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Diffusive Gradients in Thin Films Technique Equipped with a Mixed Binding Gel for Simultaneous Measurements of Dissolved Reactive Phosphorus and Dissolved Iron

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ⓢ *Supporting Information*

ABSTRACT: Developing a technique to track the release of phosphorus (P) and iron (Fe) simultaneously in sediments would be very useful in deepening our understanding of the internal loading process of P coupled with Fe cycling in aquatic systems. In this study, a new technique was established to measure simultaneously the dissolved reactive P (DRP) and dissolved Fe primarily released from sediment solids based on the diffusive gradients in thin films (DGT) theory. A mixed binding gel (ZrO-Chelex gel) used for assembling DGT was developed for simultaneous uptake of DRP and dissolved Fe(II) using amorphous zirconium hydroxide (Zr-oxide) and Chelex-100 resin as binding agents. Simultaneous measurements of DRP and dissolved Fe(II) with the ZrO-Chelex DGT were validated in solution and were independent of solution pH and ionic strength in normal environments. The capacities of the ZrO-Chelex DGT for measurements of DRP and dissolved Fe(II) were 90 μg P cm^{-2} and 75 μg Fe cm^{-2}, with the latter being greater than that (45 μg Fe cm^{-2}) observed with the Chelex-100 resin DGT commonly used in DGT measurements of metals. Microcosm experiments further confirmed the feasibility of the ZrO-Chelex DGT for simultaneous measurement of P and Fe in sediments, with a higher concentration of Fe being measured due to this method's higher capacity compared with the Chelex-100 resin DGT.
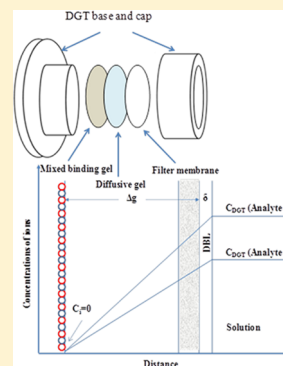
INTRODUCTION

Phosphorus is the nutrient most commonly responsible for water eutrophication and the occurrence of algal blooms.[1,2] The release of P from sediments can contribute a substantial amount of P to the water column, which can continue to support algal growth after a reduction of external P input in lakes.[3−5] The mechanisms behind the release of P from sediments involve a number of physical, chemical, and biological processes.[3] Although progress has been made to explain this phenomenon,[6] current knowledge is still largely based on the traditional concept proposed by Mortimer,[7] in which the redox of iron (Fe) plays a central role in controlling the release of P in sediments, that is, P is sorbed onto Fe(III) oxyhydroxides in oxidized sediments, and it is released when Fe(III) is reduced to Fe(II) under anoxic condition. According to this concept, both P and Fe(II) should be increasingly released to pore water from sediment solids as the redox state transitions from upper (oxic) to deeper (anoxic) sediments. Observations of this phenomenon can provide direct evidence to support the hypothesis of the control of P release by Fe cycling in sediments. However, this finding has not been available to date. Because the relevant studies were exclusively performed through ex situ analyses after collecting sediments from the lakes, this gap in the published literature can be attributed to a lack of in situ, dynamic techniques to track P and

Fe releases simultaneously in sediments. Moreover, considering the heterogeneous distribution of chemicals in sediments,[8,9] such a technique should be characterized by high resolution and short time in its measurements.

The aim of this study is to establish a new technique to track the releases of P and Fe simultaneously in sediments based on the diffusive gradients in thin films (DGT).[10,11] The DGT is an in situ, dynamic technique capable of rapid measurements of labile P, Fe, and other analytes at high spatial resolution.[8,12] This measurement relies on the diffusion-controlled flux of a solute from the surface of a DGT device to a binding phase contained within the device. Once a DGT device is deployed in sediments, an instantaneous depletion of the pore water solute occurs at the surface of the DGT device, leading to a further release of the solute from sediment solids to resupply the pore water concentration.[13] As the local supply of a solute in the pore water is usually limited during a relatively long deployment period (e.g., several days), the DGT-measured concentration is largely a result of the local release of the solute from the sediment solids.[14] Consequently, the DGT is a

potentially robust tool for detecting the simultaneous releases of P and Fe in sediments.

Generally, the ability of a DGT device to measure a solute depends on the binding phase used, which should have a sufficiently high affinity and capacity both to bind the solute and to keep its concentration at effectively zero on the surface in contact with the diffusion layer.[10] As a result, the key to simultaneously tracking the release of P and Fe in sediments with DGT is to develop a mixed binding gel for the simultaneous binding of P and Fe ions. Binding gels impregnated with single binding agents have been developed for the measurement of either dissolved reactive P (DRP) or dissolved Fe with DGT.[10,15−17] The binding agents reported were ferrhydrite or titanium dioxide (Metsorb) for P and Chelex-100 cation exchange resin for Fe. Mixed binding gels have also been developed for the simultaneous measurement of cations and anions with DGT using Chelex-100 and ferrhydrite as the binding agents.[18,19] However, the use of ferrhydrite in these gels resulted in a low capacity for DGT measurement of P, which has limited their application to environments with high P content, such as eutrophic lakes or fertilized soils.[20,21] Recently, Ding et al. developed a novel binding gel using amorphous zirconium hydroxide (Zr oxide) as the binding agent.[20] This Zr-oxide binding gel has a high capacity for DGT measurement of P compared to other gels, enabling its application to a wider variety of environments. The Zr-oxide gel has even been successfully modified to the simultaneous measurements of DRP and dissolved sulfide.[22]

In this study, a mixed binding gel (ZrO-Chelex gel) was developed for simultaneous uptake of DRP and dissolved Fe(II) using Zr-oxide and Chelex-100 as the binding agents. The performance of DGT with this binding gel was tested under laboratory conditions and compared with Zr-oxide and Chelex-100 resin DGTs, respectively, the properties of which have been well-established for the uptake of DRP (Zr-oxide) and dissolved metals (Chelex-100).

