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Environmental impact:

Phosphorus (P) is an essential macro-nutrient mainly related to water eutrophication and algal bloom, while arsenic (As) is a highly toxic trace element. Their biogeochemical cycling in the environment is considered to be closely related to the cycling of Fe. Development of a diffusive gradients in thin films (DGT) technique capable of *in situ* and simultaneous measurements of the three elements would greatly facilitate the understanding of their coupled cycling in the environment. This study developed a ZrO-Chelex DGT technique to meet this purpose. The use of this technique will significantly improve the efficiency in *in situ* monitoring of Fe, P and As in the environment. It will be a robust tool in exploring the interactions of the three elements in the biogeochemical processes.

Title: Evaluation of the diffusive gradients in thin films technique using a mixed binding gel for measuring iron, phosphorus and arsenic in the environment

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Abstract:

Simultaneous measurements of dissolved iron (Fe), phosphorus (P), and arsenic (As) were evaluated using the diffusive gradients in thin films technique equipped with a mixed binding gel impregnated with zirconium oxide and Chelex-100 (ZrO-Chelex DGT). The ZrO-Chelex binding gel exhibited rapid binding dynamics to Fe(II), P(PO_4^{3-}), and As(III)/As(V) in mixed solutions of the three elements. The bound Fe, P, and As could be quantitatively recovered using an established four-step elution procedure. Simultaneous measurements of the three elements with ZrO-Chelx DGT were validated through time-series experiments, and there was no influence of pH (4.1 to 7.1) and ionic strength (0.01 to 800 mM). The DGT capacities for As(III) and As(V) were 69.0 μg and 186 μg per device, which were much greater than those of widely-used ferrihydrite DGT. Applications in synthesized freshwaters and in sediments further confirmed its feasibility in simultaneous measurements in the environment. The present study offered that the ZrO-Chelex DGT will be a useful tool in *in situ* monitoring of Fe-P-As and assessment of their interactions in the biogeochemical processes.

Keywords: Diffusive gradients in thin films (DGT); ZrO-Chelex; Zr-oxide; passive sampling; monitoring; high resolution.

1 Introduction

There has been widespread recognition of passive sampling devices as effective tools in environmental sampling. These devices have a number of advantages over conventional spot sampling such as simplifying the operation process at the sampling site, minimizing chemical interference, and overcoming speciation changes over time.[1] Various passive sampling techniques have been developed for monitoring organic and inorganic pollutants.[2] Of these, the technique of diffusive gradients in thin film (DGT) is extensively applicable in quantitatively measuring a wide range of labile inorganic cations and anions in waters, sediments, and soils.[3,4] The DGT technique can provide the time-averaged concentration of solutes at a given deployment time based on Fick's First Law of diffusion.[5] The DGT device is mainly comprised of a diffusion-gel layer and an adsorbent-impregnated binding gel layer in which the selection of an adsorbent depends on analytical target elements. Chelex-100 has been typically used to measure labile metal species with DGT.[6] Ferrihydrite (slurry or precipitated), zirconium oxide (Zr-oxide or ZrO) and Metsorb (TiO_2) were used for measurements of oxyanions (P, As, Se etc.),[7-12] and AgI and 3-Mercaptopropyl-functionalized silica gel were used for measurements of sulfide, mercury, and As(III), respectively.[13-15]

More recently, various mixed binding gels incorporated with two different adsorbents have been developed for simultaneous measurements of multi-elements in a single DGT sampler taking the potential coexistence and reciprocal influences of elements in the complex environmental media into consideration.

For example, a mixed binding gel impregnated with ferrihydrite and Chelex-100 has been developed for measurements of As, Cd, Cu, Zn, Pb, and Mo,[16,17] zirconium hydroxide and iminodiacetate for P, As, Co, Cu, Mn, and Zn,[18] and Chelex-100 and Metsorb for trace metals and oxyanions (V, As, Mo, Sb, W, and P, etc).[19] Moreover, the combination of Zr-oxide and Chelex-100 (ZrO-Chelex) has been developed with DGT for simultaneous measurements of P and Fe(II), and Zr-oxide and AgI for P and S(II).[20,21] The Zr-oxide based DGT samplers offers significant improvements over the widely-used ferrihydrite DGT and newly developed Metsorb DGT, as reflected by greater DGT capacities, stronger tolerance to competitive ions, and longer shelf life time.[9,10,22] Furthermore, the Zr-oxide based gel has a harder rather than soft (such as the ferrihydrite and Metsorb gels), white, and opaque surface, which can be easily sliced in laboratory. As a result, they have notable advantages in high-resolution measurements of P, Fe(II) and S(II) in combination with a routine operation procedure including slicing, elution, and microcolorimetric determination, and a computer-imaging densitometry (CID) technique.[9,20] These good performances imply that the mixed binding gels impregnated with Zr-oxide enable a potentially wider application of DGT in more complex environments or over a longer monitoring time.

