodium arsenate, sodium antimonate and sodium molybdate. All oxyanion solutions were diluted from the stock solutions. To avoid possible oxidation changes, solutions were used within 1 day of preparation. All solutions used in this experiment were prepared using high purity water (18.2 M\(\Omega\) cm, Milli-Q, Millipore, USA).

A standard DGT piston device comprises a plastic base, a binding gel layer, a diffusive gel layer, a 0.14–mm–thick hydrophilic polyethersulfone membrane with 0.45 \(\mu\)m pore size, and a plastic cap with a circular 2.51 cm\(^2\) window (Zhang et al., 1998).
Preparation of slurry ferrihydrite gels. Firstly, SF was prepared by titrating 0.1 M Fe(NO$_3$)$_3$ with 1 M NaOH. To avoid an excessively high OH$^-$ concentration, which affects the binding ability of the ferrihydrite, the Fe$^{3+}$ solution was stirred vigorously to make sure the pH was <7 (Zhang et al., 1998). The dark brown-red ferrihydrite was obtained when a pH 6–7 was reached. The obtained SF was washed 3 times with high purity water and the SF was kept in the dark at 4 °C, and in water saturated conditions with a small head of overlying water. About 1.5 g of the SF, which was drained of excess water using tissue paper, was well mixed with 5 ml of the gel solution to ensure the slurry fully dispersed (Zhang et al., 1998). Afterwards, the dispersed gel solution was mixed well with 30 $\mu$L of 10% ammonium persulphate solution (daily prepared) followed by 8 $\mu$L of TEMED. Then the binding gels were cast between two pre-cleaned glass plates with a plastic spacer (0.25 mm thick) round three edges and set at 42–46 °C in an oven for 1 h. The binding gels were hydrated with the high purity water and the water changed 3–4 times during 24 h followed by storing in 0.03 M NaNO$_3$ solution for use (Warnken et al., 2004).

To prepare the diffusive gel, 10 ml of the gel solution was well mixed with 70 $\mu$L of ammonium persulphate solution (10%) followed by 25 $\mu$L of TEMED ($N,N,N',N'$-Tetramethylethylenediamine, 99%, Electron, BDH) (Stockdale et al., 2008; Luo et al., 2010). The diffusive gels were cast and hydrated as described above for the binding gels, but using 0.50 mm spacers.
2.2. DGT concentration calculation

In this study, the mass of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} or Mo\textsuperscript{VI} in the binding gel was calculated using Eq. 1 (Zhang and Davison, 1995):

\[ M = C_e \times \left( V_{gel} + V_{HNO_3} \right) / f_e \]  

(1)

Where \( C_e \) is the concentrations of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} or Mo\textsuperscript{VI} in elution samples, \( V_{gel} \) is the volume, which is 0.18 mL, of the binding gel, \( V_{HNO_3} \) is the volume of added HNO\textsubscript{3} solution, and \( f_e \) is the elution efficiency of the target element from the binding gel.

Concentration measured by DGT, \( C_{DGT} \), was calculated by Eq. 2 (Zhang and Davison, 1995):

\[ C_{DGT} = \frac{M \Delta g}{DAt} \]  

(2)

\( M \) is the mass of the target element adsorbed by the binding gel, \( \Delta g \) is the thickness of the diffusive gel, \( A \) is the area of the exposure window of the DGT device, \( D \) is the diffusion coefficient of the target element and \( t \) is the deployment time. Table S1 lists \( D \) values used in this study.

