Simultaneous sampling of phosphate, arsenate and selenate in water by Diffusive Gradients in Thin Films (DGT)

Foto: Bjørn Faafeng

Norwegian Institute for Water Research

– an institute in the Environmental Research Alliance of Norway

REPORT

Title		Serial No.	Date
Simultaneous sampling of phosphate, arsenate, and selenate in water by Diffusive Gradients in Thin Films (DGT)		4918-2004	08.12. 2004
		Report No. Sub-No. 24258.02	Pages Price 17
Author(s) Oddvar Røyset, Susanne Eich-Greatorex, Trine Aulstad Sogn, Åsgeir Rossebø Almås, Eivind Bjerke		Topic group Analytical chemistry	Distribution Open
		Geographical area	Printed NIVA

Client(s)	Client ref.
Department of Plant and Environmental Sciences, Agricultural University of Norway, P.O. Box 5003, N-1432 Ås, Norway	

Abstract

The DGT sampler was studied for simultaneous collection of phosphate, arsenate, and selenate in water. The DGT-based diffusion coefficients found were somewhat lower than the theoretical ones for free diffusion in water, but similar to what has been found earlier for phosphate and arsenate in diffusion cell experiments with the DGT membrane. Our results indicate that D sampler with the ferrihydrite adsorbent functions adequately as an adsorbent for phosphate, arsenate, and selenate in water, and may thus be used for simultaneous sampling of these three ions in water. The good performance for arsenate fills a gap in the DGT toolbox for passive sampling of high-priority trace elements, while it for selenate may prove very useful for assessing the potential for Se deficiency or toxicity in soil water.

4 keywords, Norwegian	4 keywords, English
1. DGT	1. DGT
2. P, As, Se,	2. P, As, Se,
3. Vann	3. Water
4. Prøvetaking	4. Sampling

Project manager

Research manager

Head of research department

Simultaneous sampling of phosphate, arsenate and selenate in water by Diffusive Gradients in Thin Films (DGT)

Preface

This study of Diffusive Gradients in this Films (DGT) for simultaneous sampling of phosphate (P), arsenate (As) and selenate (Se) in water, was performed in cooperation between Norwegian Institute for Water Research (Oddvar Røyset and Eivind Bjerke) and Department of Plant and Environmental Sciences (IPM), Agricultural University of Norway, P.O. Box 5003, N-1432 Ås, Norway (Susanne Eich-Greatorex, Trine Aulstad Sogn, Åsgeir Rossebø Almås), in October -December 2003.

NIVA prepared the DGT samplers, provided the DGT testchamber and the analysis of the exposed DGT by HR-ICPMS. IPM prepared the test solutions and performed the laboratory tests of the DGTs.

Oslo, 06.12.2004

Oddvar Røyset

Contents

Summary

For in-situ collection of cationic forms of labile metal ions in water, the technique of diffusive gradients in thin films (DGT), using a chelating cation-exchange resin adsorbent, has become important. For anions, only few studies have been conducted, mainly due to a lack of suitable anion-selective adsorbents. Ferrihydrite ($Fe(OH)_3$) has proved to be useful for phosphate and recently also for arsenate. In this study, we examined the potential of DGT samplers equipped with a ferrihydrite adsorbent for simultaneous collection of phosphate, arsenate, and selenate in water at two different pH values, i.e., 5 and 6. The uptake of all three ions was satisfactorily linear with time up to 3 days, whereas the uptake rate decreased slightly between 3 and 10 days exposure. The DGT-based diffusion coefficients (D_{DGT}) varied between 4 and $7*E$-06 $cm^2\,sec^{-1}$ (25 ^{o}C) for each of the three compounds. These D_{DGT} values are lower than the theoretical ones for free diffusion in water (i.e., 8.5 to 9.5 E-06 $cm^2\,sec^{-1}$), but similar to what has been found earlier for phosphate and arsenate in diffusion cell experiments with the DGT membrane. So far, no D_{DGT} values have been published for Se. We achieved acceptable 24 h detection limits (LOD 24h) of 2.5, 0.3, and 0.05 ng mL-1 for P, As, and Se, respectively. Our results indicate that the ferrihydrite adsorbent functions adequately as an adsorbent for phosphate, arsenate, and selenate in water, and may thus be used for simultaneous sampling of these three ions in water. The good performance for arsenate fills a gap in the DGT toolbox for passive sampling of high-priority trace elements, while it for selenate may prove very useful for assessing the potential for Se deficiency or toxicity in soil water.

1. Introduction

The technique of diffusive gradients in thin films (DGT), developed by Davison and Zhang (Davison and Zhang, 1994) for passive sampling of labile metal ions in aquatic environments, has proved to be useful on account of its simplicity and wide applicability. While diffusive passive samplers have become common for measurements of gases in air over the last 20 years, the DGT sampler is the first diffusive passive sampler for ions in water that takes full advantage of diffusion theory for calculations of time-averaged concentrations. Additionally, the diffusive properties are quantifiable to such an extent that accuracies in the order of 10 to 20 % can be achieved (Zhang and Davison, 1995). Since the DGT technique is based on diffusion of ions through a rather narrow-pored hydrogel, it may also serve as a speciation tool, permitting measurements of labile metal ions in solution. By 2004 more than 50 studies involving the technique have been published, where most focus have been on the high priority heavy metals Cu, Zn, Cd, Pb, Ni, and Cr, and the reactive trace metals Mn and Fe (see Davison et al. (2000) for an overview). Recently we have shown that the DGT sampler equipped with the Chelex adsorbent simultaneously collect 24 metals quantitatively and have promising properties for additional 8 elements (Røyset et al 2003).