Phosphorus (P) is an essential macro-nutrient which is often a determining factor in control of water eutrophication and algal bloom.[23] Arsenic (As) is a highly toxic trace element to organisms, which belong to the same chemical group of P.[24] They tend to occur together in the environment because of their similar physical and chemical properties. Furthermore, substantial labile fractions of inorganic P and As were found to be associated with Fe(III) oxide/oxyhydroxides in soils and sediments due to that this binding phase has great abundance, large specific surface area, and strong binding affinity for inorganic P and As ions.[25,26]Accordingly, the biogeochemical cycling of P and As is considered to be closely related to the redox cycling of Fe.[27-29] Development of a mixed binding gel-equipped DGT sampler capable of *in situ* and simultaneous measurements of the three elements at the same sampling site would greatly facilitate the understanding of their coupled cycling in the environment. Until now, the DGT technique in a sampling device for simultaneous measurements of these three elements is limited .[19] A combination of DGT with another gel technique, diffusive equilibration in thin films (DET), has been developed for simultaneous measurements of As and pore water Fe(II) in sediments. [30,31]

In the present study, we developed the ZrO-Chelex DGT for simultaneous measurements of dissolved Fe(II), dissolved reactive P (DRP, also named as dissolved molybdenum-reactive phosphorous), and dissolved As. A series of solution experiments were conducted to evaluate the performance characteristics of this DGT technique. It was then applied in synthesized freshwaters and sediments in comparison with Zr-oxide and Chelex DGTs, which have been well developed for single measurement of P, As, or Fe(II).[6,7,9,10]

2 Materials and Methods

2.1 Reagents and Solutions

The chemicals used in this study were of analytical reagent grade or greater and were supplied by SCR Co. Ltd. Stock solution (1000 mg L^{-1}) of DRP was prepared by dissolving KH_2PO_4 with anaerobic water, which was produced by heating Milli-Q water at 100°C for 10 min to remove oxygen. Separate stock solutions (1000 mg L^{-1}) of As(III) and As(V) were prepared by dissolving $NaAsO_2$ and $Na_3AsO_4 \cdot 12H_2O$ with anaerobic water, respectively. Mother solution (1000 mg L^{-1}) of dissolved Fe(II) was freshly prepared by dissolving $(NH_4)_2SO_4 \cdot FeSO_4$ with anaerobic water in order to avoid the oxidation and precipitation of Fe(II). Certified reference materials, GBW08666 and GBW08667 (National Institute of Metrology, China), were used for quality control and methodological validation for As(III) and As(V), respectively.

2.2 Gel Preparation, DGT device and Calculation

The DGT device mainly consists of the diffusive gel and binding gel layers. The DGT holder included piston and flat types used for deployments in solutions and sediments, respectively (DGT Research Limited). The diffusive gel was prepared using 15% acrylamide and 0.3% agarose-derived cross-linker following a published procedure.[6] The Chelex and Zr-oxide binding gels were prepared according to Zhang and Davison[6] and Ding et al.,[9] respectively. The ZrO-Chelex mixed binding gel was prepared by mixing 1.0 g half-dried Zr-oxide powder and 1.0 g Chelex-100 in 5 mL of gel solution containing 28.5% acrylamide (w/v) and 1.5% N, Ń-methylene bisacrylamide (w/v).[21]

All DGT holders were acid-cleaned in 10% (v/v) HNO_3 for at least 24 h, and subsequently rinsed with Milli-Q water. In the DGT assembly, a binding gel (with the binding agent's settled surface facing out) was overlain by a diffusion gel and then a filter membrane (0.13 mm thickness, Whatman, 0.45 μm pore size). The thickness of the diffusive gel in the piston-type DGT device was 0.80 mm. Only a filter membrane was used as the diffusion layer in the sediment probes in order to increase the accumulation masses of the analytes in the binding gels. All assembled DGT devices were deoxygenated with nitrogen for at least 16 h prior to use.

The DGT-measured concentration of each solute in solutions was calculated based on the well-established DGT equation.[6] The reported diffusion coefficients (D, $\times 10^{-6}$ cm^2 s^{-1}) of P, Fe(II), As(III) and As(V) at 25°C were 6.05, 6.11, 10.36 and 7.02, respectively, which were corrected to achieve their values at different temperature using the Stokes-Einstein equation.[7,10] The average diffusion coefficient of As(III) and As(V) was used to calculate the DGT-measured concentrations of total dissolved As in freshwaters and sediments.[10]

2.3 Element analysis

Concentrations of DRP and dissolved Fe(II) in solution samples were detected using the traditional molybdenum blue and phenanthroline colorimetric methods, respectively[32,33], while in eluents they were measured with a miniaturized spectrophotometry method using an Epoch Microplate Spectrophotometer (Bio Tek, Winooski, VT) according to the well-established procedures in our laboratory.[29] Arsenic analysis in solution samples and eluents were performed by an online, intermittent flow and hydride generation coupled with AFS (HG-AFS) (AF-610D, Beijing Rayleigh Analytical Instrument Corporation, China) after appropriate dilution.[10]

2.4 Performance of mixed binding gel

2.4.1 Binding kinetics

The dynamics of Fe, P, and As bindings to the ZrO-Chelex gel were tested by exposing gel discs (2.5-cm diameter) to 10 mL of mixed solutions containing 1.7 mg L^{-1} Fe(II), 0.7 mg L^{-1} DRP, and As(III) or As(V) at approximately 45 µg L^{-1}, with the ionic strength at 0.01 M $NaNO_3$ and pH at 4.5. The solutions were immediately shaken at room temperature for various time intervals ranging from 2.5 to 120 min. Respective concentrations of the three analytes in solutions before and after immersion of the gels were measured to calculate the absorbed mass of them on the gel over time.