2.3. Kinetics of Binding and Elution Efficiency

In order to check the adsorption kinetics of SF gels, the gels were loaded with a known amount of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} or Mo\textsuperscript{VI} by shaking the gels in 10 mL of 100 \( \mu \)g L\textsuperscript{-1} of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} or Mo\textsuperscript{VI}, with a matrix of 10 mM NaNO\textsubscript{3}, for various times from 0.5 min to 24 h. Concentrations of these elements in the solutions before and after gel immersion were measured using ICP-MS (PerkinElmer NexION 300X, USA) to
calculate the adsorbed elements. The SF gels loaded with different amounts of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} or Mo\textsuperscript{VI} were eluted by using different concentrations (1, 3, 4 or 5 M) of nitric acid for at least 24 h. The concentrations of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} or Mo\textsuperscript{VI} in the eluents were quantified measured by ICP–MS, after diluting the samples 100 times with ultrapure water/MQ (Luo et al., 2010). Internal standard (50 μg L\textsuperscript{-1}) was mixed with the samples/standards via online standard addition just prior to measurement. The recovery of In for all samples was between 80-120%, indicating a stable analysis run and minimal impact of matrix interferences on the measurements.

2.4. Effect of Ionic Strength, pH and Deployment Time

To test the effects of ionic strength on the measurement of DGT, triplicate SF-DGT were deployed for 4 h (measured precisely) in well stirred 2 L solution (pH 5.85) containing V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} or Mo\textsuperscript{VI} (each at 50 μg L\textsuperscript{-1}) and a range of NaNO\textsubscript{3} concentration (0, 0.1, 1, 10, 100 and 500 mM) at known constant temperatures.

In order to investigate the effects of pH on the performance of DGT, triplicate SF-DGT were deployed for 4 h (measured precisely) in 2 L solution containing 10 mM NaNO\textsubscript{3} at different pHs adjusted using 1 M HNO\textsubscript{3} and 1 M NaOH prior to spiking with V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} or Mo\textsuperscript{VI} stock solutions to 50 μg L\textsuperscript{-1}. Temperatures were also measured.

To evaluate the effect of deployment times on DGT performance characteristics,
triplicate SF-DGT were immersed in 6 L solution (pH 5.83) containing 30 μg L⁻¹ of
VV, AsV, SbV or MoVI and 10 mM NaNO₃ and then retrieved in different times (from
4 to 72 h).

2.5. Competition effect with between \( \text{VV, AsV, SbV, MoVI, PO}_4^{3-} \) and \( \text{SO}_4^{2-} \)

Competition effect among these six oxyanions in solutions was studied using
solutions with different concentration ratios of these oxyanions. Triplicate SF-DGT
were deployed for 4 h (measured precisely) in well stirred solutions (2 L): (a) 10 mM
NaNO₃, one of VV, AsV, SbV or MoVI at 10 μg L⁻¹ and the other three elements at 100
μg L⁻¹; (b) 10 mM NaNO₃, VV, AsV, SbV and MoVI at 10 μg L⁻¹, PO₄³⁻ at 100 μg L⁻¹; (c)
VV, AsV, SbV and MoVI at 50 μg L⁻¹, SO₄²⁻ at 0.1, 1, 10 and 100 mM.

2.6. Field deployment of SF-DGT devices in freshwater river

To validate the applicability of the SF-DGT in natural water, DGT devices were used
to measure VV, AsV, SbV or MoVI in the Jiuxiang River, a freshwater river located
near Nanjing University, China. The basic parameters of the river water were listed in
Table S2. Temperature and pH measured in Jiuxiang River during testing SF-DGT
were shown in Fig. S1. Six DGT devices were assembled as a hexahedral unit,
leaving the exposure windows facing outwards (Pan et al., 2015; Zheng et al., 2015),
and bound with button thermometers (Maxim Integrated Products, USA) to record
temperature of water at intervals of 1 h. The hexahedral unit was immersed in the
river water and retrieved after 5 days. Water samples were collected at 10 a.m. and 5
p.m. every day to monitor the concentrations of V^{V}, \text{As}^{V}, \text{Sb}^{V} or \text{Mo}^{VI}. The water samples were taken to the laboratory within 10 min after sampling, filtered through 0.45-mm pore size membrane and stored at 4 °C for further analysis.

