

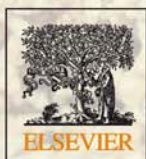
JES

JOURNAL OF
ENVIRONMENTAL
SCIENCES

ISSN 1001-0742
CN 11-2629/X

August 1, 2013 Volume 25 Number 8
www.jesc.ac.cn

Chinese GreatWall Station



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Investigation of potential interferences on the measurement of dissolved reactive phosphate using zirconium oxide-based DGT technique

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Received 04 August 2012; revised 02 November 2012; accepted 06 November 2012

Abstract

A diffusive gradients in thin films (DGT) technique based on hydrous zirconium oxide (Zr-oxide) has been recently developed for the measurement of dissolved reactive phosphate (DRP). In this study, the detailed performance of the DGT technique is reported. Spiking experiments revealed that several orthophosphate monoester compounds contributed to the Zr-oxide DGT measurements of DRP. However, such a phenomenon is unlikely to occur during field conditions due to the low concentration of organic P in typical natural waters. The presence of Cl^- (up to 106 g/L), SO_4^{2-} (up to 16 g/L), HCO_3^- (up to 817 g/L), and AsO_2^- and AsO_4^{3-} (both up to 1 mg As/L) in solutions had negligible effects on the measurement of DRP. The threshold concentrations of Cl^- , SO_4^{2-} and HCO_3^- have been increased from previous reports for the measurements of DRP using other adsorbent-based DGT techniques. The capacity for DGT measurements of DRP decreased with increasing solution pH (4.2–9.2). The lowest capacity ($95 \mu\text{g P/cm}^2$ at pH 9.2) was still greater than that of other DGT techniques that are usually used for the measurement of DRP ($2\text{--}12 \mu\text{g P/cm}^2$). The Zr-oxide binding gel could be stored for up to 2 years without any aging effect. This period of validity was considerably longer than the ferrihydrite binding gel that is commonly used in present DGT devices (6 months). The field application revealed that the concentrations of DRP measured in three fresh water samples using the Zr-oxide DGT technique were in agreement with those of the traditional colorimetric method.

Key words: diffusive gradients in thin films (DGT) technique, zirconium oxide (Zr-oxide), dissolved reactive phosphate (DRP), interference, soil, water

DOI: 10.1016/S1001-0742(12)60140-5

Introduction

The diffusive gradients in thin films (DGT) technique is a passive sampling technique that was originally developed for *in situ* measurement of trace metal concentrations in waters (Davison and Zhang, 1994; Zhang and Davison, 1995). This method has been successfully used to measure kinetically labile species of metals, semimetals, sulfides and phosphorus in soils and aquatic systems (Davison and Zhang, 2012). A typical DGT sampler consists of a polyacrylamide diffusive gel, a binding gel and a filter membrane to protect the gels. The diffusive gel is placed on top of the binding gel and covered with a membrane filter that is in contact with the bulk solution. The binding gel rapidly and irreversibly accumulates the target analytes and acts as a zero sink (Zhang and Davison, 1995). This gel is generally comprised of a gel layer that is incorporated

with a specific binding agent. The choice of binding agent depends on the target analytes to be measured. The most popular binding agents include a chelating resin (Chelex 100, Bio-Rad) for the measurement of trace metals (Scully et al., 2004; Zhang and Davison, 1995; Wu et al., 2011), ferrihydrite for anions (e.g., P and As) (Zhang et al., 1998; Österlund et al., 2010) and AgI for sulfides (Teasdale et al., 1999).

Once the DGT device is deployed, the target analyte sequentially passes through the filter membrane and the diffusive gel (with a combined thickness of Δg) and is trapped in a binding gel. A concentration gradient is quickly established within the diffusive layer. After a deployment time (t , sec), the accumulated mass (M , mg) of the analyte in the binding gel is related to its solution concentration (i.e., C_{DGT} , mg/L) according to Eq. (1).

$$C_{\text{DGT}} = \frac{M \times \Delta g}{D \times A \times t} \times 1000 \quad (1)$$

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where, D is the diffusion coefficient of the analyte in the diffusive layer, and A is the exposed surface area of the DGT device.

M is calculated according to Eq. (2) if it can be eluted using a known volume of effluent (V_e , L).

$$M = \frac{C_e(V_e + V_{\text{gel}})}{f_e} \quad (2)$$

where, C_e (mg/L) is the concentration of the analyte in the eluate determined using an appropriate analytical method, V_{gel} (L) is the volume of the binding gel, and f_e is the recovery rate from the elution (Zhang and Davison, 1995).

As a promising tool for measuring labile analytes in the environment, DGT should consistently perform under a wide range of natural conditions. The characterization of the performance of a DGT technique is generally limited to laboratory conditions, although various factors may interfere with the DGT measurement when it is applied to *in situ* measurements. These interferences can result from changes in the diffusion process of the target analyte within the diffusive layer or changes in the binding properties of the binding phase for the target analyte. Previous studies have focused on the low ionic strength in solutions and freshwaters, which lowered the uptake of metal ions by DGT through decreasing their diffusive coefficients in the diffusive gels (Scally et al., 2006). Furthermore, the dynamics and capacity of the binding phases for the binding analytes were observed to be significantly affected by a range of factors, including aging effects of the binding phases, competitive ions and organic ligands (Luo et al., 2010; Panther et al., 2011; Moorlegghem et al., 2011; Tankéré-Muller et al., 2012; Österlund et al., 2012). Because of the complex background in natural environments, it is vitally important to investigate the potential interferences to the DGT measurement, especially when a new DGT technique is applied under *in situ* conditions.