The Chelex adsorbent is a general-purpose chelator with high selectivity for a large number of divalent and trivalent metal cations. It works well both in fresh water and in seawater with high concentrations of the major element cations Na, K, Ca, and Mg. While the DGT technique is widely used for metal cations, only few studies have so far been published on the collection of anionic compounds (Zhang et al. 1998, Fitz et al. 2003). General-purpose adsorbents with high selectivity for a broad range of anions are scarce. For instance, anion exchangers usually have both low binding strength and low selectivity for potential target ions compared to major matrix ions such as chloride. Therefore, it has been necessary to develop more specific adsorbents. An important requirement is that the adsorbent must be in a chemical form that does not dissolve during exposure. For sulfide ions, silver iodide (AgI) precipitates have proved useful (Teasdale et al. 1999). A gel, impregnated with a suspension of ferrihydrite ($Fe(OH)_3$) colloids, has proved to be an efficient adsorbent for phosphate ions, as phosphate forms stable precipitates with iron/iron hydroxide (Zhang et al. 1998) . Similarly, oxidized inorganic As species may bind strongly to iron hydroxides, e.g., in sediments, and a recent study showed promising results using the ferrihydrite adsorbent for sampling of arsenate in water (Fitz et al. 2003). Both As and Se exhibit several oxidation states in natural systems. In oxidized environments, the most common inorganic species of As are arsenite (As(III), $H_xAsO_3^{(3-x)-}$) and arsenate (As(V), $H_xAsO_4^{(3-x)-}$), and of Se selenite (Se(IV), $H_xSeO_4^{(2-x)-}$) and selenate (Se(VI), $H_xSeO_4^{(2-x)-}$). Additionally, organic species of both Se (Se(-II)) and As (As(-III)) may be present. Among the inorganic Se species, selenite seems to bind more strongly to iron hydroxides than selenate (McBride, 1994, Hamdy et al.1977).

Phosphate, arsenate, and selenate are anions important for either nutrient uptake or toxicity studies in soil and water systems. A sampler for free phosphate ions may be useful for both plant nutrient studies in agriculture and for assessing the growth potential of algae in aquatic systems. In the case of arsenate, the ferrihydrite adsorbent may help to complete the "toolbox" for passive sampling of high-priority trace elements using the DGT technique, as the Chelex-based DGT sampler works well for Pb, Cd, Cu, Zn, Ni, and Cr(III). Selenium is characterized by a narrow concentration range between potential deficiency and toxicity in crops for animal or human consumption. Thus, a sampler that is able to detect dissolved oxidized forms of Se ions in soil pore water, may become very useful. Moreover, one of the advantages of the DGT sampler is the possibility to time-integrate the concentration of bioavailable ions (Zhang et al. 2001), which is a useful property for predicting biological effects (Almås et al. 2004). Plants take up Se predominantly in the inorganic oxidized forms

selenate and selenite, although also organically bound Se, e.g., Se-methionine, may be taken up (Terry et al. 2000). Due to less effective binding to hydroxides, selenate is usually the main inorganic Se form available for plant uptake (Singh, 1991), but the extent of Se uptake also depends on the presence of competing ions such as sulfate for selenate and phosphate for selenite (Hopper et al 1999). A passive sampler, collecting selenate and/or selenite, may thus become a useful tool for predicting the potential bioavailability of Se, especially under aerobic soil conditions.

It is beyond the scope of this work to cover all As and Se species that may occur in water and soil systems, or to fully describe all speciation issues necessary to understand the potentials for adsorption to an adsorbent such as ferrihydrite. Neither can all environmental implications related to plant uptake and toxicity be considered. From the discussion above, however, it should be clear that there is no straightforward solution to designing an adsorbent which can collect all inorganic oxidized species of As and Se in water. While ferrihydrite seems to be a useful DGT adsorbent for sampling of phosphate (Zhang et al. 1998) and arsenate (Fitz et al. 2003), no studies using the DGT technique for sampling of Se species in water have been published. So far, ferrihydrite is the only DGT adsorbent commercially available with potential for simultaneous collection of the anionic species of these three elements in water. The aim of our work was

    i)   to study the performance of this adsorbent for simultaneous sampling of phosphate, arsenate, and selenate and

    ii)   to determine diffusion coefficients of phosphate, arsenate, and selenate, if the performance was satisfactory.

We first need to establish basic knowledge of uptake rates of the sampler by determining DGT-based diffusion coefficients (D_{DGT}), which we achieve in a laboratory test system (Røyset et a.,l 2003). These diffusion coefficients are directly related to the use of the sampler and are more relevant than those achieved from diffusion cells or from thermodynamic data because they also include the actual uptake of an ion by the adsorbent. Recent developments of plasma-chemical analysis methods (High Resolution Inductively Coupled Plasma Mass Spectrometry -HR-ICP-MS) facilitate simultaneous determinations of P, As, and Se with high sensitivity and selectivity. We examined this technique for the development of efficient multi-element analysis methods of these elements collected by the sampler.