■ EXPERIMENTAL SECTION

Principles of Simultaneous Measurement with DGT. Details of the DGT theory have been previously reported.[10,12] A typical DGT device consists of a binding gel overlain by a diffusion gel and a membrane filter that is used as an extension of the diffusion layer in contact with the solution or surrounding environment (Figure 1). During the deployment of DGT, an analyte in the bulk environment diffuses through the diffusive boundary layer (DBL, thickness δ) in solution and the diffusive layer (thickness Δg) and is subsequently bound to the binding layer. The accumulating mass of the analyte (M) in the binding gel can be calculated according to eq 1 when it is eluted using a known volume of elution solution (V_e).

$$M = \frac{C_e(V_g + V_e)}{f_e} \tag{1}$$

where C_e is the concentration of the analyte in the elution solution, V_g is the volume of the gel, and f_e is the elution efficiency.

The DGT-measured concentration (C_{DGT}) of the analyte, which is interpreted as a mean concentration at the surface of the DGT device over the deployment time (t), can be calculated from the accumulated mass (M) using eq 2:
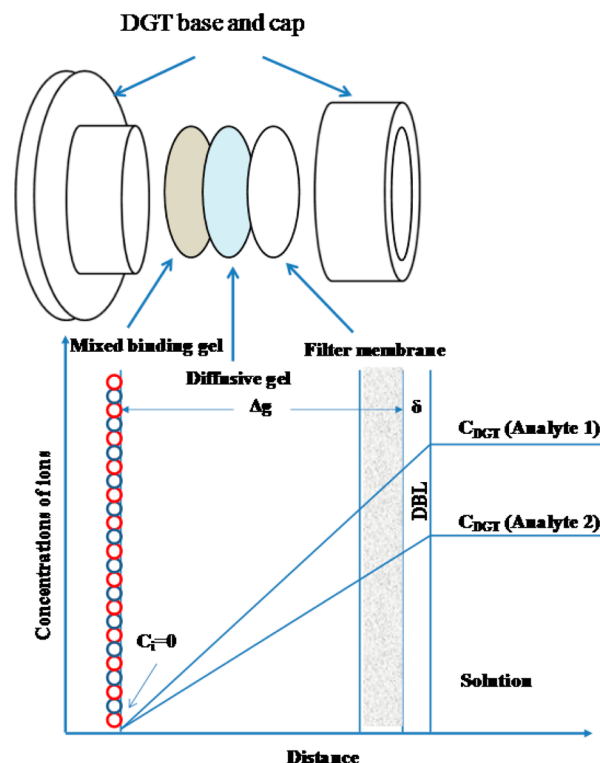

Figure 1. Schematic view of a DGT device equipped with a mixed binding gel layer for simultaneous measurements of two analytes.

$$C_{DGT} = \frac{M(\Delta g + \delta)}{DAt} \tag{2}$$

where A is the exposed surface area of the DGT device, and D is the diffusion coefficient of the analyte in the diffusive layer. The DBL can be neglected when a 0.8 mm thick diffusive gel is used in a standard DGT solution device or when the DGT is deployed in soil or sediment systems.[23] eq 2 is therefore simplified to

$$C_{DGT} = \frac{M\Delta g}{DAt} \tag{3}$$

As the diffusive gel commonly used in the present DGT device (a polyacrylamide gel cross-linked with an agarose derivative) is uncharged at an ionic strength greater than 10 nM,[24] both cations and anions can diffuse freely within it under the defined conditions. When a mixed binding layer is used in a DGT device for taking up different analytes, the DGT can be used for simultaneous measurements of those analytes in a single assay.

Gel Preparation and DGT Deployment. The diffusive gel was prepared with 15% acrylamide and 0.3% agarose-derived cross-linker following published procedures.[24] The mixed binding gel (ZrO-Chelex gel) for simultaneous uptake of DRP and dissolved Fe(II) was prepared based on a modification of the Zr-oxide binding gel.[20] A weight of 1.0 g half-dried Zr-oxide was added into 5 mL of a gel solution composed of 28.5% acrylamide (w/v) and 1.5% N,N-methylene bisacrylamide (w/v). The mixture was thoroughly ground in an agate mortar. A weight of 1.0 g Chelex-100 (Bio-Rad., 200−400 mesh, sodium form) was added and mixed well followed by an addition of 8 μL of N,N,N′,N′-tetramethylethylenediamine (TEMED, Amresco, ultrapure grade) catalyst and 16 μL of freshly prepared ammonium persulfate (Amresco, ACS grade)

initiator (10%, w/v). After mixing, the solution was immediately cast between two glass plates separated by a 0.4 mm plastic space. The glass plate assembly was placed in a refrigerator at 3 ± 1 °C for 0.5 h to let the zirconium hydroxide and Chelex-100 settle to one side of the gel, and the assembly was later transferred to an oven at 45 ± 1 °C to allow the gel to polymerize for 0.5 h. The gel sheet removed from the glass plates was soaked in deionized water for at least 24 h (the water was replaced 2−3 times) and stored in deionized water prior to use. The thickness of the gel remained at 0.4 mm after hydration. The amounts of Chelex-100 in the gel was 0.18 ± 0.01 g cm^{-3}.