Recently, a DGT technique was developed for the measurement of dissolved reactive phosphate (DRP) based on the use of a new binding gel that has a high capacity

for binding phosphate (Ding et al., 2010). This binding gel was prepared using hydrous zirconium oxide (Zr-oxide) as the binding agent. This compound is known to have a high selectivity and great capacity for absorbing phosphate compared to other materials (Chitrakar et al., 2006; Rodrigues et al., 2011). The resulting Zr-oxide DGT technique has a considerably higher capacity (> 50 times) for DRP uptake than that of the ferrihydrite-based DGT technique, which has been commonly used in present DGT devices. The new Zr-oxide based DGT technique has been extended to high-resolution, two-dimensional measurements of DRP and dissolved sulfide (Ding et al., 2011, 2012). However, the potential interferences to the DGT measurement of DRP in the environment have not currently been investigated.

In this study, we extended the performance test of the Zr-oxide DGT technique for DRP measurements under laboratory conditions and in natural waters. The influences of several potential environmental factors on the DGT measurements of DRP were investigated, including the interferences from various P compounds and major competitive ions, the effect of solution pH on the DGT capacity, and the effect of aging on the Zr-oxide binding gel. The performance of this technique for *in situ* measurements of DRP was also examined in 3 natural waters through comparison with the traditional colorimetric method.

1 Materials and methods

1.1 Reagents, materials, and solutions

ZrOCl₂·8H₂O (AR, Sinopharm Chemical Reagent Co., Ltd.) was used for preparing the hydrous Zr-oxide and the Zr-oxide binding gel. Potassium dihydrogen phosphate (KH₂PO₄, AR Sinopharm Chemical Reagent Co., Ltd.) was used to prepare the P stock solution (100 mg/L). Thirteen model P compounds were selected to investigate their possible effects on the DGT measurements of DRP based on the Zr-oxide binding gel, whose basic properties and sources are listed in **Table 1**.

Table 1 Basic information for selected phosphorus compounds

Compounds	Phosphate type	Purity	Source
Sodium pyrophosphate	Polyphosphate	98%	SCRC
Sodium hexametaphosphate	Polyphosphate	—	SCRC
Sodium polyphosphate	Polyphosphate	—	Sigma
4-Nitrophenyl phosphate disodium	Orthophosphate monoester	—	Sigma
myo-Inositol hexakisphosphate	Orthophosphate monoester	—	Sigma
Adenosine 5' monophosphate	Orthophosphate monoester	—	Sigma
D-glucose-6-phosphate	Orthophosphate monoester	98%	Sigma
L-α-phosphatidyl choline	Orthophosphate diester	BR	Sigma
Deoxyribonucleic acid	Orthophosphate diester	—	Sigma
(R)-(-)-1,1'-Binaphthyl-2,2'-diyl-hydrogen phosphate	Orthophosphate diester	98%	Sigma
Creatine phosphate	Phosphonate	98%	Sigma
2-Aminoethyl phosphonic acid	Phosphonate	99%	Sigma
Adenosine 5' triphosphate	Organic polyphosphate	98%	Sigma

SCRC: Sinopharm Chemical Reagent Co., Ltd., China; —: no data; BR: biological reagent.

The diffusive gel was prepared using 15% acrylamide and 0.3% agarose-derived cross-linker according to standard procedures (Zhang and Davison, 1995). The Zr-oxide binding gel was prepared based on the procedure reported by Ding et al. (2010). The half-dried hydrous zirconium oxide was prepared from the precipitation of a $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution (25 g/L). The gel solution was cast at 60°C by mixing 0.9 g of the half-dried Zr-oxides into 3.6 mL of a gel solution composed of 28.5% acrylamide (W/V), and 1.5% *N,N'*-methylene bisacrylamide (W/V) plus 4 μL of a tetramethylethylenediamine catalyst and 100 μL of a freshly prepared ammonium persulfate initiator (10%, W/V). The thickness of the gel was 0.40 mm after hydration in deionized water.

The DGT devices were assembled using standard piston-type DGT holders with a 2 cm diameter exposure window (DGT Research Ltd.) (Zhang and Davison, 1995). The Zr-oxide binding gel was placed at the bottom of the holder (the Zr-oxide settled surface up), covered in sequence with the diffusive gel and a 0.14 mm cellulose nitrate filter membrane (Whatman, 0.45 μm pore size).

1.2 Elution procedure and phosphorus analysis

The P in the Zr-oxide binding gel was eluted with 1 mol/L NaOH after deployment of the DGT. Each gel disc (2.5 cm diameter) was immersed in 20 mL of a NaOH solution. The solution was stirred in an oscillator for 16 hr. The eluents were diluted 5–10 times and adjusted to a pH of 7.0. The concentrations of DRP in the diluted eluents or in other solutions were measured using a miniaturized molybdenum blue method with 96-microwell plates and an Epoch Microplate Spectrophotometer (BioTek, USA) (Ding et al., 2011). The limit of detection of this colorimetric method was 0.002 mg P/L. The mass of P (M) in the gel was calculated according to Eq. (2) using an elution factor (f_e) of 0.95 (Ding et al., 2010).