3. Results and discussion

3.1. DGT Blanks and Detection Limits

Blank concentrations were evaluated by determining the mass of oxyanions existing in SF gels in DGT devices which were left assembled for the same time as the deployed DGT devices. Blank concentrations of DGT devices were calculated from the measured masses of analytes on the SF gel assuming a deployment time of 24 h at 25 °C with a 0.89 mm thick diffusive layer including a 0.14 mm filter membrane. As for development of a new analysis method, method detection limits (MDL), calculated as three times the standard deviation of the blank concentrations, is necessary. Table 1 lists the calculated blank concentrations and MDL of SF-DGT (n=7). These data were lower than those reported by Luo et al. (2010), probably due to the higher quality of the chemicals used in this study, suggesting that high purity of chemicals can decrease the gel blank concentrations and MDLs considerably. Furthermore, these lower MDL and gel blank concentrations indicate that SF-DGT have a greater performance potential than previously thought.

SF-DGT deployments measured by ICP-MS analysis are sufficiently reproducible and free from contamination and analysis interferences to enable high accuracy, high
precision, and high sensitivity analysis of V^V, As^V, Sb^V or Mo^VI in natural samples.

However, matrix effects can be a problem, particularly, for determination of As by ICP-MS, since the eluent from SF gels can be highly enriched in dissolved Fe^{2+}. However, in this study, a 100 times dilution of the eluent prior to measurement, overcame any potential measurement interferences for As or other elements. The total amount of ferrihydrite per resin gel disc is about 500 mg, based on ferrihydrite being completely dissolved during elution, the maximum concentration of Fe^{2+} in the sample after dilution would be 5 mg L^{-1}, which is a loading that ICP-MS systems can accommodate, as long as isotopes of iron are not measured directly as this could impact on the detector lifetime.

3.2. Elution Efficiency and Kinetics of Binding

How to efficiently elute these oxyanions from SF gels is a prerequisite of accurate DGT measurement. Strong acids can digest and destroy the structure of the gels for complete release of elements from the binding layer. Previous studies showed that 0.25 M H_2SO_4 were used to elute SF gels for P^V and concentrated HCl (Panther et al., 2008a, b) or HNO_3 (Fitz et al., 2003; Sogn et al., 2008) for As^V and Se^VI. However, higher concentrations of acid used means greater dilutions steps are required for ICP-MS analysis, hence decreasing concentrations of target elements in samples and increasing the uncertainty of analysis, especially at lower concentrations. 1 M HNO_3 is commonly used to elute elements from several binding gels, including PF gels (Luo et al., 2010), and chelex gels (Scally et al., 2006). Here, 1 M HNO_3 was firstly chosen
to elute $V^{V}$, $As^{V}$, $Sb^{V}$ and $Mo^{VI}$ from SF gels. However, the elution efficiency of $As^{V}$ and $Mo^{VI}$ were relatively low (Table 2). Then higher concentrations (3, 4 and 5 M) of nitric acid were trialed. The findings were that, the elution efficiencies of $V^{V}$, $As^{V}$, $Sb^{V}$ or $Mo^{VI}$ are not significantly different when either 3, 4 or 5 M HNO$_3$ is used. The elution efficiencies ($f_e$) of $As^{V}$, $Sb^{V}$ or $Mo^{VI}$ were stable at ~0.9 while $V$ was slightly lower at around 0.81. In this study, 4 M HNO$_3$ was used for elution of all elements from the SF gels.

SF gels immersed into solutions containing 100 $\mu$g L$^{-1}$ of $V^{V}$, $As^{V}$, $Sb^{V}$ or $Mo^{VI}$ accumulated about 70% of the total amount of the dissolved elements in the first 10 min (Fig. 1.). The mass accumulated after 60 min was similar to that measured at 24 h. Similar time dependency trends were observed in PF gels and other binding layers (Luo et al., 2010; Zhou et al., 2016). In the first 10 min, the relationship between the accumulated mass of the element and time is almost linear. It provides direct evidence that binding of the target element to the SF gels within DGT is sufficiently fast to ensure that its concentration at the interface of the diffusive gel close to the binding gel is effectively zero (Luo et al., 2010). For instance, the measured mass of $V^{V}$ accumulated within 10 min corresponds to a flux of 32.03 ng cm$^{-2}$ min$^{-1}$, which is a far greater flux than is measured through the diffusion layer of a DGT device deployed in solution containing 1 mg L$^{-1}$ $V^{V}$ (5.41 ng cm$^{-2}$ min$^{-1}$).