2.4.2 Elution efficiencies

ZrO-Chelex gel discs were placed in 10 mL of mixed solutions containing Fe(II), DRP, and As(III) or As(V) with their respective concentrations ranging from 0.1 to 4 mg L^{-1} at 0.01 M $NaNO_3$ and pH 4.5. The solutions were shaken for 24 h. Afterwards, the gels were retrieved and eluted using a three-step or four-step elution procedure based on published methods (Fig. 1).[10,21] In the three-step elution procedure, the gel was first exposed to 10 mL of 1.0 M HNO_3 and shaken for 24 h to elute Fe. The gel was rinsed using 10 mL of deionized water for 2 h to remove residual acid from the gel surface, and then exposed to 1.8 mL of 1.0 M NaOH for shaking 24 h to elute P/As(III)/As(V). In the four-step elution procedure, the first three steps were the same as those of the three-step procedure. The gel was then exposed to 1.8 mL of mixed solution composed of 1.0 M NaOH and 1.0 M H_2O_2 (1.0 M NaOH-1.0 M H_2O_2) for shaking 24 h to further elute As(III)/As(V). Then, the eluents of 1.0 M NaOH and 1.0 M NaOH-1.0 M H_2O_2 were mixed together with the same volume for analysis of As(III)/As(V).

2.5 Performance Test of the ZrO-Chelex DGT

2.5.1 Time dependence of DGT uptake

The time dependence of DGT uptake was investigated by deploying DGT units in 10 L of 0.01 M $NaNO_3$ solution containing 0.83 mg L^{-1} Fe(II), 0.61 mg L^{-1} DRP, and 50 µg L^{-1} As(III) or As(V) at pH 4.5 for time intervals ranging from 4 to 24 h. The temperature in the solutions was stabilized at 22 °C. In order to prevent Fe(II) oxidation and precipitation, the mixed solutions were cautiously prepared by first deoxygenating in a well-sealed container with high-purity nitrogen for 16 h, followed by additions of the corresponding mother solutions of Fe(II), DRP and As(III)/As(V). The pH values of solutions were adjusted with dilute HNO_3 and NaOH to 4.5 and stabilized overnight with high-purity nitrogen prior to DGT deployment. The solutions were well mixed using a magnetic stirrer during the experiment. At each retrieval time, three duplicate DGT devices were removed and rinsed with deionized water. The Fe(II), DRP, and As(III)/As(V) accumulated in the binding gel were eluted using the four-step elution procedure as mentioned earlier.

2.5.2 The effects of pH and ionic strength

The effects of pH on uptakes of the three elements by ZrO-Chelex DGT were examined under a pH range of 4.0 to 7.0. Higher pH will cause oxygenation and precipitation of dissolved Fe(II) in the solutions.[21] The DGT units were deployed for 12 h in 2 L of 0.01 M $NaNO_3$ solutions containing approximately 0.50 mg L^{-1} Fe(II), 1.0 mg L^{-1} DRP, and 50 µg L^{-1} As(III) or As(V). The final pH of the solutions was adjusted to different values (4.06-7.11). The effects of ionic strength on DGT uptakes of the three elements were examined by deploying ZrO-Chelex DGT units for 12 h in 2 L of a series of solutions with different $NaNO_3$ concentrations ranging from 0.01 to 800 mM. The solutions contained approximately 0.8 mg L^{-1} Fe(II), 1.0 mg L^{-1} DRP, and 50 µg L^{-1} As(III) or As(V) at pH 4.5. In two sets of experiments, the solution temperature was stabilized at 23 ^{o}C.

2.5.3 DGT capacities for As(III) and As(V)

The ZrO-Chelex DGT capacities for measurements of P and Fe have been measured previously.[21] In this study, the DGT capacities for As(III) and As(V) were determined by deploying the DGT units in 0.01 M $NaNO_3$ solutions at pH 6.3 containing different concentrations of As(III) (0.5-20 mg L^{-1}) for 11 h or As(V) (5-100 mg L^{-1}) for 8 h. Solution temperature was stabilized at 24 ^{o}C.

2.6 ZrO-Chelex DGT deployment in synthesized waters

The freshwaters were synthesized in a laboratory according to the methods by Langmuir, [34] whose compositions were 0.38 mmol L^{-1} Ca^{2+}, 0.058 mmol L^{-1} K^+, 0.29 mmol L^{-1} Mg^{2+}, 0.46 mmol L^{-1} Na^+, 0.23 mmol L^{-1} Cl^-, 0.12 mmol L^{-1} SO_4^{2-}, 1.12 mmol L^{-1} NO_3^- , 0.98 mmol L^{-1} HCO_3^- and pH 7.2. The freshwater samples were spiked with 1.47 mg L^{-1} Fe(II), 0.63 mg L^{-1} DRP, and 100 µg L^{-1} inorganic As with the same amount of As(III) and As(V) (i.e. the 1:1 ratio of As(III) to As(V)). The ZrO-Chelex DGT units were deployed at 26°C for different times ranging from 4 to 24 h, respectively. Single Zr-oxide and Chelex DGTs were simultaneously deployed for comparison.