Two other binding gels were prepared for comparison. The Zr-oxide binding gel was prepared following the published procedure.[20] The amount of Zr-oxide added in the stock gel solution was reduced to the same as in this study. The Chelex-100 binding gel (known as resin gel) was prepared according to Zhang and Davison.[10] A 2 g quantity (wet weight, equal to 0.8 g without washing) of Chelex-100 was added to a volume of 5 mL gel solution. The amounts of Chelex-100 in the gel was 0.09 ± 0.01 g cm^{-3}.

The surface images of the ZrO-Chelex and Chelex-100 gels were observed by an optical microscope (Oxympus BX51). The ZrO-Chelex gel was stained using a potassium permanganate solution (1‰, weight/volume) for 4 h before observation to visualize the particles of Chelex-100. The distribution densities of Chelex-100 on their surfaces were determined by counting the particle number per area.

Two different DGT holders (DGT Research Ltd.) were used for DGT assembly and deployment. A piston-type DGT holder with a 2 cm diameter exposure window was used for the solution test. A flat probe with a 1.8×16 cm (width × length) exposure window was used for deployment in sediments. In both types of DGT assemblies, the binding gel (with the binding agents' settled surface facing out) was covered sequentially by a diffusion gel and a 0.13 mm cellulose nitrate filter membrane (Whatman, 0.45 μm pore size). The thickness of the diffusive gel in the piston-type DGT unit was 0.80 mm, while a 0.40 mm thick diffusive gel was used in the sediment probes to increase the masses of DRP and Fe(II) accumulated in the binding gels during the deployment period. All the DGT holders were acid-cleaned in 10% (v/v) HNO$_3$ (AR grade) for at least 24 h and rinsed thoroughly with deionized water prior to use. All the DGT assemblies were freshly deoxygenated with nitrogen for at least 16 h prior to their deployments.

Binding Kinetics and Elution. Three different types of binding gels (ZrO-Chelex, Zr-oxide, and Chelex-100) were cut into 2.5 cm diameter discs, the size of which was the same assembled in the solution DGT units. The kinetics of DRP binding to ZrO-Chelex and Zr-oxide gels were examined by immersing the gel discs in 5 mL of a KH$_2$PO$_4$ solution containing 0.2 mg P L^{-1} and 0.03 M NaNO$_3$ at pH 7.0, while the kinetics of Fe(II) binding to ZrO-Chelex and Chelex-100 gels were examined by immersing the gel discs in 5 mL of (NH$_4$)$_2$SO$_4$·FeSO$_4$ solutions containing 0.2 mg Fe(II) L^{-1} and 0.03 M NaNO$_3$ at pH 4.5. The solutions were immediately shaken at room temperature for various time intervals ranging from 5 min to 2 h. Concentrations of DRP and dissolved Fe(II) remaining in the solutions were measured before immersion and after retrieval of the gel discs from the solutions using molybdenum blue and phenanthroline colorimetric methods,[25,26] respectively.

Elution of P and Fe from the Zr-oxide gel was tested using a three-step extraction procedure. Mixed solutions used for uptake of DRP and dissolved Fe(II) by the gels were freshly prepared using KH$_2$PO$_4$ and (NH$_4$)$_2$SO$_4$·FeSO$_4$. Concentrations of DRP and dissolved Fe(II) in these solutions varied from 0.1 to 2.0 M, with the ionic strength at 0.03 M NaNO$_3$ and a pH value of 4.5. Each solution was deoxygenated with nitrogen for 16 h. A gel disc was later immersed in 20 mL of a solution contained in a well-sealed plastic tube. After 10 h of shaking, the gel disc was retrieved and immersed in 20 mL of 1.0 M HNO$_3$ for 16 h of shaking to elute Fe bound in the gel. The gel was immersed into 20 mL of deionized water for 2 h to remove residual acid followed by 20 mL of 1.0 M NaOH for 16 h of shaking to elute P bound in the gel. The amounts of P and Fe bound by each gel disc were determined by the differences of their concentrations in mixed solutions before and after the gel immersions. The elution efficiencies for P and Fe were the ratio of the eluted amounts to the amounts bound in the gels.

Characteristics of DGT Performance in Solutions. *Validation of Simultaneous Measurements with the DGT.* The simultaneous measurements of DRP and dissolved Fe(II) with the ZrO-Chelex DGT were examined by employing the diffusive layer (sum of the diffusive gel and filter membrane) with thickness of 0.43 mm, 0.53 mm, 0.67 mm, 0.77 mm, 0.93 mm, respectively. The DGT units were deployed for 4 h in a 0.03 M NaNO$_3$ solution containing approximately 0.23 mg L^{-1} P and 0.72 mg L^{-1} Fe(II) at pH 4.5. To minimize the loss of Fe(II) through oxidation and precipitation, the solutions were prepared with deionized water purged with high-purity nitrogen (Supporting Information Figure S1). The solutions were later stabilized overnight followed by DGT deployment with continuous purging of high-purity nitrogen. No obvious changes in concentrations of dissolved Fe(II) were detected in all solutions during the DGT deployment. After retrieval of the DGT, the bound P and Fe in the ZrO-Chelex gel were eluted using the three-step extraction procedure as described above.