2. Material and methods

2.1 Theory – diffusion

Here, we will only give a short overview over some important aspects of diffusion with respect to DGT experiments. For more detailed information on diffusion theory we refer to textbooks such as Cussler's excellent monograph (Cussler, 1997). The principle of diffusive sampling relies on the formation of a steady-state concentration gradient and diffusion-controlled mass transport across a diffusive membrane. Fick's first Law of diffusion describes the flux of molecules (dm/dt) along a concentration gradient (dC/dz) where D (cm^2 sec^{-1}, specific for each ion) is the coefficient of diffusion (eq 1).

$$Flux = \frac{dm}{dt} = -D \cdot \frac{dC}{dz} \qquad (1)$$

If the sampler adsorbent is an efficient sink for ions (i.e., the concentration of ions at the adsorbent surface approximates zero and no back-diffusion occurs), time-integrated mass uptake at time t (m(t) can be determined from eq 2:

Time-integrated uptake $$m(t) = Co \cdot t \cdot D \cdot \frac{A}{L} \quad (2)$$

where Co is the concentration of ions outside the sampler, while the terms, L (the thickness) and A (the cross section area of the diffusion membrane), are constants which are specific to the design of the passive sampler. For calculation of time-averaged concentration of ions outside the sampler during passive sampling, eq 2 is solved for Co (eq 3).

Time-averaged concentration $$Co = \frac{m}{t} \cdot \frac{L}{DA} \quad (3)$$

For any particular passive sampler, the L term in eq 3 needs to comprise the total thickness of the diffusion layer by taking into account the special geometric design and sampling properties. In our study, L includes the thickness of the gel diffusion membrane (G, mm), the filter (f, mm), and the diffusive boundary layer (δ, mm), thus forming eq 4.

Time-averaged concentration $$Co = \frac{m}{t} \cdot \frac{(G + f + \delta)}{DA} \quad (4)$$

The thickness of the diffusive boundary layer depends on water flow rate along the membrane surface and distance from the edge of the surface. We developed a model4 which estimate it to 0.1 mm in the middle of the sampler's window at a water flow rate of 10 cm sec^{-1}. For the DGT units used in our experiments, the dimensions of these terms are G=0.80, f=0.12 and δ=0.10 mm, respectively, so that L=(G+f+δ) equals 1.02 mm.

The DA/L term in eq 2 represents the uptake rate factor (cm3 sec^{-1}). For metal ions with typical D values of 5E-6 cm^2 sec^{-1}, uptake rates are in the order of 12 mL per 24 h at 25 $^{\circ}$C (using the typical DGT sampler dimensions for L and A (Røyset et al. 2003). The uptake rate is here defined as the volume of water "diffusively emptied" of ions per unit of time.

The constants G, f, δ, and A in eq. 4 and the analytical results obtained for m and Co at time t (samples withdrawn at the different exposure times, see later) were used as input parameters when calculating D for As, Se and P. Diffusion coefficients are also temperature-dependant, during the experiments the temperature is recorded and corrected (Røyset et al. 2003). Similarly to Li and Gregory (2002), we used diffusion coefficients estimated from property-limiting equivalent conductance (LEC), based on data tabulated by Robinson and Stokes (1959), for comparison. Additionally, we compared the results with data from diffusion cell experiments.

2.2 DGT experiments

Regular DGT moldings made of polyethylene were used (DGT Research Ltd, Lancaster, UK). The adsorbent was composed of an agarose polyacryalamide (APA) hydrogel (0.4 mm) doped with ferrihydrite (Fe(OH)$_3$) colloids, while an open pore APA diffusion membrane (0.8 mm), both supplied by DGT-Research., were used. On top of the diffusion membrane a 0.45 µm membrane filter (Millipore polysulfone) was placed for protection.

In our study, we determined the adsorption of phosphate, arsenate, and selenate by the ferrihydrite adsorbent at two different pH values, 5 and 6, representing common pH conditions in water and soil

systems. The DGT units were exposed to the respective test solution for 1, 3, and 10 days at a room temperature of 20°C.

The exposure chamber, which has been described earlier (Røyset et al. 2003), were filled with 50 L 0.01 M $NaNO_3$ (p.a. Merck), and spiked with commercially available plasma-chemical calibration solutions (High Purity Standards (HPS), Charleston, USA) at 1000 µg mL^{-1} each of the ionic forms PO_4^{3-}, AsO_4^{3-} and SeO_4^{2-} to obtain 10 ng mL^{-1} final concentration of As, P, and Se. After mixing, the pH of the two test solutions was adjusted to near 5 and 6, respectively, by adding ultra pure NaOH. The pH was recorded during the course of the experiment. The water used in all steps was deionized water from a Millipore MilliQ system. The exposure chamber was equipped with rotors of 20 cm in diameter, connected by a shaft to an electric motor on top of the chamber. The rim of the rotor plate allowed for up to twelve assembled DGT units to be fixed, and the periphery velocity of the plate was fixed to 0.1 m sec^{-1} during the experiment. The latter was to ensure a constant water fluid velocity and thus a predictable diffusive boundary layer for all DGT units.