2.7 ZrO-Chelex DGT deployment in microcosm

A microcosm with homogeneous sediment was created in a laboratory to further test the replicability of ZrO-Chelex DGT for simultaneous measurements of Fe, P, and As. Single Zr-oxide and Chelex DGTs were used for comparison, respectively. Sediments (~10 cm) and overlaying waters were collected on March 28, 2014, from Taihu Lake, which is one of the largest freshwater lakes in China. The sediments were thoroughly mixed into a uniform sludge, and placed in a plastic tank to a depth of approximately 20 cm. The overlaying water was gently poured into the surface of the homogeneous sediments to reach a depth of approximately 15 cm. The established microcosm was kept in a bath incubator at room temperature for two months prior to DGT deployment.

Two ZrO-Chelex DGT probes were fixed back to back with a Zr-oxide and Chelex DGT probe, respectively. The combined DGT samplers were deoxygenated overnight with high-purity nitrogen and then inserted into the microcosm for 24 h. After retrieval of the samplers, the binding gels were sliced at 2.0-mm resolution. Each slice of ZrO-Chelex gel was eluted using the four-step elution procedure, with 400 μL of each eluent (Fig. 1). Also, each slice of the Zr-oxide and Chelex gels was eluted using 400 μL of 1.0 M NaOH and 1.0 M HNO_3, respectively. [6, 9]

2.8 Statistical analyses

The DGT-measured concentrations of the three elements between ZrO-Chelex DGT and single Zr-oxide DGT/Chelex DGT in freshwaters and sediments were compared using independent-samples *T* test with SPSS 10.0 statistical package for Windows.

3 Results and Discussion

3.1 Binding kinetics

It is required that the binding gel used in DGT measurement must rapidly take up target analytes and maintain the concentrations with zero at its surface over the deployment period.[3] The binding kinetics of Fe(II), DRP and As to the ZrO-Chelex gel was examined in mixed solutions containing 1.7 mg L^{-1} Fe(II), 0.7 mg L^{-1} DRP, and 45 μg L^{-1} As(III) or As(V). As shown in Fig. 2, the uptakes of the three elements by ZrO-Chelex gels approximately increased linearly within the first 10 min, followed by slow increases up to 60 min. After that, most of them (>95%) were taken up by the gels. The result demonstrates that the binding dynamics of Fe(II), DRP, and As to the ZrO-Chelex gel are high enough to satisfy the requirement in DGT measurement.

3.2 Elution efficiencies

Previous studies have demonstrated that 1.0 M HNO_3 and 1.0 M NaOH were effective in eluting Fe and P/As from the Chelex and Zr-oxide gel, respectively.[6,9,10] In this study, a three-step elution procedure based on the uses of the two agents was initially set up to elute the accumulated Fe(II), DRP, and As(III)/As(V) in the ZrO-Chelex mixed gel (Fig. 1). The results showed a stable efficiency rate of 89 ± 3.3 % for Fe(II) and 95 ± 2.5 % for DRP in the presence of As(III) (Fig. 3a). The efficiency rate of As(III) was maintained at 86 ± 1.8 % when the accumulation mass of As(III) was lower than 2 μg, while it began to decrease after that. The lowest efficiency rate was only 29% at the greatest accumulation mass of As(III) (40 μg). A further examination showed that the coexistence of DRP rather than Fe(II) caused this phenomenon, but the mechanism remained unclear. In contrast, the elution efficiency of As(V) remained stable at 85 ± 1.7% with the increase of its accumulation mass (Fig. 3b). The elution efficiencies of Fe(II) and P in the presence of As(V) were similar to those in the presence of As(III) (Fig. 3b). Average efficiency rates of 89% and 95% could be used in DGT calculation for Fe(II) and DRP, which agreed well with published elution values of Fe(II) and DRP in the absence of As(III)/As(V).[21]

In order to overcome the problem in elution of As(III), a further elution (Step 4 in Fig. 1) using a mixed solution of 1.0 M NaOH-1.0 M H_2O_2 was performed following the above elution steps, and this extract was used for analysis of As(III) and As(V) after combination with the NaOH eluent (Step 3). This elution produced stable elution efficiencies of 85 ± 0.9 % for As(III) and 85 ± 2.2 % for As(V) with the increase of their accumulation masses in the gels (Fig. 3). The addition of H_2O_2 may oxygenate As(III) to As(V) in this gel and thus promote the elution efficiency of As(III). As a result, the rate of 85% could be used in DGT calculation for both As(III) and As(V) or total inorganic As. This value was slightly lower than 88% in elution of As(III)/As(V) or total inorganic As from the Zr-oxide gel.[10] Because the concentration of DRP in the NaOH-H_2O_2 eluent could not be measured using spectrophotometric method due to the interference of H_2O_2,[35] it was necessary to employ the four-step elution procedure for simultaneous measurements of Fe(II), DRP, and As.