Effects of pH and Ionic Strength. The effect of pH on the ZrO-Chelex DGT measurement was investigated by deploying the ZrO-Chelex DGT units into a series of 2 L well-stirred solutions containing 0.03 mol L^{-1} NaNO$_3$, approximately 1 mg L^{-1} DRP and 0.5 mg L^{-1} dissolved Fe(II) at 24 °C. The pH values in these solutions were adjusted to 4.0, 4.5, 5.1, 5.6, 6.3, 6.9, and 7.5, respectively. Examination of a pH value higher than 7.5 could not be performed because of unavoidable oxygenation and precipitation of dissolved Fe(II) under this pH condition. The effect of ionic strength on the ZrO-Chelex DGT measurement was investigated by deploying the ZrO-Chelex DGT units into a series of 2 L well-stirred solutions containing approximately 1.0 mg L^{-1} DRP, 0.90 mg L^{-1} dissolved Fe(II) and different concentrations of NaNO$_3$ ranging from 10 nM to 0.5 M. The pH values of these solutions were adjusted to 4.5. All of the solutions were prepared and protected with continuous purging of high-purity nitrogen as mentioned earlier. The deployment time of DGT was set at 4 h for both experiments.

Capacity for DGT Response. The DGT capacity for measurement of DRP was determined by exposing the ZrO-Chelex and Zr-oxide DGT units to a series of 2 L, well-stirred, 0.03 M NaNO$_3$ solutions containing different DRP concentrations ranging from 9.4 to 117 mg P L^{-1} at pH 7. The DGT capacity for measurement of dissolved Fe(II) was determined by exposing the ZrO-Chelex and Chelex-100 DGT units to a

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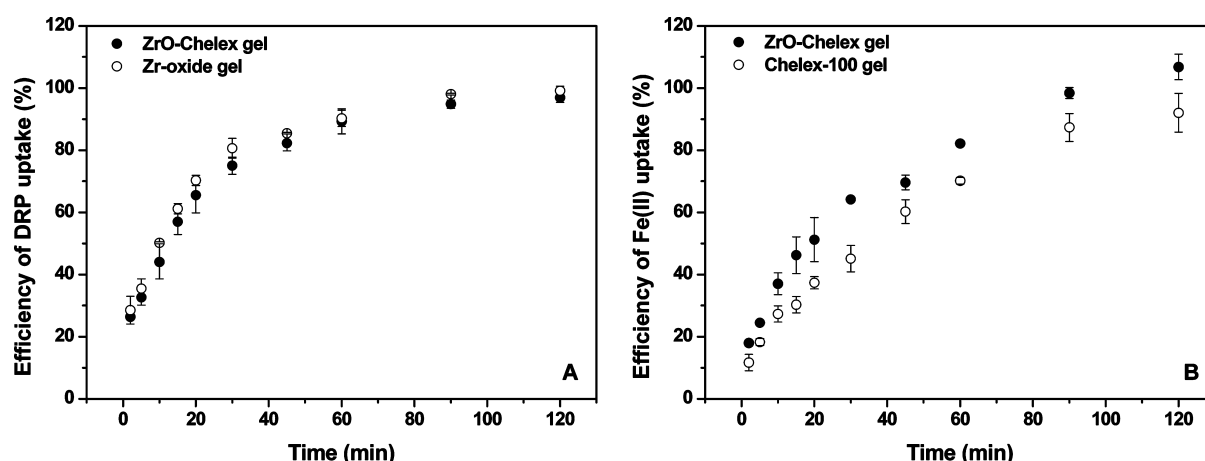dx.doi.org/10.1021/es401822x | Environ. Sci. Technol. 2013, 47, 10477−10484

Figure 2. Dynamic bindings of DRP (A) and dissolved Fe(II) (B) to the ZrO-Chelex gel in comparison with those of the Zr-oxide and Chelex-100 gels. Values are mean ± SD of three replicates.

series of 2 L, well-stirred 0.03 M, $NaNO_3$ solutions containing different dissolved Fe(II) concentrations ranging from 4.7 to 58 mg Fe L^{-1} at pH 4.5. The deployment time of DGT was set at 6 h for both experiments.

Field Application. A microcosm with homogeneous sediments was created to test the replicability of ZrO-Chelex DGT on simultaneous measurements of DRP and dissolved Fe(II) in sediment profiles. Surface sediments (∼10 cm) were collected on June 10, 2012 from a eutrophic region of Taihu Lake (31° 30′58.2″ N, 120°11′33.8″ E). The sediments were placed in a plastic tank to a depth of approximately 20 cm after thoroughly mixing them into a uniform sludge. The overlaying water later was gently poured onto the surface of the sediment to a depth of approximately 15 cm. The microcosm was kept in a bath incubator at 25 °C for three weeks. Two sets of ZrO-Chelex DGT probes were bound back to back with a Zr-oxide and a Chelex-100 DGT probe, respectively. The combined DGT probes were deoxygenated with nitrogen overnight and then inserted into the microcosm for 48 h. After retrieval of the probes, the binding gels were dissected at 1.0 mm intervals. Each piece of the ZrO-Chelex gel was eluted using the three-step procedure, using a 200 μL volume of each eluent. Each piece of the Zr-oxide and Chelex-100 gels was eluted with 200 μL of 1.0 M NaOH and 1.0 M HNO_3, respectively. Concentrations of DRP and dissolved Fe in the eluates were measured with a miniaturized spectrophotometry method using the Epoch Microplate Spectrophotometer (BioTek, Winooski, VT), with the analytical parameters reported elsewhere.[27]