3.3. Effect of Ionic Strength and pH on DGT performance
The effects of different ionic strength on uptake of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} and Mo\textsuperscript{VI} by SF-DGT are shown in Fig. 2. In the solution containing 0.1, 1, 10, and 100 mM HNO\textsubscript{3}, the ratios, $R$, of DGT measured to solution concentrations of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} or Mo\textsuperscript{VI} were in an acceptable range except for As\textsuperscript{V} at 100 mM. However, all the $R$ values were significantly lower than 1 for deployment in solutions without added NaNO\textsubscript{3} and $R$ values of As\textsuperscript{V} and Mo\textsuperscript{VI} declined substantially when the concentration of NaNO\textsubscript{3} reached 500 mM (Fig. 2). Since when diffusive gels are very well washed, they have a very small positive charge (Warnken et al., 2005), which in solutions of very low ionic strength gives rise to Donnan portioning at the gel-solution interface (Yezek and van Leeuwen, 2004; Yezek et al., 2008), and there can be a consequent lowering of the effective diffusion coefficient of oxyanion species. Because the ionic strength of seawater is approximate 700 mM, the technique is not appropriate for saline water deployments if it is used to measure As\textsuperscript{V} and Mo\textsuperscript{V}. However, since the ionic strength in fresh and most wastewaters is lower than 100 mM (Turner et al., 1981; Glass and Silverstein, 1999), SF-DGT can effectively measure these elements in these water bodies.

For pH in the range of 4.87-8.01, the ratio of SF-DGT measured concentration to solution concentration of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} or Mo\textsuperscript{VI} was within the acceptable ranges (1.0 ± 0.1). But the $R$ value of V\textsuperscript{V} at pH 3.86 is low. Even at pH of 4.87, the $R$ value of V\textsuperscript{V} is inaccurate (Fig. 3). This is likely due to different ionic forms corresponding to different pH situations. In the Supplementary data (Fig. S3), at pH lower than 5.5,
most of $V^V$ in solution exists as $VO^{2+}$ with positively charged species dominating while $V^V$ is existed as $HVO_4^{2-}$ when pH is higher than 5.5. Because the SF gel surface is positively charged below pH 5.5, the binding of positively charged species can be expected to be weak. At higher pH, the $C_{DGT}/C_{soln}$ of $As^V$, $Mo^{VI}$ and $V^V$, $Sb^V$ were greatly reduced when pH was increased to 8.97 and 9.90 respectively. The lower zero point of charge (zpc) of ferrihydrite of 8 compared to 9 for goethite is due to proton binding mainly occurring at singly coordinated surface groups (Hiemstra and Van Riemsdijk, 2009). The specific inner-sphere binding of arsenate can lower the zpc (Goldberg and Johnston, 2001). However, the change in zpc within the binding gel of DGT is likely to be slight, as the concentrations of the anion are lowered by binding and constrain diffusional supply. When the charge on the surface of SF gels becomes negative, there is likely to be much weaker adsorption of oxyanions. In conclusion, the excellent R values recorded for a wide pH range (4.87-8.01) shows a good application prospect of SF-DGT in acidic to alkaline waters.

3.4. Effect of Deployment Time on DGT performance

The measured mass of $V^V$, $As^V$, $Sb^V$ or $Mo^{VI}$ accumulated by SF-DGT increased linearly with deployment time over 72 h and agreed well with the theoretical values calculated from the known solution concentrations ($30 \mu g \ L^{-1}$ of $V^V$, $As^V$, $Sb^V$ or $Mo^{VI}$ and 10 mM $NaNO_3$) (Fig. S2). A previous study reported that the rate of mass accumulation of $As^V$ by SF-DGT decreased after 24 h, indicating a possible deterioration of sorption of the SF gels during deployment (Sogn et al., 2008).
However, there was no such effect appearing in SF-DGT investigated in this study (Fig. S2) inferred performance characteristics of SF-DGT did not change within 72 h.