2.3 Sampling of test solutions and DGT units

To check possible experimental artifacts, such as loss of elements due to surface adsorption or an unsustained rate of element supply to maintain a constant concentration adjacent to the DGT-membrane surface, solution samples were taken at the start, and after 1, 3, and 10 days. We used a size charge fractionation procedure, collecting three types of samples: total (T), filtered (F, 0.45 µm Millipore filter) and filtered / cation-exchanged (FCE). This procedure resulted in the following three fractions: particles/colloids (P = T-F), cationic labile ions (L = F-FCE) and anionic forms (FCE), and may describe precipitation processes (formation of particles/colloids) as well as ensuring that the added species stayed in the anionic form. The solution samples were preserved with nitric acid (0.5 % vol/vol), and element concentrations determined by HR-ICP-MS.

After exposure, the ferrihydrite gels from the DGT units were eluted with 1 mL concentrated nitric acid (high purity quality, Merck Suprapure 65 %), mixed, left overnight, and then diluted with water to a final volume of 10 mL. Some dissolved gel precipitated when water was added. To avoid clogging problems during analysis, the samples were left to settle, and then the clear solution was decanted off.

2.4 HR-ICP-MS analyses

Element concentrations in the extracts and the samples from the test solution were determined by HR-ICP-MS (Thermo Finnigan Element 2). We developed a method based on our experience with a 57 element procedure optimized for environmental analysis of water, biota and sediments, as described earlier (Røyset et al. 2003). For the analysis of the ferrihydrite extracts, the method comprised most major elements (to gain information of possible matrix effects), and P, As, and Se (medium resolution for P31 and high resolution for As75 and Se77/Se82). The acidity of the calibration solutions was similar to that of the extracts from the DGT-samples or from the water samples.

3. Results and Discussion

3.1 Performance of HR-ICP-MS analyses

Expected major components in the extraction solution of the adsorbents are Fe (from the ferrihydrite), C (from the dissolved membrane) and other constituents of the adsorbent or the membrane. Typical concentrations of major components in the 10 mL extracts were (in $\mu g\ mL^{-1}$): Fe (40-50), C (10-30), Na (5-10), Ca (0.1-0.2), K (0.05), Mg (0.01-0.03), Al (<0.01), and Mn/Cu/Zn (<0.005). Carbon may affect the determination of As, but only at considerably higher concentration than those encountered here. The results above indicate that the extracts of the ferrihydrite adsorbent cause few interference problems when using well-designed HR-ICP-MS procedures.

3.2 Stability of the anionic compounds in the test solutions

The control measurements of the test solutions are shown in Table 1. All measurements of P, As, and Se in the total fraction (T) were between 9 and 11 $ng\ mL^{-1}$, with an average just above 10 $ng\ mL^{-1}$. The filtered (F) and filtered plus cation-exchanged (FCE) fractions were also in the same range as the total fraction (T). All the three fractions were very similar, indicating that no serious wall adsorption, precipitation, or contamination problems were encountered during the experiments. Since the size charge fractionation results showed that all the phosphate, arsenate, and selenate ions passed the filter plus the cation exchanger, it is likely that phosphate, arsenate, and selenate all stayed in the anionic form. For the estimation of the diffusion coefficients we used the average concentration from all the three fractions, since all were very similar.

3.3 Elution efficiency

Dilute sulphuric acid (approximately 0.5 M) has been recommended for elution of the ferrihydrite adsorbent, when applying the molybdate blue colorimetric method for determination or phosphate[5]. For plasma-chemical methods, nitric acid is a more convenient matrix than sulphuric acid. With concentrated nitric acid, we achieved high and reproducible elution efficiencies (95 to 99 %) for the Chelex adsorbent (Røyset et al. 2003). Therefore concentrated nitric acid was also used for the elution of the ferrihydrite adsorbent. The stability of phosphate, arsenate, and selenate complexes with iron (III) is very low at a pH near 0 (Lindsay, 2001), because the anions are fully protonated (i.e., H_3PO_4, H_3AsO_4, and H_2SeO_4). Thus, it is reasonable to assume 100 % elution efficiency when using concentrated nitric acid.

3.4 Detection limits and precision

The instrumental detection limit of HR-ICP-MS is in the range of 0.01 to 0.1 $ng\ mL^{-1}$ for P, As, and Se, at the instrumental resolutions used: P31(MR), As75(HR) and Se77(HR). The blank values for P were satisfactorily stable (Table 2) but higher (68 ±11 $ng\ mL^{-1}$) than expected, possibly due to contamination of the adsorbent or the equipment used. The blanks of 0.6 $ng\ mL^{-1}$ ±0.24 for As and 0.3 $ng\ mL^{-1}$ ±0.24 for Se, were satisfactorily low. These values corresponded to a limit of detection (LOD) normalized to 24 h exposure (24 h LOD) of 2.5, 0.032, and 0.054 $ng\ mL^{-1}$ for P, As, and Se, respectively. The 24 h LOD for P is appropriate for eutrophic waters, but somewhat high compared to the requirements for determination of phosphate in oligotrophic waters (1 $ng\ P\ mL^{-1}$ is needed), while the LODs for As and Se are more satisfactory compared to normal environmental requirements. Se concentrations (19) in river waters in low-Se regions are usually in the range < 0.002-0.11 $ng\ mL^{-1}$, and As concentrations in non-polluted river waters (Schwertmann et al 1989) are usually between 0.1 and 0.2 $ng\ mL^{-1}$.