3.3 Test of ZrO-Chelex DGT performance

Validation of DGT performance was performed through examining time-series uptakes of three elements by ZrO-Chelex DGT in mixed solutions containing Fe(II), DRP, and As(III) or As(V). As presented in Fig. 4, accumulation masses of both Fe(II) and DRP in the presence of As(III) or As(V) increased linearly with the deployment period. The ratios of measured masses to those theoretically predicated using the DGT equation were 0.98 ± 0.03 and 0.99 ± 0.02 in the presence of As(III) and 0.97 ± 0.02, and 0.97 ± 0.03 in the presence of As(V), respectively. The ratios were well within the acceptable limit of 1.00 ± 0.10 for DGT experiments.[6] The DGT uptake of As(III) or As (V) was also in accordance to the theoretical predication, in which the measured-to-predicted ratios were 1.07 ± 0.01 or 1.06 ± 0.03. Therefore, these results confirmed the suitability of ZrO-Chelex DGT for simultaneous measurements of Fe(II), DRP, and As(III) or As (V) in solutions.

The effects of pH and ionic strength on ZrO-Chelex DGT for simultaneous measurements of three elements were examined by deploying DGT in mixed solutions containing Fe(II), DRP, and As(III) or As(V) at different pH (4.1-7.1) or ionic strength (0.01-800 mM). As depicted in Fig. 5, their concentrations measured by DGT corresponded well with those in solutions, with all measured-to-predicted ratios within 1.00 ± 0.10. These results demonstrate that the DGT uptakes of three elements were independent of solution pH and ionic strength. Earlier studies have shown that the Zr-oxide DGT for single measurements of DRP and As(III)/As(V) worked well under a wide pH range (2.0 -10) and ionic strength (0.01 -750 mM), [9,10] while measurements with Chelex DGT were unaffected at pH 5-8.3 and ionic strength 0.01-1 M.[6] Accordingly, the ZrO-Chelex DGT can be applied in typical environments.

3.4 ZrO-Chelex DGT capacities for As

Previous studies have reported that the capacity of ZrO-Chelex DGT for Fe(II) was greater than that observed with single Chelex DGT commonly used for measurements of metals, and its value for DRP was only slightly lower than that with single Zr-oxide DGT.[21] In this study, the capacities of this DGT in measurements of As(III) and As(V) were further measured by deploying the DGT units in 0.01 M $NaNO_3$ solutions containing different concentrations of As(III) or As(V). A linear and theoretically predictable response was obtained with As(III) and As(V) concentrations up to 5 mg L^{-1} and 30 mg L^{-1}, respectively (Fig. 6). Their capacities were determined at 69.0 μg and 186 μg per DGT device. Although both values were 43% of those measured by the single Zr-oxide DGT, they were still much higher than those of the ferrihydrite DGT (22.5 to 34.5 μg for As(III) and 15 to 87 μg for As(V)) and Metsorb DGT (8.5 μg for As(III) and 82 μg for As(V) respectively).[10] It means that ZrO-Chelex DGT could be applied either in the environment containing higher concentrations of inorganic As or with a longer monitoring time.

3.5 ZrO-Chelex DGT deployment in waters

The performance of ZrO-Chelex DGT was originally tested in synthesized freshwaters. Chelex and Zr-oxide DGTs were used for comparison, since they have been well established for single measurements of Fe and P/As.[6,7,9,10] As the synthesized freshwaters simultaneously contained As(III) and As(V), total inorganic As was measured in combination with the use of the four-step elution procedure (Fig. 1). The results showed consistent accumulation masses of three elements measured between different DGTs over deployment time (Fig. 7). Moreover, all DGT-measured accumulation masses corresponded well to those theoretically predicted from the actual concentrations of three elements in waters (Fig. 7), there was no significant (P>0.05) difference between them. It verified the feasibility of ZrO-Chelex DGT in simultaneous measurements of Fe(II), DRP, and dissolved As in waters.

3.6 ZrO-Chelex DGT deployment in sediments

Deployment of ZrO-Chelex DGT in microcosm was performed to further test whether this DGT could be used well in simultaneous measurements of Fe(II), DRP, and dissolved As in sediments. The depth-concentration profiles of DRP, Fe(II), and inorganic As measured by three different DGTs are shown in Fig. 8. Concentrations of DRP shared the same shape between ZrO-Chelex and Zr-oxide DGTs, reflected by a slight increase from the overlying water to a depth of -20 mm (the minus represents the position below the sediment-water interface), a sharp increase to a depth of -50 mm, and a stable stage to the bottom. The profile of dissolved inorganic As by ZrO-Chelex DGT also corresponded well with that by single Zr-oxide DGT, reflected by a sharp increase from the sediment-water interface to a depth of -30 mm, followed by a stable or slightly increasing stage to the bottom. A change in concentration of Fe(II) similar to DRP appeared above the depth of -50 mm, followed by a slight increase from -50 mm to the bottom, while ZrO-Chelex and Chelex DGTs agreed well in measurements. Totally, simultaneous measurements of Fe(II), DRP, and dissolved As by ZrO-Chelex DGT had good agreements with those by other two DGTs. Statistical analysis also showed that no significant (P>0.05) difference was observed between them. These findings confirmed the feasibility of ZrO-Chelex DGT in simultaneous measurements of the three elements in sediments.