■ RESULTS AND DISCUSSION

Preparation of the ZrO-Chelex Gel. Both the Zr-oxide and Chelex-100 binding gels have been well-characterized for use in DGT measurements of DRP and dissolved metals, respectively.[10,20,28] The gels can take up the corresponding analytes rapidly, allowing the concentrations of the dissolved analytes to remain effectively zero at the interface between the binding and diffusive gels over the DGT deployment period. However, their combination in a thin gel layer will let them overlay each other on the gel surface, which may block their respective binding sites and decrease the capacity of the mixed ZrO-Chelex gel in DGT measurement. To alleviate this problem, the amount of Zr-oxide added to 5 mL of gel solution for preparation of the binding gels was reduced from 2.5 g in the original Zr-oxide gel to 1.0 g in the present study.

This reduction could also help cast the gel by keeping the solids impregnated in the gel to a minimum. Measurement of DRP with DGT resulting from this change should be satisfactory in normal environments, taking the high capacity of the Zr-oxide in binding DRP into consideration.[20,28] Optimization of the addition of Chelex-100 was then performed by increasing its added amounts from 0.6 to 1.2 g in the gel solutions to increase the capacity of the produced ZrO-Chelex gel to absorb as much dissolved Fe(II) as possible. Increasing the amount of Chelex-100 to 1.0 g successfully produced a ZrO-Chelex gel with good physical strength for DGT use. However, the addition of 1.2 g Chelex-100 made the mixture notably viscous and difficult to inject into the 0.4 mm plastic spacer. Consequently, the added amount of Chelex-100 was set at 1.0 g for the preparation of the ZrO-Chelex gel, which was higher than the 0.8 g used for the preparation of the Chelex-100 gel.

An image of the ZrO-Chelex gel prepared with additions of 1.0 g Zr-oxide and 1.0 g Chelex-100 is shown in Supporting Information Figure S2, accompanied by that of the Chelex-100 gel for comparison. The circular Chelex-100 particles can be clearly viewed in the Chelex-100 gel because the region around each particle is transparent. The Chelex-100 particles in the ZrO-Chelex gel can also be clearly viewed as scarlet spots after staining with potassium permanganate. These particles were embedded in the gel and surrounded by the amorphous Zr-oxides. The visualization of the Chelex-100 particles in this gel demonstrated that they had partly settled onto the surface of the gel during the gel casting, which would facilitate the uptake of dissolved Fe(II) during the DGT deployment. The distribution density of the Chelex-100 was 42 ± 4 particles per mm^2 in the ZrO-Chelex gel based on counting them in eight images, which was greater than the 32 ± 4 particles observed in the Chelex-100 gel. This difference was attributed to a higher amount of Chelex-100 in the ZrO-Chelex gel (twice as much as that in the Chelex-100 gel).

Binding Kinetics and Elution. To investigate whether the ZrO-Chelex gel could act as a zero sink for DGT measurement comparable to the combined function of Zr-oxide and Chelex-100 gels, the binding kinetics of DRP and dissolved Fe(II) to this gel were investigated by immersing it in stirred DRP and Fe(II) solutions with concentrations of 0.2 mg P L^{-1} and 0.2 mg Fe L^{-1}, respectively. The Zr-oxide and Chelex-100 gels were simultaneously investigated for comparison. The results showed that the uptake of DRP and dissolved Fe(II) by each binding
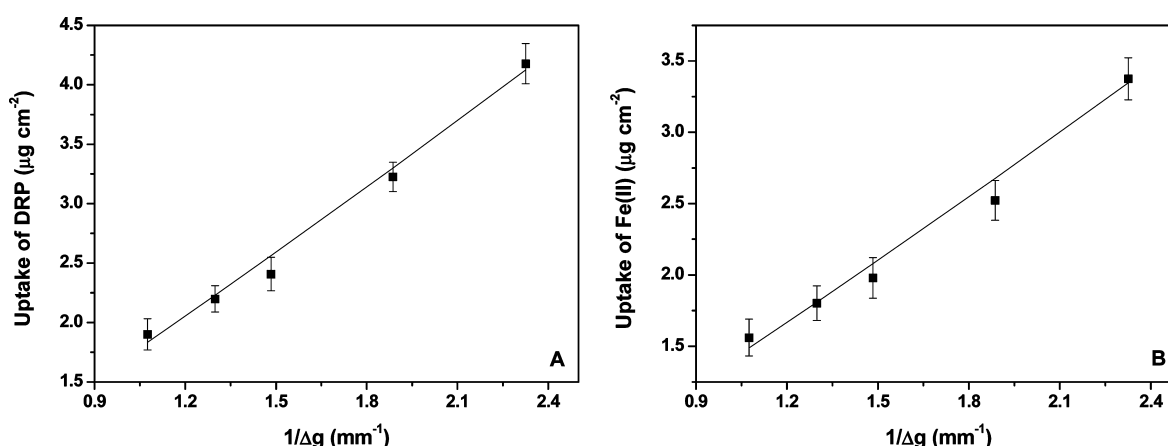
Figure 3. Changes in uptakes of DRP (A) and dissolved Fe(II) (B) by the ZrO-Chelex DGT with the thicknesses of the diffusive layer in the DGT devices. The line is the theoretical response calculated using eq 3. Values are mean $\pm$ SD of three replicates.
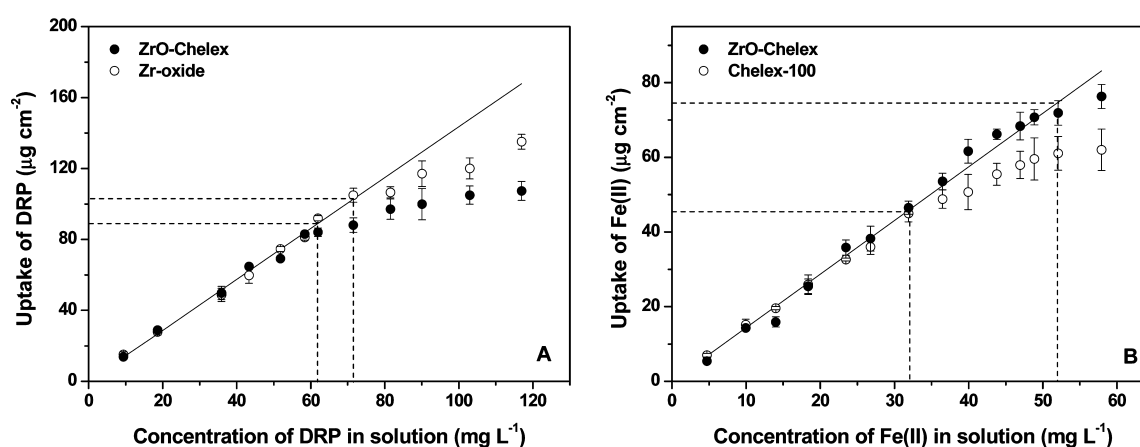