Additionally, re-examining of the possible contamination source, may reduce the high blanks observed here especially for P, and increasing the exposure time is another way to get lower LODs (Table 2). The sampling precision with standard deviations between 10 and 20 % is in the same range as found earlier for the Chelex-based DGT for metals (Røyset et al. 2003).

Table 1.
Determination of P, As, and Se in the test solution of the exposure chamber over the   experimental period of 10 days, using a size charge fractionation (SCF) procedure yielding   total (T), filtered (F), and filtered plus cation-exchanged (FCE) concentrations

Size charge	Exposure time (h)	pH 5.1			pH 6.3		
		P	As	Se	P	As	Se
T	0	10.8	10.9	10.9	10.2	11.6	11.4
F	0	11.6	11.2	10.8	10.8	11.2	10.8
FCE	0	11.4	11.1	11.4	11.0	11.3	11.1
T	24	11.2	11.1	10.6	10.3	10.7	11.7
F	24	11.5	11.3	11.0	10.5	11.0	10.2
FCE	24	11.1	11.2	11.4	10.7	11.1	11.3
T	72	10.4	11.4	11.7	10.8	10.9	11.1
F	72	10.6	11.4	11.4	11.0	11.6	10.6
FCE	72	10.3	11.2	10.4	11.2	11.2	10.6
T	240	9.7	11.2	11.3	10.5	10.9	10.3
F	240	8.9	11.4	10.6	10.1	10.9	10.9
FCE	240	9.2	10.9	11.1	10.8	11.1	11.8
Average		10.7	11.1	11.0	10.6	11.2	11.0
SD		0.3	0.2	0.5	0.9	0.2	0.4

Concentrations are in ng mL^{-1}.

Table 2.
P, As, and Se contents of the ferrihydrite adsorbent membrane from unexposed DGT units, and estimated detection limits

	Content [a]		Limit of detection (LOD) [b]	
	Ave (ng)	SD (ng)	24h (ng ml^{-1})	7d (ng ml^{-1})
P	68	11	2.5	0.3
As	0.64	0.14	0.032	0.005
Se	0.31	0.24	0.054	0.008

[a]   Total amount extracted from unexposed membranes in ng per membrane (7 replicates).
[b]   The LOD 24h (7d) is calculated by eq 4 based on three times the standard deviation of the
    blanks and an exposure time of 24h (7d), using our D_{DGT} diffusion coefficients in Table 3.

3.5 Sampling capacity and exposure time considerations

The surface charge of Fe-oxides changes with pH, and the point of zero (PZC) charge ranges between pH 7 and pH 9. It is known (Sager 2002), however, that specific ion adsorption of polyvalent anions such as HPO_4^{2-} may reduce the PZC down to near pH 5. Although the latter effect is not investigated here, we suggest it to be of minor importance since the element concentrations used are low (in the range of 10 nmol L^{-1}). Since the pH of the exposure solution in this experiment was controlled to be near 5 and 6, surface charge of the Fe-oxide is most likely positive in the form of $Fe(OH)_2^+$.

Zhang and Davison (1998) found a capacity of 6-7 µg of P per membrane of this type (ie about 0.2 µmol of P). We do not have other capacity data for the ferrihydrite adsorbent, but the following assumptions can be made: The 10 mL extracts from single adsorbent membranes contained about 50 µg mL^{-1} of Fe (see data for major elements in the membrane extracts above), i.e 500 µg per membrane (about 9 µmol Fe). Assuming that each Fe atom yield one $Fe(OH)_3$ unit, the maximum possible absorption sites of the membrane are 9 µmol. According to the measured capacity of about 0.2 µmol above, only about 2 % of the $Fe(OH)_3$ units are available as adsorption sites ($Fe(OH)_2^+$ units).

The DGT units were exposed to a concentration of 10 ng mL^{-1} of P, As and Se which sums up to about 0.5 nmol mL^{-1} (0.0005 µmol mL^{-1}). At this concentration and a capacity of about 0.2 µmol, the adsorbent may theoretically collect ions from a volume of about 400 L before saturation. At a sampling rate of approximately 50 mL day^{-1} (about 15 mL per day per ion), we may estimate a total exposure time of 8 days before overloading.

However, if we consider phosphate alone at 10 ng ml^{-1}, we may estimate (0.2µmol / 0.0003µmol) a capacity of about 600 L, which at a sampling rate of 15 mL day^{-1}, equal to a total exposure time of about 40 days. Since phosphate in most situations is the dominating ion (most often 10-100 times higher than As and Se), the maximum exposure time is controlled by this ion. Based on these assumptions we can recommend deployment times from 1 to 4 weeks, which must be adjusted to the expected free phosphate concentration at the tested site.