4 Conclusions

Evaluation of ZrO-Chelex DGT has shown that it had good performance in simultaneous measurements of Fe(II), DRP, and dissolved As, reflected by a rapid dynamic of the binding gel in simultaneously taking up the three targets, a theoretically-predicted uptake with DGT irrespective of pH (4.1-7.1) and ionic strengthen (0.01-800 mM), and a greater DGT capacity in measurements of the three elements compared to other DGTs. Application of ZrO-Chelex DGT in synthesized freshwater and sediments, compared to other developed DGTs, further confirmed its feasibility in simultaneous measurements. Accordingly, the efficiency in *in situ* monitoring of Fe(II), DRP, and dissolved As will be significantly improved by using this technique. It will also be a robust tool in exploring the interactions among the three elements in the biogeochemical processes.

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Figure captions

Figure 1 Elution procedure for target elements.

Figure 2 Binding kinetics of ZrO-Chelex gel to Fe(II), DRP, and As(III)/As(V) in mixed solutions of Fe(II), DRP, and As(III) (a) or Fe(II), DRP, and As(V) (b). Values are means ± SD of three replicates.

Figure 3 Elution efficiencies of Fe(II), DRP, and As(III)/As(V) bound to the ZrO-Chelex gel immersed in mixed solutions of Fe(II), DRP, and As(III) (a) or Fe(II), DRP, and As(V) (b) using a three-step or four-step elution procedure. Values are means ± SD of three replicates.

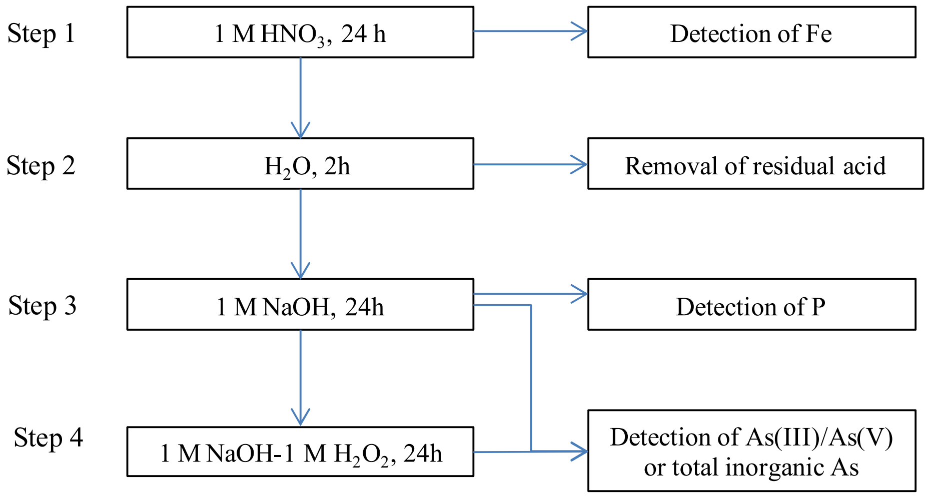
Figure 4 ZrO-Chelex DGT response to Fe(II), DRP, and As(III)/As(V) over deployment time in mixed solutions of Fe(II), DRP, and As(III) (a) or Fe(II), DRP, and As(V) (b). The line in the figure is the theoretical response calculated using the DGT equation. Values are means ± SD of three replicates.

Figure 5 Effects of pH (a and b) and ionic strength ($NaNO_3$) (c and d) on ZrO-Chelex DGT response to Fe(II), DRP, and As(III)/As(V) in mixed solutions of Fe(II), DRP, and As(III) or Fe(II), DRP, and As(V). The *y*-axis in the figure represents the ratio of DGT-measured concentration of target element (C_{DGT}) to their concentration in well-stirred solutions (C_{sol}). The two dashed lines show within the accepted values of 1.0 ± 0.1 for DGT.

Figure 6 Uptakes of As(III) and As(V) by ZrO-Chelex DGT over As concentrations. The straight lines show the theoretical prediction calculated using the DGT equation. Values are means ± SD of three replicates.

Figure 7 Accumulated masses of Fe(II), DRP, and dissolved As measured by ZrO-Chelex DGT as compared with those obtained with single Zr-oxide DGT/Chelex DGT in synthetic freshwaters spiked with 1.47 mg L^{-1} Fe(II), 0.63 mg L^{-1} DRP, and 100 µg L^{-1} dissolved As with the same amount of As(III) and As(V)(i.e. the 1:1 ratio of As(III) to As(V)). The straight lines show the theoretical prediction calculated using the DGT equation. Values are means ± SD of three replicates.

Figure 8 The vertical concentration-based distributions of Fe(II), DRP, and dissolved As measured by ZrO-Chelex DGT in a homogenized sediment profile. Zr-oxide and Chelex DGTs were used for comparison in single determination of P/As and Fe. The dotted line in the figure indicates the sediment-water interface with zero.