Figure 4. Changes in uptakes of DRP (A) and dissolved Fe(II) (B) by the ZrO-Chelex DGT with their concentrations in solution. The Zr-oxide and Chelex-100 DGTs were used for comparison. The lines are the theoretical responses calculated using eq 3. The horizontal and vertical dashed lines show the capacities and the respective concentrations. Values are mean $\pm$ SD of three replicates.

gel increased linearly with time for the first 20 min, followed by a slow increase until 120 min. There was no obvious difference in the binding dynamics of DRP between the ZrO-Chelex and Zr-oxide gels (Figure 2A). A complete uptake of DRP was obtained for both gels after 120 min. This demonstrated that the addition of Chelex-100 in the ZrO-Chelex gel did not affect the binding kinetics of DRP to the Zr-oxide.

The uptake of dissolved Fe(II) onto the ZrO-Chelex gel was obviously faster than that of the Chelex-100 gel, which showed a complete uptake of dissolved Fe(II) after 120 min in contrast to a 90% removal efficiency for the Chelex-100 gel (Figure 2B). The stronger binding of Fe(II) by the ZrO-Chelex gel was consistent with a higher distribution density of the Chelex-100 particles in the gel compared with the Chelex-100 gel. Furthermore, it has been found that Zr-oxide absorbs metal cations under neutral and alkaline conditions,[29−31] which should contribute to the binding of dissolved Fe(II) by the ZrO-Chelex gel. A further study is required to examine this contribution.

The 1.0 M HNO$_3$ and 1.0 M NaOH solutions, respectively, have been used for the elution of metals from the Chelex-100 gel and DRP from the Zr-oxide gel.[10,20] In this study, a three-step procedure composed of the sequential uses of 1.0 M HNO$_3$, deionized water and 1.0 M NaOH was tested to elute Fe(II) and DRP from the ZrO-Chelex gel. The first elution

using 1.0 M HNO$_3$ obtained a stable efficiency of 88 $\pm$ 2% for Fe(II) (Supporting Information Figure S3), whereas negligible amounts of DRP (<2% of the total amounts in the gel) was removed during this elution process. This efficiency was higher than the 70% elution of Fe(II) from the Chelex-100 gel.[10] Similar phenomena have been observed by Mason et al. for the elution of Fe from a mixed binding gel impregnated with ferrhydrite and Chelex-100.[18] After washing the residual gel using deionized water, the third elution of the ZrO-Chelex gel using 1.0 M NaOH obtained a total recovery 98 $\pm$ 2% for DRP (Supporting Information Figure S3). This efficiency was even higher than the value of 95% for elution of DRP from the Zr-oxide gel.[20] The result indicated that the use of a three-step elution procedure is reasonable for the elution of Fe(II) and DRP from the ZrO-Chelex gel, with elution factors of 0.88 and 0.98, respectively, adopted for the calculation of dissolved Fe(II) and DRP mass accumulated in the gel.