1.3 Effects of various P compounds on the DGT measurement

To examine the possible interferences of various organic and inorganic P compounds on the DRP measurements using the Zr-oxide DGT technique, the DGT units were exposed to 4 L solutions that contained 1 mg/L P (KH_2PO_4), 0.03 mol/L NaNO_3 and each model P compound, which are listed in Table 1, with the concentration of each model compound similar to P-PO_4^{3-} . Each solution was vigorously stirred at 23°C until the concentration of DRP became stable. The pH of the solution was maintained at 6.3 ± 0.1 . The DGT units were deployed in these solutions. Three units for each treatment were retrieved after a deployment time of 4 hr. The deployment times for the hexametaphosphate, adenosine 5' triphosphate and creatine phosphate treatments were prolonged to 62 hr. The accumulated mass of P in the binding gels was measured as mentioned above.

To determine whether the tested P compounds degraded during the elution process with 1 mol/L NaOH, each P solution for the DGT deployment was immediately collected after the retrieval of the DGT devices. The pH of the solution was adjusted to that of the 1 mol/L NaOH solution. The solutions were vigorously stirred at 20°C for 16 hr, as performed during the elution procedure. The concentration of DRP in each solution was detected using the miniaturized molybdenum blue method after adjusting the pH of the solution to a neutral value (~ 7).

1.4 Effects of various anions on the DGT measurement

To examine the possible interferences of various anions (Cl^- , SO_4^{2-} , HCO_3^- , AsO_2^- and AsO_4^{3-}) on the DRP measurements using the Zr-oxide DGT technique, the DGT devices were deployed in 4 L solutions that contained 1 mg/L P (KH_2PO_4) and 0.03 mol/L NaNO_3 mixed with increasing concentrations of Cl^- (1.1–105.8 g/L), SO_4^{2-} (1.5–16.2 g/L), HCO_3^- (11.8–816.7 mg/L), and AsO_2^- and AsO_4^{3-} (5×10^{-4} –1 mg As/L) at 20°C. The upper concentration limits for these ions were greater than those observed in typical natural waters (Kallay et al., 1993; Smedley and Kinniburgh, 2002). The DGT devices for each concentration treatment were retrieved in triplicate after a deployment time of 4 hr. The DRP loaded in the binding gel was eluted using 1 mol/L NaOH for 16 hr. The concentrations of DRP in the eluents were detected using an ICP-AES for the AsO_2^- and AsO_4^{3-} treatments and the molybdenum blue method for other treatments. The accumulated mass (M) of P in the binding gels was calculated using Eq. (2).

1.5 Effect of pH on the DGT capacity

To determine the effect of pH on the capacity of the Zr-oxide DGT technique, the DGT devices were deployed in 4 L solutions that contained 20 mg/L P (KH_2PO_4) and 0.03 mol/L NaNO_3 at different pH values (from 4 to 9). Before immersion of the DGT devices, the pH values of the solutions were initially adjusted to 4.0, 7.0 and 9.0. The solutions were vigorously stirred at 20°C for 3 days, and the pH of the solution was adjusted several times until it remained constant. The resulting pH values were 4.2, 7.1 and 9.2, respectively. The DGT devices at each pH treatment were retrieved in triplicate at different times varying from 2 to 72 hr. The accumulated mass of P (M) in the binding gels was calculated using Eq. (2).

The effects of pH on the binding efficiency of the gel were investigated by immersing the gel discs in 20 mL of KH_2PO_4 solutions that contained 20 mg/L P and 0.03 mol/L NaNO_3 . The pH value of the solutions was adjusted between 2 and 12 using dilute HCl and NaOH solutions. After stirring for 24 hr, the pH value of each solution was measured. The amount of DRP bound in the gels was calculated from the difference between the phosphate concentrations in the solutions before and after binding by

the gel discs.

1.6 Aging effect on DGT capacity

To examine the possible aging effect of the Zr-oxide binding gel on the capacity of the DGT technique, the DGT devices were assembled using three different types of Zr-oxide binding gels. One of the gels was freshly produced, and the other two gels were stored in a 0.03 mol/L NaNO₃ solution at a low temperature (2–4°C) for 1 and 2 years after production, respectively. The assembled DGT devices were deployed in 4 L solutions that contained 21 mg/L P (KH₂PO₄) and 0.03 mol/L NaNO₃ at a pH of 7.0 at 19°C. The DGT devices were retrieved in triplicate at different times varying from 2 to 25 hr.

1.7 Field performance of DGT in natural waters

To determine the performance of the Zr-oxide DGT technique for DRP measurements in natural waters, field deployments were performed in three freshwater sites located in Lake Taihu, Lake Chaohu and the Nanfei River. The location for each site is provided in **Table 2**. The piston-type DGT devices were deployed 50 cm beneath the surface of the water. To calculate the thickness of the diffusive boundary layer (DBL) for each site, the deployed DGT devices were assembled with diffusive gels of various thicknesses (Zhang et al., 1998; Panther et al., 2010). The DGT devices were retrieved after 4 days. The accumulated mass (*M*) of P in the Zr-oxide binding gels was used to calculate the concentration of DRP (*C*_{DGT}) in the waters using Eq. (1). Temperature, salinity and pH were measured every 12 hr *in situ* using a YSI water analyzer. Water samples were collected every 12 hr by pumping the water from the same depth. Each water sample was immediately filtered through a 0.45 µm cellulose nitrate membrane (Whatman) and was frozen before analysis. The concentrations of DRP in water samples were determined using the molybdenum blue method. The concentrations of SO₄²⁻ and HCO₃⁻ in selected samples were determined using an ion chromatographic method. The concentration of total As was determined using an ICP-MS.