3.5. Competition Effects

SF-DGT was immersed in a series of synthetic solutions with different concentrations of oxyanions to test possible competition effects between these oxyanions. Table 3 showed that R values obtained at different concentration ratios of $V^V$, $As^V$, $Sb^V$, $Mo^{VI}$ and $PO_4^{3-}$ were in an acceptable range (0.9–1.1), indicating that no significant interference from these oxyanions existed and possible competition effects between these oxyanions make no difference to SF-DGT. When $SO_4^{2-}$ were at 0-10 mM, the ratio of SF-DGT measured concentration to solution concentration of $V^V$, $As^V$, $Sb^V$ or $Mo^{VI}$ was within the acceptable ranges (1.0 ± 0.1) (Fig. 4). However, when the concentration of $SO_4^{2-}$ increased to 100 mM, the R values of $Mo^{VI}$ and $Sb^V$ were slightly lower than 0.9. As usual, in the groundwater, the concentration of $SO_4^{2-}$ was between 0.005 and 5 mM (Morales et al., 2000). The competition of $SO_4^{2-}$ is not a problem if SF-DGT is used in the groundwater.

3.6. The application of SF-DGT devices in freshwater river

Test experiments of SF-DGT under different conditions in the laboratory showed that the SF-DGT is likely to be a reliable tool for measuring $V^V$, $As^V$, $Sb^V$ and $Mo^{VI}$ in waters. To prove this proposition working in the field, concentrations of these four elements were measured using SF-DGT devices deployed in the Jiuxiang River and
compared with those determined using an active sampling method. The average concentrations of four elements in the river acquired by active sampling at 10 am and 5 pm from day 1 to 5 were $2.37 \pm 0.02$, $3.55 \pm 0.04$, $3.11 \pm 0.07$, and $0.68 \pm 0.02 \mu g L^{-1}$ for V, As, Sb and Mo, respectively, which were comparable to those found in the lagoon of Venice (the concentrations of V, As, Sb and Mo were 0.69-3.21, 1.42-2.27, 0.14-0.52, and 6.50-10.62 $\mu g L^{-1}$, respectively) (Turetta et al., 2005) and the Sacramento River in California (the concentrations of V, As, Sb and Mo are 9.1, 2.8, 0.26, and 2.6 $\mu g L^{-1}$, respectively) (Taylor et al., 2012).

The averaged DGT-measured concentrations of V$^V$, As$^V$, Sb$^V$ and Mo$^{VI}$ were close to the averaged concentrations measured by active sampling, whose R values were at 1.00, 0.99, 1.02 and 1.00, respectively. Meanwhile, as shown in Fig. 5, even though the concentrations in water fluctuated slightly with the time, the most of water concentrations (black points) were located between two dotted black lines (representing maximum and minimum DGT measured concentrations). It indicated the range of DGT-measured concentrations were consistent with the concentrations measured by active sampling method. The averaged values provided by DGT could substitute for high frequency grab sampling.

4. Conclusions

According to the adsorption kinetics of SF gel, the adsorption rates were high enough to meet the technical requirement of DGT. SF-DGT deployments measured by
ICP-MS analysis enable high accuracy, high precision, and high sensitivity analysis of $V^V$, $As^V$, $Sb^V$ and $Mo^{VI}$. For eluent, 4M HNO$_3$ was found to be optimum, with steady elution efficiency at around 90%. SF-DGT has an excellent performance in a broad pH ranges 4.87-8.01, especially at around pH 6. Furthermore, the SF-DGT detection limits are lower than concentrations of $V^V$, $As^V$, $Sb^V$ and $Mo^{VI}$ in a number of typical natural water, and in normal conditions competition between the oxyanions is not an issue. In general, all the above advantages, combined with a long sampler storage life, make this method convenient for using in a wide range of matrixes, which include rivers, wastewaters, synthetic solutions, sediments and wetland soils.