Validation of ZrO-Chelex DGT in Solution. An investigation was performed to ensure whether the ZrO-Chelex DGT could be used for simultaneous measurements of DRP and dissolved Fe(II) in solution. This study was conducted via a comparison between the measured and theoretically predicted uptake of DRP and dissolved Fe(II) by changing the thickness of the diffusive layer in the assembly of the DGT devices. After 4 h of DGT exposure, both of the measured masses of DRP and
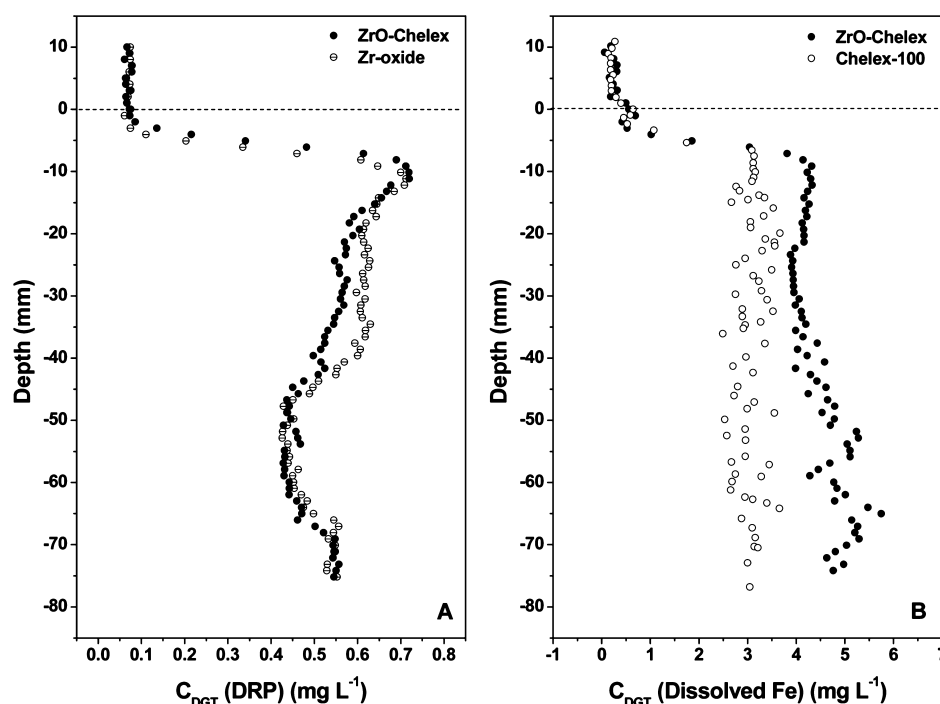
Figure 5. Concentrations of DRP (A) and dissolved Fe (B) measured by the ZrO-Chelex DGT in a homogenized sediment profile. The Zr-oxide and Chelex-100 DGTs were used for comparison. The location of the sediment−water interface is represented by zero.

dissolved Fe(II) increased linearly with the reciprocal of the thickness of the diffusive layer (Figure 3). The experimental data agreed with the theoretical prediction calculated using eqs 1 and 3, with measured-to-predicted ratios of 0.99 ± 0.07 ($n = 15$) for DRP and 1.00 ± 0.08 ($n = 15$) for dissolved Fe(II). Therefore, these results validated the use of the ZrO-Chelex DGT for the simultaneous measurements of DRP and dissolved Fe(II) in solutions. Their agreement also demonstrated that the errors caused by neglecting the DBL could be ignored.

Effects of pH and Ionic Strength on ZrO-Chelex DGT Measurement. The effects of pH and ionic strength on the ZrO-Chelex DGT measurement were examined by deploying DGT in solutions containing dissolved Fe(II) and DRP at different pH (4.0−7.5) or ionic strength (10 nM−0.5 M) (Supporting Information Figure S4). The results showed that concentrations of DRP and dissolved Fe(II) measured by DGT corresponded with those in solutions, with measured-to-predicted ratios of 1.01 ± 0.05 ($n = 21$) and 1.01 ± 0.04 ($n = 21$) for pH and 1.00 ± 0.04 ($n = 18$) and 1.01 ± 0.06 ($n = 18$) for ionic strength, respectively. This finding demonstrates that the DGT uptakes of DRP and dissolved Fe(II) were independent of solution pH and ionic strength. Because the feasibility of the Zr-oxide and Chelex-100 DGTs in measurements of DRP and dissolved metals has been examined under a wide pH range,[10,20] the ZrO-Chelex DGT can be applied to their measurement in many normal field environments.

The Capacity of the ZrO-Chelex DGT. The capacity of the ZrO-Chelex DGT was investigated by deploying the DGTs in stirred solutions with various DRP and dissolved Fe(II) concentrations ranging from 9.4 to 117 mg P L^{-1} at pH 7.0 and from 4.7 to 58 mg Fe L^{-1} at pH 4.5. The Zr-oxide and Chelex-100 DGTs were simultaneously deployed for comparison. A linear and theoretically predictable response was obtained with the DRP concentration up to 62 mg L^{-1} and 72 mg L^{-1} for the ZrO-Chelex and Zr-oxide DGTs, respectively (Figure 4A).

Their capacities were calculated at 90 μg P cm^{-2} (ZrO-Chelex) and 102 μg P cm^{-2} (Zr-oxide), corresponding to DRP concentrations of 16 mg L^{-1} and 18 mg L^{-1}, respectively, in solutions assuming a deployment time of 24 h at 25 °C for a typical DGT device (0.8 mm thick diffusive gel and 0.13 mm filter). Although the value of 90 μg P cm^{-2} was lower than that of the Zr-oxide DGT reported previously and in this study (100−130 μg P cm^{-2} under neutral pH condition),[20,28] it was still much greater than those of the other DGTs simultaneously used for DRP (7−12 μg P cm^{-2}).[15−18,32]

A linear and theoretically predictable response was also obtained with the dissolved Fe(II) concentration up to 52 mg L^{-1} and 32 mg L^{-1} for the ZrO-Chelex and Chelex-100 DGTs, respectively (Figure 4B). Their capacities were calculated at 75 μg Fe cm^{-2} (ZrO-Chelex) and 45 μg Fe cm^{-2} (Chelex-100), corresponding to Fe(II) concentrations of 13 mg L^{-1} and 8 mg L^{-1}, respectively, in solutions assuming a deployment time of 24 h at 25 °C for a typical DGT device. The greater capacity of the ZrO-Chelex DGT was consistent with the higher density of Chelex-100 particles in the ZrO-Chelex gel compared with the Chelex-100 gel, which significantly facilitates Fe measurement with DGT in environments containing higher concentrations of dissolved Fe.