2 Results and discussion

2.1 Effects of various interfering P compounds

In addition to inorganic orthophosphate, there are diverse P compounds present in natural aqueous systems. These compounds are generally classified as inorganic and or-

ganic P. Pyrophosphate and long-chain polyphosphate are inorganic P compounds that are commonly found in natural environments, whereas organic P compounds include various compounds such as orthophosphate monoesters, orthophosphate diesters (e.g., phospholipids and nucleic acids), phosphonates and organic polyphosphate (Cade-Menun, 2005). Moorleghem et al. (2011) reported that several organic P compounds were detected as DRP using the ferrihydrite-based DGT technique because of their hydrolysis during elution from the ferrihydrite binding gel with 1 mol/L HCl. In contrast to the ferrihydrite-based DGT technique, 1 mol/L NaOH solution was used as the eluent in the Zr-oxide based DGT technique. It is possible that some P compounds may hydrolyze during the alkaline elution process and contribute to the DRP measured using the DGT technique.

Among the 13 investigated P compounds, the concentrations of DRP measured by DGT (*C*_{DGT}) were nearly equivalent to those in the original solutions (*C*_{DRP}) for 10 of the added compounds, including hexametaphosphate, adenosine 5' triphosphate and creatine phosphate. The concentration ratios of these compounds (*C*_{DGT}/*C*_{DRP}) varied within 1.0 ± 0.1, which are values acceptable for DGT measurements (**Table 3**). Prolonging the DGT deployment time for the hexametaphosphate, adenosine 5' triphosphate and creatine phosphate treatments to 62 hr revealed that the masses of DRP measured using the Zr-oxide DGT technique also agreed with their corresponding theoretical predictions (**Fig. 1**), which further confirmed that these compounds had negligible effects on the DGT measurements of DRP despite the short deployment time used above.

The negligible effects of these compounds were consistent with their stability under strong alkaline conditions. When the solutions that contained these 10 P compounds were adjusted to a pH of 14 and stirred for 16 hr, which is a procedure that simulates the elution process, the resulting concentrations of DRP (*C*'_{DRP}) were consistent with those measured in the original solutions, with their ratios (*C*'_{DRP}/*C*_{DRP}) varying within 1.00 ± 0.10 (**Table 3**). This result implies that these P compounds remained stable or at least did not degrade into inorganic phosphate during the alkaline elution process because only this form of P can react with a molybdate reagent to produce a blue complex for spectrophotometric determination (Murphy and Riley, 1962). Consequently, these compounds did not contribute additional DRP to the DGT measurements.

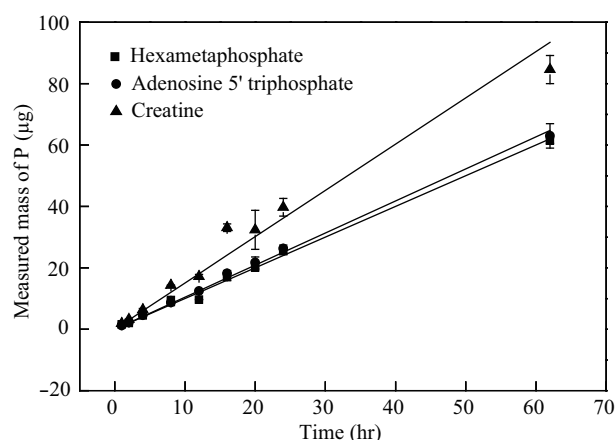
The concentrations of 4-nitrophenyl phosphate

Table 2 Basic information of sampling sites

Sampling sites	Salinity (‰)	pH	Temperature (°C)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	As (µg/L)
Lake Taihu (31°30'58.2''N, 20°11'20.7''E)	0.17	7.8	25.4	37.2	101.3	32.1	7.6
Lake Chaohu (31°38'6.9''N, 117°22'48.79''E)	0.14	7.6	23.1	24.4	132.6	35.9	1.9
Nanfei River (31°48'15.6''N, 117°23'7.4''E)	0.27	6.9	26.4	68.1	155.2	51.4	28.2

Table 3 Concentrations of DRP measured using the colorimetric method in P solutions without (C_{DRP}) and with strong alkaline coexistence (C'_{DRP}) and using the Zr-oxide DGT technique (C_{DGT})