Trace element, oxyanions are a contamination risk for waters globally. (Ikem et al., 2003; Behbahaninia, 2006; Shikazono et al., 2012; Ficken and Byrne, 2013). So, convenient and easy-to-operate methods for oxyanions detection are especially needed. Meanwhile, for the research community, understanding of the fine-scale mobilization processes occurring at the mineral, soil and sediment-water interfaces are crucially important (Zhang et al., 2016). This extension in functionality of an existing and widely used method presents a new opportunity for improving the way we measure oxyanions in autochthonous and allochthonous systems to improve environmental and human health risk assessment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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Table 1
Calculated Blanks, Method Detection Limits (MDL=3σ_{blank}) and Instrumental Detection Limits for V^{V}, As^{V}, Sb^{V} and Mo^{VI} for SF-DGT.

<table>
<thead>
<tr>
<th></th>
<th>Gel blank (µg L^{-1})</th>
<th>MDL (µg L^{-1})</th>
<th>IDL (µg L^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.014 ± 0.003</td>
<td>0.009</td>
<td>0.0005</td>
</tr>
<tr>
<td>As</td>
<td>0.016 ± 0.003</td>
<td>0.009</td>
<td>0.0006</td>
</tr>
<tr>
<td>Sb</td>
<td>0.038 ± 0.012</td>
<td>0.036</td>
<td>0.0009</td>
</tr>
<tr>
<td>Mo</td>
<td>0.155 ± 0.004</td>
<td>0.012</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Table 2
Elution efficiencies of V$^V$, As$^V$, Sb$^V$ and Mo$^{VI}$ from SF gels using 1 mL of different concentrations (1, 3, 4, or 5 M) of HNO$_3$. Values were means ± standard errors of three replicates.

<table>
<thead>
<tr>
<th></th>
<th>1M HNO$_3$</th>
<th>3M HNO$_3$</th>
<th>4M HNO$_3$</th>
<th>5M HNO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.81 ± 0.01</td>
<td>0.82 ± 0.05</td>
<td>0.81 ± 0.04</td>
<td>0.80 ± 0.04</td>
</tr>
<tr>
<td>As</td>
<td>0.50 ± 0.03</td>
<td>0.89 ± 0.02</td>
<td>0.89 ± 0.02</td>
<td>0.89 ± 0.01</td>
</tr>
<tr>
<td>Sb</td>
<td>0.80 ± 0.02</td>
<td>0.91 ± 0.05</td>
<td>0.91 ± 0.04</td>
<td>0.91 ± 0.05</td>
</tr>
<tr>
<td>Mo</td>
<td>0.56 ± 0.01</td>
<td>0.87 ± 0.03</td>
<td>0.90 ± 0.03</td>
<td>0.92 ± 0.02</td>
</tr>
</tbody>
</table>
Table 3. $C_{\text{DGT}}/C_{\text{sohn}}$ of V$^V$, As$^V$, Sb$^V$ and Mo$^{VI}$ measured by SF-DGT deployed in solutions containing 10 mM NaNO$_3$, one of V$^V$, As$^V$, Sb$^V$ or Mo$^{VI}$ at 10 $\mu$g L$^{-1}$ and the other three elements at 100 $\mu$g L$^{-1}$ or V$^V$, As$^V$, Sb$^V$ or Mo$^{VI}$ at 10 $\mu$g L$^{-1}$ and PO$_4^{3-}$ at 100 $\mu$g L$^{-1}$.