3.6 Calculations of diffusion coefficients

Diffusion coefficients have been estimated with diffusion cell experiments (Fitz et al. 2003, Teasdale et al. 1999), or calculated based on LEC data (Li and Gregory, 2002). Diffusion coefficients based on LEC express free diffusion in water without the restriction imposed by a gel membrane. Using diffusion cell experiments, we get data for diffusion through the membrane, and the diffusion coefficient includes the restriction to diffusion by the membrane.

The diffusion coefficients obtained from our laboratory study represent a combination of the diffusion rate of ions through the diffusive gel membrane and the binding ability of the receiving adsorbent. The coefficients are therefore most precisely denoted as DGT-effective diffusion coefficients (D_{DGT}). For elements, for which the adsorbent is not 100 % efficient, back-diffusion may occur and the D_{DGT}-value obtained will be lower than diffusion coefficients calculated from LEC data (D_{LEC}) or measured in diffusion cells (D_{DC}). With the approach used in this study, it is difficult to establish reliable diffusion coefficients for elements with substantial back-diffusion, Previously (Røyset et al. 2003) we concluded that the resistance in the diffusive gel was about 10 to 15 % based on the fact that D_{DGT} values were 10 to 15 % lower than D_{LEC}-values for elements with an expected quantitative absorption. Thus, if D_{DGT}-values are 20 % lower than D_{LEC}-values, we may assume that a substantial back-diffusion occurs that prevents quantitative absorption. We therefore suggest that exposure tests with ferrihydrite loaded in DGT molders are most appropriate for determining diffusion coefficients related to the DGT-technique. Such "conditional" diffusion constants show which elements are quantitatively adsorbed by the sampler's adsorbent. Data from diffusion cells or LEC calculations are necessary for evaluating if

absorption is quantitative. However, the DGT sampler may still be useful even if absorption is not quantitative. Provided that both absorption and back-diffusion are linear with time, the sampler will collect and accumulate ions, but the sampler then becomes a more qualitative sampling tool.

Table 3.
Diffusion coefficients (D_{DGT}) as determined after 24, 72, and 240 h (1, 3 and 10 d) exposure of DGT units, equipped with a ferrihydrite adsorbent, in the test chamber, and compared to literature data from diffusion cell experiments (D_{DC}) or limiting equivalent conductance (D_{LEC}).

	pH 5.1						pH 6.3					
Species *a*	$H_2PO_4^-$		$H_2AsO_4^-$		SeO_4^{2-}		$H_2PO_4^-$		$H_2AsO_4^-$		SeO_4^{2-}	
Ave/RSD *b*	Ave	RSD	Ave	RSD	Ave	RSD	Ave	RSD	Ave	RSD	Ave	RSD
D_{DGT} 24 h	7.35	7.1	5.34	1.2	5.86	3.6	5.63	12.7	4.96	15.0	5.15	18.6
D_{DGT} 72 h	5.65	15.7	4.60	16.3	5.28	14.9	6.35	25.4	5.60	25.7	6.17	22.4
D_{DGT} 240 h	4.93	14.4	4.27	13.5	4.87	9.5	5.32	15.1	4.61	18.7	5.05	14.6
D_{DGT} Mean	5.98	20.8	4.74	11.6	5.34	9.3	5.46	9.2	5.05	20.5	5.46	11.4
D_{DC} *c*	6.05		5.92				6.05		5.92			
D_{LEC} *d*	8.46		9.05		9.46		8.46		9.05		9.46	

a   Predominant form of the added P, As and Se at the pHs during the tests.
b   The statistics for Ave(rage) and RSD are based on three replicates.
c   Earlier D_{DC} values for phosphate6 and for arsenate7
d D_{LEC} data from Robinson and Stokes16. The data represent the species $H_2PO_4^-$ for P, $H_2AsO_4^-$ for As, and SeO_4^{2-} for Se.

Table 3 shows the diffusion coefficients obtained in this study, as well as literature data from LEC calculations and values determined by diffusion cell experiments with the same type of APA hydrogel as used in our DGT experiments. Our D_{DGT}-values are similar to D_{DC}-values for phosphate (Zhang et al. 1998) and for arsenate (Fitz et al 2003). The closest agreement is achieved for phosphate, where the figures for D_{DGT} (5.98 at pH 5 and 5.76 at pH 6) and for D_{DC} (6.05) are within the experimental error. For arsenate, the deviation between D_{DGT} (5.34 at pH5 and 5.35 at pH6) and D_{DC} (5.92) is larger. For selenate, no D_{DC}-values have been published so far, while the LEC value is 9.46 E-06.

The D_{LEC}-values for phosphate, arsenate, and selenate reported in Table 3 are in the range of 8.5 to 9.5E-06 cm^2 sec^{-1}, and are thus 20 to 50 % higher than our D_{DGT} values. There may be several explanations for this:

Firstly, all the three elements are oxyanions of di- and three-protic acids, for which diffusion coefficients decline with increasing degree of protonation. Diffusion is an ionic property that first of all depends on molecular size (the larger the ion, the larger the resistance to movement through the solvent).