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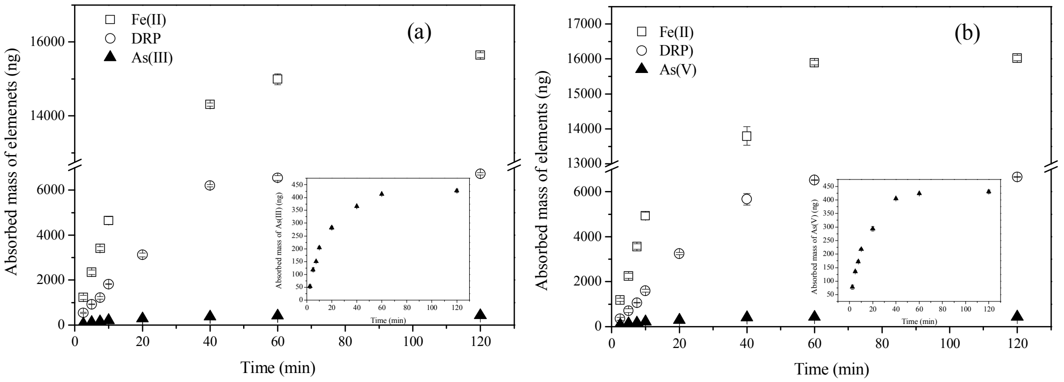

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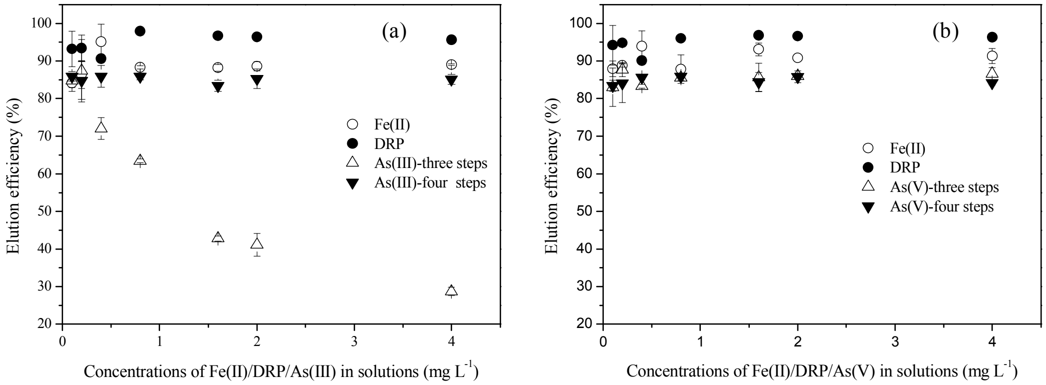

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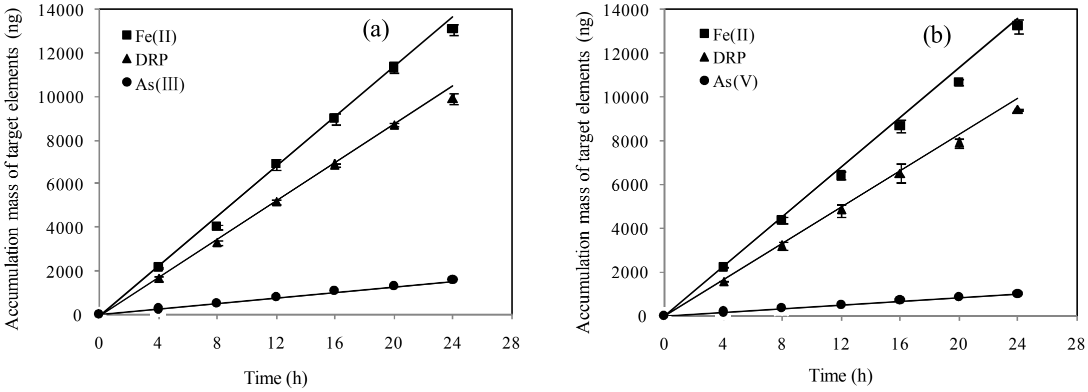

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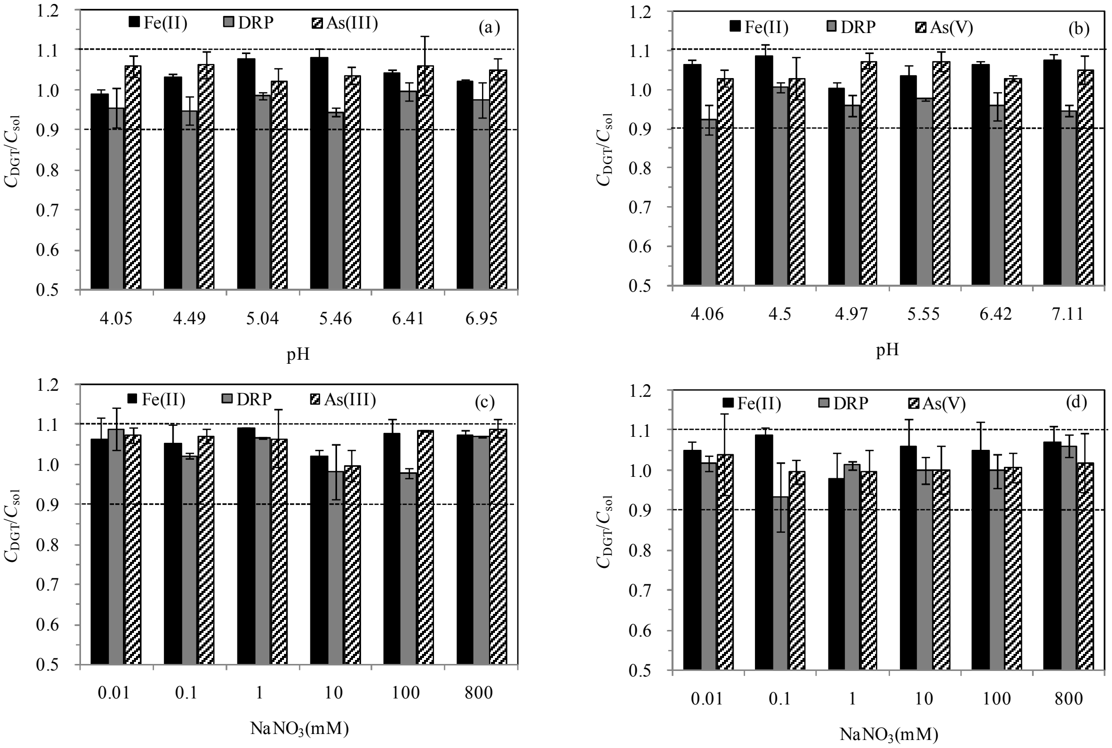