<table>
<thead>
<tr>
<th>Solution</th>
<th>V</th>
<th>As</th>
<th>Mo</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.90 $\pm$ 0.01</td>
<td>1.04 $\pm$ 0.02</td>
<td>1.01 $\pm$ 0.03</td>
<td>1.00 $\pm$ 0.02</td>
</tr>
<tr>
<td>2</td>
<td>0.95 $\pm$ 0.04</td>
<td>0.95 $\pm$ 0.02</td>
<td>0.99 $\pm$ 0.05</td>
<td>1.02 $\pm$ 0.05</td>
</tr>
<tr>
<td>3</td>
<td>0.99 $\pm$ 0.08</td>
<td>0.93 $\pm$ 0.08</td>
<td>0.92 $\pm$ 0.01</td>
<td>1.03 $\pm$ 0.09</td>
</tr>
<tr>
<td>4</td>
<td>1.04 $\pm$ 0.02</td>
<td>0.92 $\pm$ 0.06</td>
<td>0.97 $\pm$ 0.06</td>
<td>0.95 $\pm$ 0.01</td>
</tr>
<tr>
<td>5</td>
<td>0.96 $\pm$ 0.07</td>
<td>0.96 $\pm$ 0.02</td>
<td>0.98 $\pm$ 0.03</td>
<td>1.05 $\pm$ 0.08</td>
</tr>
</tbody>
</table>

1: V$^V$ 10 $\mu$g L$^{-1}$, others 100 $\mu$g L$^{-1}$; 2: As$^V$ 10 $\mu$g L$^{-1}$, others 100 $\mu$g L$^{-1}$; 3: Mo$^{VI}$ 10 $\mu$g L$^{-1}$, others 100 $\mu$g L$^{-1}$; 4: Sb$^V$ 10 $\mu$g L$^{-1}$, others 100 $\mu$g L$^{-1}$; 5: V$^V$, As$^V$, Sb$^V$ or Mo$^{VI}$ 10 $\mu$g L$^{-1}$, PO$_4^{3-}$ 100 $\mu$g L$^{-1}$.
**Fig. 1.** Mass of V\(^{V}\), As\(^{V}\), Sb\(^{V}\) or Mo\(^{VI}\) accumulated by SF gels immersed in solutions containing 100 \(\mu\)g L\(^{-1}\) V\(^{V}\), As\(^{V}\), Sb\(^{V}\) and Mo\(^{VI}\) for different immersion times. Error bars are calculated from the standard deviation of replicates (n=3).
Fig. 2. Effect of concentrations of supporting electrolyte, NaNO₃, on the ratio of concentrations measured by SF-DGT, $C_{DGT}$, to deployment solution concentrations of $V^V$, $As^V$, $Sb^V$ and $Mo^{VI}$, $C_{soln}$. These measurements were performed in the pH of 5.85. Error bars represent the standard deviation of three replicates. The solid horizontal line and dotted horizontal lines represent target values of 1.0±0.1.
Fig. 3. Effect of pH on the ratio of concentrations of V\textsuperscript{V}, As\textsuperscript{V}, Sb\textsuperscript{V} and Mo\textsuperscript{VI} measured by SF-DGT, $C_{DGT}$, to deployment solution concentrations, $C_{soln}$. These measurements were performed in the presence of 10 mM NaNO\textsubscript{3}. Error bars represent the standard deviation of three replicates. The dotted horizontal lines represent target values of 1.0±0.1.
Fig. 4. Effect of competition with SO$_4^{2-}$ (0.1, 1,10 and 100 mM) on the ratio of concentrations of V$^V$, As$^V$, Sb$^V$ and Mo$^{VI}$ measured by SF-DGT, $C_{DGT}$, to deployment solution concentrations, $C_{soln}$. These measurements were performed in the presence of 10 mM NaNO$_3$. Error bars represent the standard deviation of three replicates. The dotted horizontal lines represent target values of 1.0±0.1.
Fig. 5. Measurement of $V^V$, $As^V$, $Sb^V$ and $Mo^{VI}$ concentrations by two methods at different sampling times in Jiuxiang River. The black points represent the concentrations measured by active sampling method. The solid red line represents the average concentration of $V^V$, $As^V$, $Sb^V$ and $Mo^{VI}$ from active sampling method during the five days. The solid black line means the average concentration of $V^V$, $As^V$, $Sb^V$ and $Mo^{VI}$ measured by SF-DGT and the upper and lower dotted black lines mean the maximum and minimum DGT measured concentrations.