Compounds	C_{DRP} (mg/L)	C'_{DRP} (mg/L)	C_{DGT} (mg/L)	$C'_{\text{DRP}}/C_{\text{DRP}}$	$C_{\text{DGT}}/C_{\text{DRP}}$
Sodium pyrophosphate	2.05	2.14	2.06	1.04	1.01
Sodium hexametaphosphate	1.48	1.41	1.53	0.95	1.03
Sodium polyphosphate	1.88	2.07	1.70	1.10	0.90
4-Nitrophenyl phosphate disodium	1.15	1.97	1.66	1.71	1.44
<i>myo</i> -Inositol hexakisphosphate	1.10	1.04	1.17	0.95	1.06
Adenosine 5' monophosphate	1.05	2.38	2.24	2.27	2.13
D-glucose-6-phosphate	1.24	1.72	2.20	1.39	1.77
L- α -phosphatidyl choline	1.12	1.19	1.10	1.06	0.98
Deoxyribonucleic acid	1.11	1.19	1.03	1.07	0.93
(R)-(-)-1,1'-Binaphthyl-2,2'-diyl-hydrogen phosphate	1.06	1.10	1.14	1.05	1.08
Creatine phosphate	2.05	2.06	2.16	1.00	1.05
2-Aminoethyl phosphonic acid	1.49	1.55	1.54	1.04	1.03
Adenosine 5' triphosphate	1.34	1.28	1.44	0.96	1.08

**Fig. 1** Accumulated masses of DRP in the DGT devices as a function of deployment time in solutions that contained 1 mg/L P and similar concentrations of hexametaphosphate, adenosine 5' triphosphate, and creatine. The straight line is the theoretical response calculated using Eq. (1).

disodium, adenosine 5' monophosphate, and D-glucose-6-phosphate (all belonging to the class of orthophosphate monoesters) measured using the Zr-oxide DGT technique were greater than those in the original solutions, and the $C_{\text{DGT}}/C_{\text{DRP}}$ ratios varied from 1.44 to 2.13 (Table 3). It could be demonstrated that these three compounds partially contributed to the DRP measured using the Zr-oxide DGT technique. The additional DRP measured using the DGT technique most likely resulted from the hydrolysis of these compounds during the elution process with 1 mol/L NaOH. This assumption was verified by the hydrolysis of 4-nitrophenyl phosphate disodium, adenosine 5' monophosphate, and D-glucose-6-phosphate under strong alkaline conditions (Table 3). The C'_{DRP} values of these compounds were significantly greater than those measured in the original solutions, with the ratios ($C'_{\text{DRP}}/C_{\text{DRP}}$) varying from 1.39 to 2.27. It is evident that these compounds should degrade into inorganic orthophosphate under strong alkaline conditions during the elution process and further contribute to the DRP

measured using the Zr-oxide DGT technique.

2.2 Effects of various anionic interferences

To satisfy the requirement that the binding gel should act as a zero sink for DGT measurements throughout the deployment period, the binding gel must adsorb the target analytes rapidly and irreversibly. Previous studies have investigated the binding kinetics of phosphate to the Zr-oxide gels and confirmed a rapid process for this uptake (Ding et al., 2010). In addition, the Zr-oxide binding gel has a high capacity to maintain the diffusion-adsorption process during the DGT deployment. However, the DGT response may change in the presence of various competing ions under field conditions. As the uptake of ions (primarily Cl^- , SO_4^{2-} , HCO_3^- , AsO_4^{3-} and AsO_3^{3-}) by hydrous Zr-oxide has been reported in published literature (Bortun et al., 2010; Hang et al., 2012), these ions may compete with DRP for binding sites in the Zr-oxide gel and decrease the rate or capacity for adsorbing DRP and may further affect the measurements of DRP using the Zr-oxide DGT technique.

To examine the possible interferences of the major competing ions on the DRP measurements using the Zr-oxide DGT technique, a series of experiments were conducted where the DGT units were deployed in 4 L solutions that contained 1 mg/L P (KH_2PO_4) and increasing concentrations of ions at 0.03 mol/L NaNO_3 and 20°C. Over the ion concentration ranges investigated, there were no significant differences between the concentration of DRP measured using the DGT technique, and the concentration of the original solution (C_{sol}), and their ratios were within the range of 0.9–1.1 (Fig. 2).

The observed minimal effects from Cl^- and SO_4^{2-} were caused by the high specificity of the hydrous Zr-oxides for phosphate. Chitrakar et al. (2006) reported that the distribution coefficient (k_d , the ratio of ion uptake by an absorbent to ion concentration in solution at equilibration) of phosphate in seawater by hydrous Zr-oxide is 1.3×10^5 mL/g, which is considerably greater than 0.4 mL/g for Cl^-