Microcosm Deployment. A microcosm with homogenized sediments was created to test the use of ZrO-Chelex DGT for simultaneous measurements of DRP and dissolved Fe in sediment profiles. Homogenized sediments were used to avoid the inherent heterogeneities in sediment and to facilitate comparisons with the Zr-oxide and Chelex-100 DGTs. The profiles of DRP and dissolved Fe(II) in the sediment profiles measured by the three different DGTs are shown in Figure 5. The two DRP mass-depth profiles measured by the ZrO-Chelex and Zr-oxide DGTs generally agreed (Figure 5A), reflected by a sharp increase in DRP concentration from the sediment-water interface (SWI) to a depth of −10 mm (the

Table 1. Summary of the Features of the Zr-Oxide, Chelex-100 and ZrO-Chelex Binding Gels used for DGT Measurements of DRP and Dissolved Fe(II)

features	Zr-oxide gel	Chelex-100 resin gel	ZrO-Chelex gel
appearance	white, opaque, and smooth surface	opaque except for the position distributing Chelex-100 particles	white, semiopaque, and visible distribution of Chelex-100 particles
flexibility	hard and not easy to deform	easy to elastically extend	hard and not easy to deform
elution procedure	elution of P for 16 h using 1.0 M NaOH, with elution efficiency of 0.95[a]	elution of Fe for 16 h using 1.0 M HNO_3, with elution efficiency of 0.70[b]	elution of Fe for 16 h using 1.0 M HNO_3 and then P for 16 h using 1.0 M NaOH, with elution efficiencies of 0.88 and 0.98, respectively
capacity for DGT response	95 μg P cm^{-2} to >330 μg P cm^{-2} at pH 4.2–9.2[c]	45 μg Fe cm^{-2} at pH 4.5	90 μg P cm^{-2} at pH 7.0, 75 μg Fe cm^{-2} at pH 4.5
suitable conditions for DGT deployments	pH 2–10, ionic strength ≥10 nM[a]	Refer to other metals[b]	similar to the Zr-oxide and Chelex-100 gels

[a]From ref 20. [b]From ref 10. [c]From ref 28.

minus sign represents the depth below the SWI), a slight decrease to a depth of −50 mm and, later, a slight increase to the bottom of the depth. These findings demonstrate the feasibility of the ZrO-Chelex DGT in measurement of DRP in sediments.

There was general agreement between the two Fe mass-depth profiles measured by the ZrO-Chelex and Chelex-100 DGTs from a depth of 10 mm above the SWI to a depth of −7 mm (Figure 5B). Concentration of dissolved Fe measured by ZrO-Chelex DGT remained stable from a depth of −7 to −30 mm followed by a slight increase to the bottom, while concentration of dissolved Fe measured by the Chelex-100 DGT remained stable along the whole profile from a depth of −7 mm to the bottom. More importantly, concentrations of dissolved Fe measured by the Chelex-100 DGT (3.08 ± 0.29 mg Fe L^{-1}) were significantly lower than those measured by the ZrO-Chelex DGT (4.49 ± 0.46 mg Fe L^{-1}) from the depth of −7 mm to the bottom. Because the accumulated masses of Fe in the Chelex-100 gel (39 ± 4 μg Fe cm^{-2}) approached its DGT capacity (45 μg Fe cm^{-2}), the lower concentrations of dissolved Fe measured by the Chelex-100 DGT were likely caused by the oversaturation of the Chelex-100 binding gel from accumulation of Fe. The vertical fluctuation of the measured Fe concentrations also reflected the local difference of the Chelex-100 gel in DGT capacity. The results demonstrated the superiority of the ZrO-Chelex DGT in measurement of dissolved Fe due to its higher capacity for DGT response.

General Appraisal. The features of the three binding gels used in DGT are summarized in Table 1. Overall, the newly developed ZrO-Chelex binding gel takes advantages of the Zr-oxide gel and overcomes the shortcomings of the other gels, which have a low capacity for DRP measurement. The performance of this DGT is also superior to that of the Chelex-100 DGT because of a higher capacity to measure dissolved Fe, reflected in the difference between the measured concentrations of dissolved Fe in the sediment profile using the two DGTs observed in this study (Figure 5). Additionally, the recovery rate of Fe was notably enhanced by the three-step elution of the ZrO-Chelex gel compared to the elution of the Chelex-100 gel, which can reduce errors in calculation on Fe mass accumulated in the binding gels. As a consequence, the ZrO-Chelex DGT should be an effective tool in the simultaneous measurement of DRP and dissolved Fe in sediments. As the binding agents impregnated in the ZrO-Chelex gel can take up a range of cations and anions besides P and Fe, the ZrO-Chelex DGT has the potential to be extended to simultaneous measurements of other analytes in single assays in the near future.

ASSOCIATED CONTENT

Ⓢ Supporting Information
A schematic diagram of a system for testing the DGT performance in solutions; Surface images of the ZrO-Chelex and Chelex-100 gels; Recovery of DRP and dissolved Fe(II) from elution of the ZrO-Chelex gel; Effects of solution pH and ionic strength on the measurements with the ZrO-Chelex DGT. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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