Secondly, ionic species interact with polar solvents such as water, i.e., the larger the charge/size ratio, the larger the interaction and resistance to movement. The latter is very important for cationic species,

but to a smaller extent also for anions, as interactions between anions and water molecules are weaker than those for cations. There is little knowledge about the pH dependence of diffusion coefficients of these polyprotic anionic species, but Robinson and Stokes (1959) have reported separate D_{LEC} data for $H_2PO_4^-$ and HPO_4^{2-}, i.e., 8.46E-06 ($H_2PO_4^-$) and 7.34E-06 (HPO_4^{2-}), showing that higher ionic charge reduces the diffusion coefficient. The pK values of orto-phosphoric acid of 2.12 (pK_1 for $H_3PO_4^-$ /$H_2PO_4^-$), 7.21 (pK_2 $H_2PO_4^-$/HPO_4^{2-}), and 12.4 (pK_3 HPO_4^{2-}/PO_4^{3-}) show that H_2PO_4- is the dominating ionic species of phosphate between pH 5 and 6, so that a comparison with a diffusion coefficient of 8.46E-06 is the most reasonable. For arsenic acid, the respective pK-values are 2.25, 6.77 and 11.60, while for selenic acid the pK_2 is 1.92. Thus, in the pH range from 5 to 6, the expected dominating As and Se species are $H_2AsO_4^-$ and SeO_4^{2-}. Robinson and Stokes' LEC data 17 are for $H_2AsO_4^-$ and SeO_4^{2-}, so that the D_{LEC} values in Table 3 are for the same individual species as for the dominating species in our test solution.

With respect to the adsorption strength of these anions to the ferrihydrite adsorbent, it is well known that phosphates forms strong complexes with ferric oxides in the pH range 4 to 6. Iron oxide complexes of low solubility have been reported for arsenate6 and to a lower extent for selenite (McBride, 1994, Hamdy et al. 1977). The solubility of the iron complexes increases in the order phosphate = arsenate < selenate (McBride, 1994, Schwertmann, 1989). This is supported by the fact that the difference between D_{LEC} and our D_{DGT} values increases in the order phosphate, arsenate, and selenate (Table 3).

Figure 1.
Uptake curves for the DGT sampler equipped with the ferrihydrite adsorbent, over a period of 10 days (240 h) for P (● ○), As (■ □), and Se (▲ △), using open symbols at pH 5.1 and filled symbols at pH 6.4.
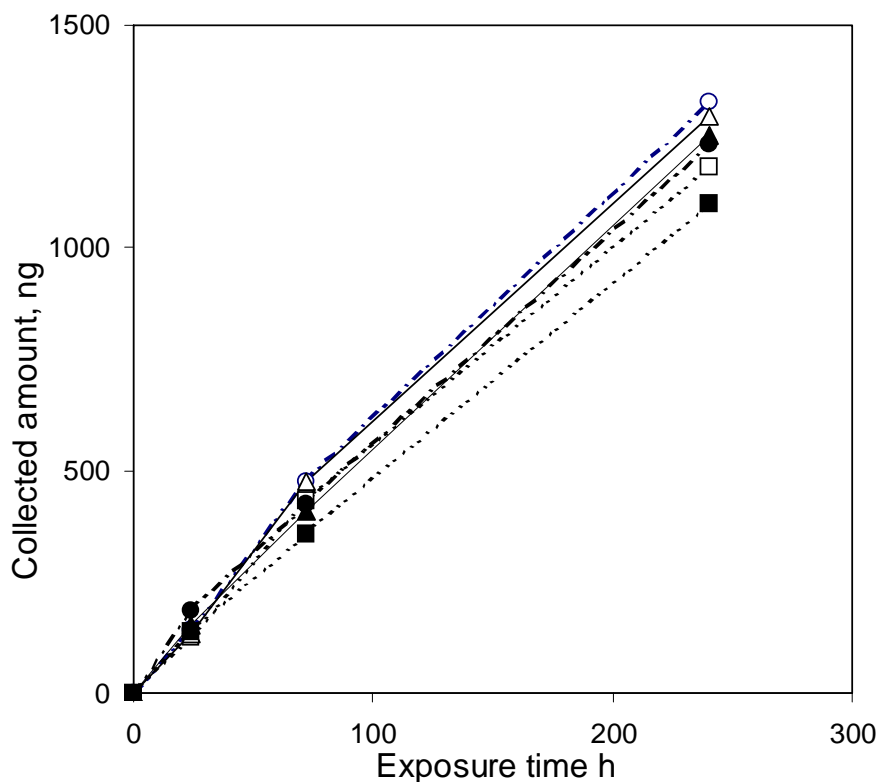
4. Conclusions

The DGT sampler with the ferrihydrite adsorbent for simultaneous sampling of phosphate, arsenate, and selenate shows promising performance. The matrix achieved from the adsorbent of the sampler is easy to analyze by HR-ICP-MS. Detection limits and sampling precision are acceptable, although some improvements are desirable especially to lower the detection limit for P.

DGT-based diffusion coefficients for phosphate and arsenate are comparable to those found earlier in diffusion cells experiments using the same membrane, but 20 to 50 % lower than those for diffusion of free ions in water obtained from LEC data. For selenate, this is the first data reported for DGT-based diffusion coefficients. They are in a similar range as for phosphate and arsenate, but 30 to 50 % lower than those achieved from LEC data. For Se and As, the use of ferrihydrite-based DGT sampling is more complicated than for phosphate, because the aqueous speciation may change between different oxidation states (e.g., selenite/selenate and arsenite/arsenate) under normal environmental conditions. Since selenite seems to be more strongly adsorbed to ferrihydrite than selenate, the sampler may be expected to collect both selenite and selenate. The diffusion coefficients for these two selenium species are expected to be in the same range, as both have approximately the same molecular size and charge.