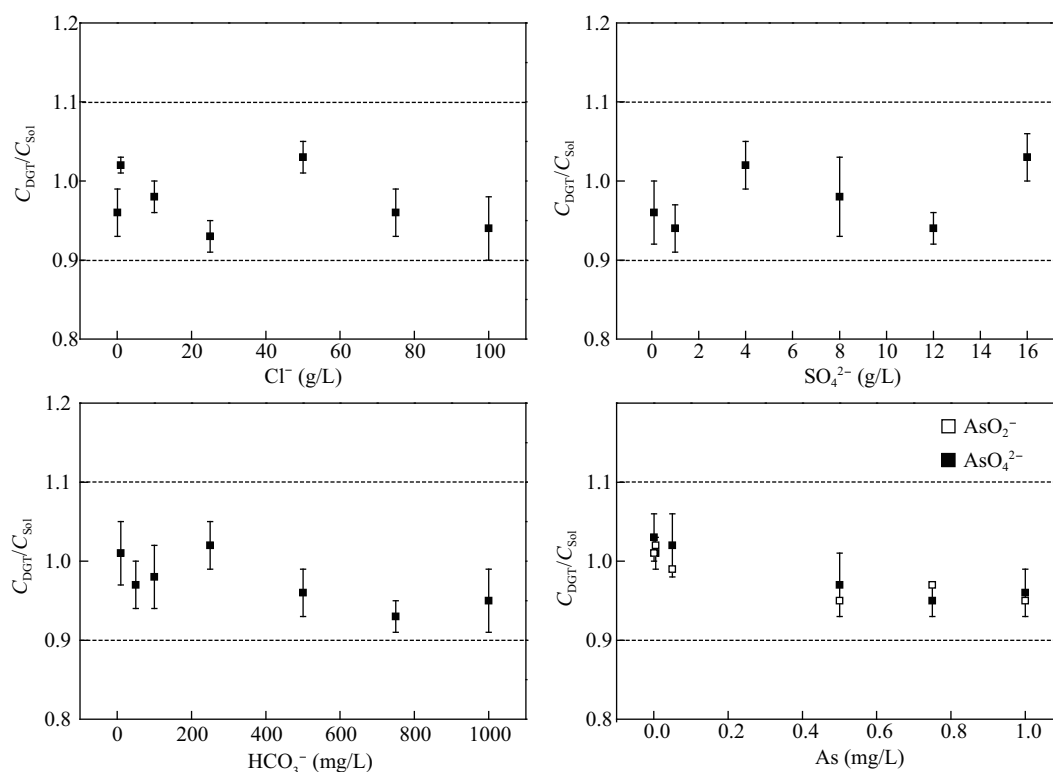


Fig. 2 DGT response under various ionic interferences. C_{DGT} and C_{sol} are the concentrations of DRP measured using the Zr-oxide DGT technique and the colorimetric method, respectively.

and 7 mL/g for SO_4^{2-} . Mason et al. (2008) and Panther et al. (2011) have examined the competitive effects of Cl^- (up to 1.5 and 47.9 g/L, respectively) and SO_4^{2-} (up to 0.6 and 5.4 g/L, respectively) on the DGT measurements of DRP using ferrihydrite- and metsorb-impregnated binding gels with the same result; however, Panther et al. (2011) observed a strong interference from HCO_3^- (up to 347.7 mg/L) for the ferrihydrite-impregnated binding gel. The upper concentration limits of Cl^- , SO_4^{2-} and HCO_3^- used in this study were considerably greater than those used by Mason et al. (2008) and Panther et al. (2011). Therefore, the tolerant concentration limit of these ions has been increased from previous reports for the DGT measurements of DRP.

The observed minimal effects of AsO_2^- and AsO_4^{3-} should be restricted to the conditions examined in this study. Because the hydrous Zr-oxide is known to have a high selectivity to adsorb both phosphate and inorganic As ions (Chitrakar et al., 2006; Bortun et al., 2010; Rodrigues et al., 2011; Hang et al., 2012), a competitive effect would appear in the DRP measurements using the Zr-oxide DGT technique when the concentrations of AsO_2^- and AsO_4^{3-} are continuously increased. Because the typical concentrations of As in freshwaters are less than 10 $\mu\text{g/L}$ and frequently less than 1 $\mu\text{g/L}$ (Smedley and Kinniburgh, 2002), its competition would not affect the DGT measurements of DRP in most cases. However, considerably higher concentrations of As (up to 5 mg/L) have been observed in groundwa-

ter and mine drainage waters (Smedley and Kinniburgh, 2002), and measurements using the DGT technique should be performed with caution in these situations.

2.3 DGT capacity under different pH conditions

Because a dependence on pH has been observed for the uptake of phosphate by hydrous Zr-oxide (Chitrakar et al., 2006; Rodrigues et al., 2011), the pH value should be a vital factor that influences the uptake of P by the Zr-oxide DGT. Therefore, the capacity of the Zr-oxide binding gel for the DGT deployment was examined at different pH levels (4.2, 7.1 and 9.2). The accumulated mass of DRP linearly increased with an increase of the deployment time during all pH conditions, which was in agreement with theoretical predictions using Eq. (1) (**Fig. 3a**). This trend remained constant for 72 hr under a pH of 4.2. However, notable deviations were observed under pH 7.1 and pH 9.2 when the deployment time exceeded 28 hr and 20 hr, respectively. The deviations revealed that the binding gel had reached saturation from the DGT uptake of DRP under conditions of pH 7.1 and 9.2. The Zr-oxide DGT capacity, which is defined as the greatest accumulated mass of P in the linear region, could be estimated as > 330, 130, and 95 $\mu\text{g P/cm}^2$ under the pH 4.2, 7.1, and 9.2, respectively. These values were considerably greater than those of the commonly used ferrihydrite (2 $\mu\text{g P/cm}^2$ at pH 7.0) (Zhang et al., 1998) and other recently developed binding gels (7–12 $\mu\text{g P/cm}^2$ under neutral pH conditions) for DGT