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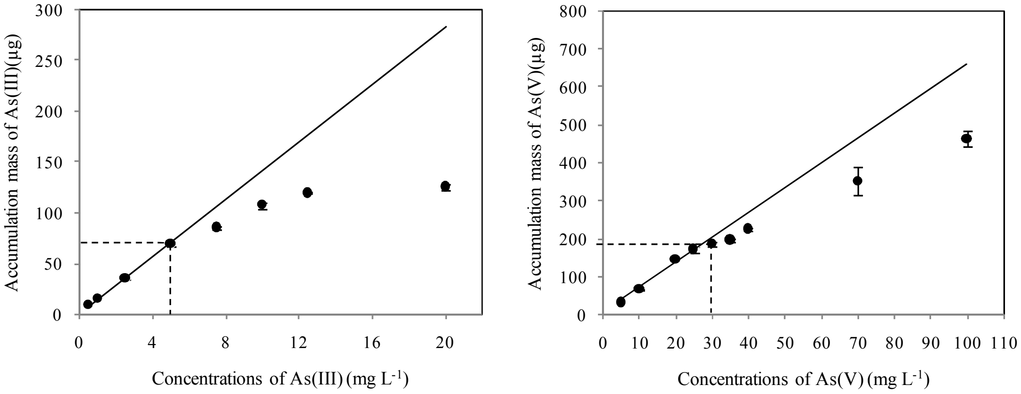

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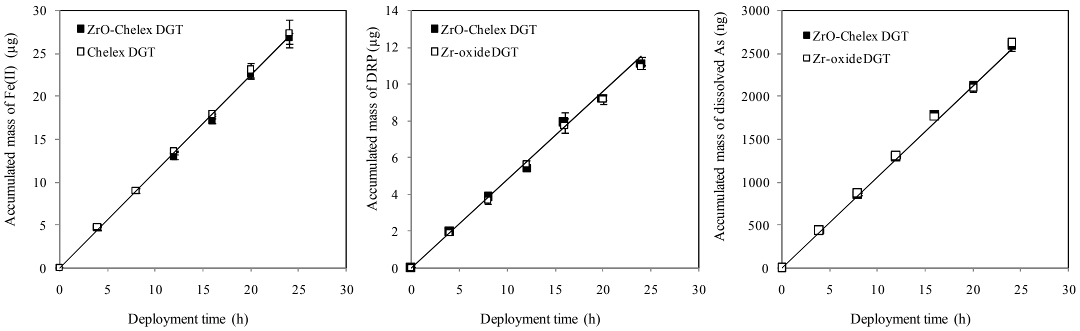

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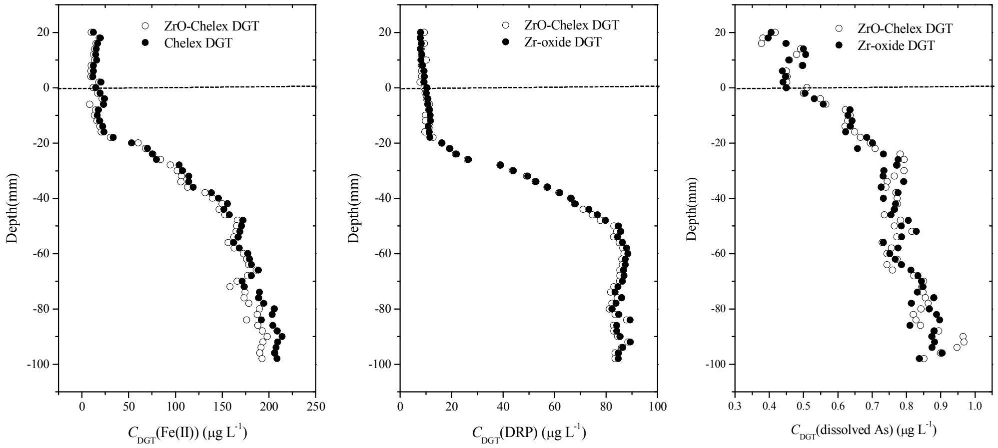

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