Our results shows that the sampler collects both arsenate and selenate, but more research is necessary to understand the samplers performance with respect to the different oxidized inorganic species of As and Se. Our diffusion coefficients achieved are not as quantitatively precise as desired, but they may be appropriately accurate for environmental studies as they are obtained from in-situ experiments with the sampler. As the labile oxidized species of P; As and Se are the environmentally most reactive ones, the sampler may be used in environmental studies of these elements.

One critical point in the use of this sampler for arsenate and selenate, is the capacity. In many situations such as in pore waters from agricultural soils and in run off from soils, phosphate is present at much higher levels than arsenate and selenate. The selectivity of phosphate for the ferrihydrite adsorbent is similar to that for arsenate and selenate. Thus, the total adsorption capacity is controlled by the major anion, which in most circumstances is phosphate. This has to be taken into consideration when estimating the maximum deployment time. However, this also means that this sampler has it largest potential for free phosphate ions in water, as it is easiest to control the risk for overload for this ion.

5. References

Davison, W.; Zhang, H. In-situ speciation measurements of trace components in natural-waters using thin-film gels, *Nature*., **1994**, 367, 546-548.

Zhang, H.; Davison, W. Performance-characteristics of diffusion gradients in thin-films for the in-situ measurement of trace-metals in aqueous-solution*, Anal. Chem.* 1995, 67, 3391-4000.

Davison, W.; Fones, G.; Harper, M.; Teasdale, P.; Zhang, H. Dialysis, DET and DGT: In situ diffusive techniques for studying water, sediments and soils. In *In situ monitoring of aquatic systems: Chemical analysis and speciation*; Buffle, J.; Horvai, G. (eds.), John Wiley & Sons: New York, 2000, pp 495-569.

Garmo, O. A.; Royset, O.; Steinnes, E.; Flaten, T. P. Performance study of diffusive gradients in thin films for 55 elements, *Anal. Chem.* **2003**, 75, 3573-3580.

Zhang, H.; Davison, W.; Gadi, R.; Kobayashi, T. In situ measurement of dissolved phosphorus in natural waters using DGT, *Anal. Chim. Acta.* **1998**, 370, 29-38.

Fitz, W. J.; Wenzel, W. W.; Zhang, H.; Nurmi, J.; Stipek, K.; Fischerova, Z.; Schweiger, P.; Kollensperger, G.; Ma, L. Q.; Stingeder, G. Rhizosphere characteristics of the arsenic hyperaccumulator Pteris vittata L. and monitoring of phytoremoval efficiency, E*nvironm. Science Techn..* **2003**, 37, 5008-5014.

Teasdale, P. R.; Hayward, S.; Davison, W.; In situ, high-resolution measurement of dissolved sulfide using diffusive gradients in thin films with computer-imaging densitometry *Anal Chem.* **1999**, 71, 2186-2191.

McBride, M. B.; *Environmental chemistry of soils*; Oxford University Press: New York, USA, 1994.

Hamdy, A. A.; Gissel-Nielsen, G. *Z. Planzenernähr. Bodenkd.* **1977**, 140, 63-70.

Zhang, H.; Zhao, F.-J.; Sun, B.; Davison, W.; McGrath, S. P.; A new method to measure effective soil solution concentration predicts copper availability to plants, *Environ. Sci. Technol.*, **2001**, 35, 2602-2607.

Almås, Å. R., Bakken, L.R. and Mulder, J. (2004)., Changes in tolerance of soil microbial communities in Zn and Cd contaminated soils, *Soil Biology and Biochemistry,* 36, 2004, 805-813.

Terry, N.; Zayed, A. M.; de Souza, M. P.; Tarun, A. S. Selenium in higher plants *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **2000**, 51, 401-432.

Singh, B.R. *Fert. Res.* **1991**, 30, 1-7.

Hopper, J. L.; Parker, D. R. Plant availability of selenite and selenate as influenced by the competing ions phosphate and sulphate, *Plant Soil* **1999**, 210, 199-207.

Cussler, E. L. *Diffusion: Mass transfer in fluid systems*, 2nd ed.; Cambridge University Press: Cambridge, UK, 1997.

Li, Y.; Gregory, S., Diffusion of ions in sea water and in deep-sea sediments, *Geochim. Cosmochim. Acta*. **2002**, 38, 703-714.

Robinson, R. A.; Stokes, R. H. *Electrolytic solutions*, Butterwords Publications Ltd: London, UK, 1959.

Lindsay, W. L. *Chemical equilibria in soils*, Blackburn Press: Caldwell, NJ, USA, 2001.

Schwertmann, O.; Taylor, R. M. In *Minerals in soil environments.* 2nd ed.; Dixon, J.B.; Weed, S.B. (eds.), Soil Science Society of America Book Series: WI, USA, 1989, pp 379-438.

Sager, M. (2002). Vertical mobility of selenium, arsenic and sulfur in model soil columns, *Die Bodenkultur,* 53(2) 2002, 83-103.