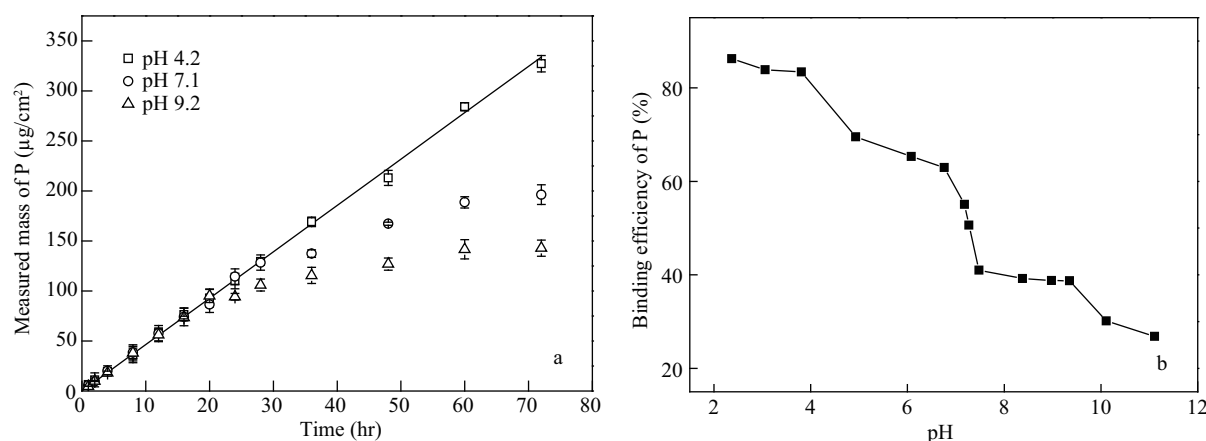


Fig. 3 Effects of pH on the DGT measurement of DRP (a) and the binding efficiency of the Zr-oxide gel for DRP (b). The straight line in (a) is the theoretical response calculated using Eq. (1).

measurements of DRP (Panther et al., 2010; Santner et al., 2010). The lowest capacity for the Zr-oxide DGT at pH 9.2 could be converted to a concentration of 17 mg/L in solution assuming a deployment time of 24 hr at 25°C with a 0.8 mm thick diffusive gel and a 0.14 mm filter, which considerably exceeds the concentrations of DRP in various natural waters. Consequently, the negative effect of pH would not affect the field use of this technique over the environmental pH range (4–9).

To clarify why the Zr-oxide DGT capacity decreased with the increase of solution pH, the uptake of phosphate by the Zr-oxide gel was investigated at different pH values (from 2 to 11). The result of this measurement revealed a strong dependence of the binding efficiency for phosphate by the Zr-oxide gel on the solution pH, and the binding efficiency decreased from greater than 85% at pH 2 to less than 10% at pH 11 (Fig. 3b). The decrease in the binding efficiency of the Zr-oxide gel was evidently responsible for the decrease in the Zr-oxide DGT capacity with the increase in the solution pH. The adsorption of phosphate on Zr-oxide primarily occurs through the formation of the outer sphere complex between the phosphate and hydroxyl groups within Zr-oxide (Chitrakar et al., 2006; Rodrigues et al., 2011). As the dominant phosphate species are H_2PO_4^- at pH 2–4 and HPO_4^{2-} at pH 6–10, a lower pH value causes the Zr-oxide surface to carry more positive charge and attract more charged monovalent H_2PO_4^- in solution. The surface charge of the adsorbent changes to a more negative value at higher pH, which results in electrostatic repulsion of the more negatively charged HPO_4^{2-} .

2.4 Aging effect

The binding efficiency of the Zr-oxide binding gel may vary with its storage time because of changes in reactivity of the impregnated binding agent. This change can affect the DGT measurements by changing the capacity of the binding gel for the DGT response. In this study, the possible effects because of aging on the Zr-oxide DGT technique were examined by comparing the performance

of the DGT that contained Zr-oxide binding gels that were stored for different periods after production (no storage and storage of 1 and 2 years). The accumulated mass of DRP linearly increased with the increase of deployment time for all of the binding gels when the deployment time reached 25 hr (Fig. 4). All of the data agreed with the theoretical predictions according to Eq. (1). Therefore, there was no evident aging effect on the Zr-oxide DGT capacity, and the Zr-oxide binding gel can be used for up to 2 years after production of the gel.

The ferrihydrite binding gel that is commonly used in the present DGT technique has a period of validity of 6 months (suggested by DGT Research Ltd.). A considerably shorter period of validity (38 days) was achieved by Luo et al. (2010) for DGT measurements of As using a precipitated ferrihydrite binding gel. The aging effects of the ferrihydrite-based DGT technique reflect the fact that the binding sites within the impregnated ferrihydrite in the gels decreased in number or reactivity with time. This decrease was attributed to the progressive conversion of ferrihydrite to goethite or hematite or a mixture of the two

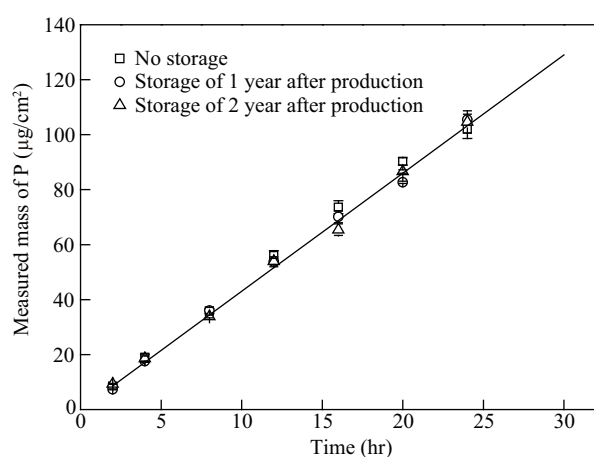


Fig. 4 DGT measured mass of DRP in the Zr-oxide gel as a function of deployment time using gels with different storage times. The straight line is the theoretical response calculated using Eq. (1).

(Luo et al., 2010). The fresh hydrous Zr-oxide used in this study would undergo intra- and inter-particle condensation reactions upon aging, which will result in a decrease in the sorption capacity due to the loss of free hydroxyl groups within the gel. However, examining the aging effect of the Zr-oxide gels using a very high concentration of P (21 mg/L) revealed that this binding agent is considerably more stable than ferrihydrite and has a much longer period of validity for the use of this technique.

2.5 Field performance of DGT in natural waters

The performance of the Zr-oxide DGT technique for the measurement of DRP in natural waters was examined by deploying the DGT units in three freshwater sites for 4 days. The basic information of each sampling site is provided in **Table 2**. The pH values in the waters were approximately 7.0, from which the DGT capacity for DPR measurements was estimated to be $130 \mu\text{g P/cm}^2$ (**Fig. 3a**). The greatest concentrations of dissolved Cl, SO_4^{2-} , HCO_3^- and As in these waters were considerably less than their upper concentration limits used for the investigation of their effects on the DGT measurements of DRP.

The concentrations of DRP measured using the molybdenum blue method (C_{sol} , with RSD) were $59.2 \pm 6.7 \mu\text{g/L}$ (11.3%), $87.6 \pm 9.8 \mu\text{g/L}$ (11.2%), and $210.3 \pm 38.5 \mu\text{g/L}$ (18.3%) for Lake Taihu, Lake Chaohu, and River Nanfei, respectively, while using the Zr-oxide DGT technique (C_{DGT}), the concentrations were $63.1 \pm 5.1 \mu\text{g/L}$ (8.1%), $83.1 \pm 5.2 \mu\text{g/L}$ (6.3%), $224.6 \pm 30.2 \mu\text{g/L}$ (13.4%), respectively. The concentrations of the C_{sol} were similar among the two lake water samples. The C_{sol} concentrations were considerably greater in the Nanfei River, which is likely the result of pollution from sewage input (Yin et al., 2011). The detected C_{DGT} was similar to the C_{sol} for each site. An ANOVA analysis (a Tukey HSD post-hoc test) revealed that there were no significant differences between the two techniques, which indicates that the Zr-oxide DGT technique can be used to accurately measure the concentration of DRP. The variation of C_{DGT} ranged from 6% to 13%, which is better than that of C_{sol} (11%–18%). This result demonstrates an advantage of DGT passive sampling relative to direct measurements, which provides a time-integrated mean concentration at a fixed sampling position, whereas the direct measurement is based on the use of spot samples with considerable variation.

The consistency of C_{DGT} with C_{sol} revealed that the hydrolysis from organic and other inorganic P compounds did not significantly contribute to the DRP measurements using the Zr-oxide DGT technique. This result may be due to a low proportion of these compounds in natural waters. Measurements using ^{31}P NMR indicated that the P species in a freshwater river and five freshwater lakes is primarily inorganic orthophosphate, and other P fractions observed in these waters are mainly orthophosphate monoesters and deoxyribonucleic acid, which represent less than 20% of

the total dissolved P (Cade-Menun et al., 2006; Reitzel et al., 2009). A comparison of the DGT measurement with ion chromatography and colorimetric methods also revealed that the P in surface water is mostly present as orthophosphate and phosphate sorbed onto inorganic colloids, and the fraction of organic P is negligible (Moor-legend et al., 2011).

3 Conclusions

Several organic P compounds (belonging to the class of orthophosphate monoesters) partly contributed to the DRP measured using the Zr-oxide DGT, but various tested anions (Cl^- , SO_4^{2-} , HCO_3^- , AsO_2^- and AsO_4^{3-}) had minimal effects on the measurement of DRP using the Zr-oxide DGT technique. Furthermore, it was observed that the pH of the solution significantly affected the capacities of the Zr-oxide binding gel in the DGT technique. The capacities of the Zr-oxide binding gel in the DGT technique for DRP measurements decreased with the increase of the solution pH (4.2, 7.1, 9.2), with the estimated values of >330 , 130, and $95 \mu\text{g P/cm}^2$, respectively, which were considerably greater than those of the ferrihydrite binding gel that is commonly used for DGT measurements of DRP. In addition, it was observed that no aging effect of Zr-oxide binding gel adversely affected its binding performance when the Zr-oxide binding gel was stored in a 0.03 mol/L NaNO_3 solution at a low temperature (2–4°C) for 2 years. The concentrations of DRP measured using the Zr-oxide DGT technique agreed with those measured directly by the colorimetric method in three freshwater samples. The results provided evidence that the new zirconium oxide-based DGT technique is a promising, reliable and robust tool for *in situ* measurements of DRP in the environment.

Acknowledgments

This study was sponsored by the National Natural Scientific Foundation of China (No. 41001334, 41001325), the Project of Knowledge Innovation for the 3rd period, the Chinese Academy of Sciences (No. KZCX2-YW-JS304), and the Natural Scientific Foundation of Jiangsu Province, China (No. BK2010606).

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Journal of Environmental Sciences (Established in 1989)

Vol. 25 No. 8 2013

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences		Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Distributed by	
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CN 11-2629/X	Domestic postcode: 2-580		Domestic price per issue RMB ¥ 110.00

ISSN 1001-0742

