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Inorganic species of arsenic in soil solution determined by microcartridges and ferrihydrite-based diffusive gradient in thin films (DGT)

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ABSTRACT

The bioavailability of soil arsenic (As) is determined by its speciation in soil solution, i.e., arsenite [As(III)] or arsenate [As(V)]. Soil bioavailability studies require suitable methods to cope with small volumes of soil solution that can be speciated directly after sampling, and thereby minimise any As speciation change during sample collection. In this study, we tested a self-made microcartridge to separate both As species and compared it to a commercially available cartridge. In addition, the diffusive gradient in thin films technique (DGT), in combination with the microcartridges, was applied to synthetic solutions and to a soil spiked with As. This combination was used to improve the assessment of available inorganic As species with ferrihydrite(FH)-DGT, in order to validate the technique for environmental analysis, mainly in soils. The self-made microcartridge was effective in separating As(III) from As(V) in solution with detection by inductively coupled plasma optical emission spectrometry (ICP-OES) in volumes of only 3 ml. The DGT study also showed that the FH-based binding gels are effective for As(III) and As(V) assessment, in solutions with As and P concentrations and ionic strength commonly found in soils. The FH-DGT was tested on flooded and unflooded As spiked soils and recoveries of As(III) and As(V) were 85–104% of the total dissolved As. This study shows that the DGT with FH-based binding gel is robust for assessing inorganic species of As in soils.

1. Introduction

Arsenic is a ubiquitous metalloid that has accumulated in soils in numerous areas of the world. Elevated As concentrations found in the soil constitute a hazard for both human and ecosystem biota [1]. Improving the understanding of As bioavailability in soil has become a challenge, both for determining real in situ concentrations and conserving As speciation until the analysis. The bio-available forms of As are mainly the inorganic species present in the soil solution or those loosely bound to the solid phase (labile pool). Arsenite [As(III)] is predominant under flooded, anoxic conditions, while arsenate [As(V)] dominates in well aerated soils [2,3].

Soil testing methods for measuring bio-available As fractions include pore water extractions or soil extraction with dilute salts (e.g., 0.01 M $CaCl_2$) and chelates [4–6]. Arsenic speciation in such solutions are now commonly performed with HPLC–ICP–MS. Filtering solutions with cartridges has been used as a cheap and quick alternative for the time consuming HPLC analysis. More importantly, cartridges can also be used in situ during field sampling to speciate As immediately upon sampling to avoid oxidative changes in speciation during transport to the lab [7]. When passed through the cartridge, As(V) is retained on the anion exchanger in the cartridge and the neutral As(III) can be collected in the filtrate. The As(V) can be removed subsequently from the cartridge by rinsing it with a suitable salt solution. Unfortunately, commercial cartridges such as those provided by the company MetalSoft Center require large amounts of solution (40–60 ml), which usually exceed the volume of indigenous soil solution extraction (commonly <5 ml).

Soil solution concentrations of As reflect the immediately available As in soil but do not reflect the dynamics of the reactions between solid and solution [8]. The diffuse gradient in thin film technique (DGT) overcomes this issue by measuring the diffusive flux of the analyte from soil to the device. The DGT technique consists of a diffusive polyacrylamide hydrogel in front of a binding gel containing a material with high affinity for the investigated element. The diffusive gel is separated from the soil/solution by a membrane filter to protect the gels from soil particles. In the first applications of DGT, trace metals and other

Abbreviations: FH, Ferrihydrate; DGT, Diffusive gradient in thin films; DMAA, Dimethylarsinate; MMAA, Monomethylarsonate; ICP-OES, Inductively coupled plasma optical emission spectrometry

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cations were captured on a Chelex binding layer. More recently, binding layers specific for anions (e.g., P, As) were developed [9,10]. The use of DGT in soils has particular merit. The continuous removal of the analyte from the soil solution by the DGT sampler results in a depletion zone next to the DGT sampler, which in turn results in a continuous replenishment of the analyte from the solid phase to the soil solution [11] (although some soils may have a low rate of replenishment). For this reason, DGT-measured concentrations predict well the uptake of trace elements and phosphate [12,13] because they simulate plant roots by providing a sink for the analyte. An additional advantage is that the capacity of a soil to resupply an analyte from the solid phase to soil solution can be calculated by comparing C_{DGT} (the time-averaged analyte in soil solution near the DGT) to the measured concentration in the soil solution (C_{sol}) [14].

The performance of FH-based binging gels to measure As(V) in a pool of other anions, was investigated by Luo et al. [10] and Österlund et al. [15] in solution samples. These studies did neither investigate inorganic As species separately or tested the applicability of FH-based DGTs in soils. Panther and co-workers compared the potential of FH-based binding gels to measure the two inorganic As species [16]. This has been scarcely applied to soils [8,14] while the mixed arsenite/arsenate diffusion coefficients in the DGT calculations were not optimised by in situ As speciation measurements.

The objective of this study was to develop and to test a soil solution speciation technique for inorganic As. First, a Dowex-based microcartridge was developed to separate As species in small volumes and to apply it to extracted soil solutions, which was compared to a commercial cartridge. Second, the ability of FH-DGT in combination with the microcartridge was tested to measure available inorganic As(III) and As(V) species in (i) solutions with characteristics similar to soil solutions, and (ii) in soils spiked with As.

2. Materials and methods

2.1. Lab procedures

All solutions were prepared using Milli-Q water (18.2 MΩ) and chemical reagents of analytical grade were used throughout. Arsenic solutions were prepared with $NaAsO_2$ or $Na_2HAsO_4.7H_2O$ salts for As(III) and As(V), respectively.

The lab material was acid washed prior to use and subsequently rinsed with distilled and Milli-Q water. For the As(III) solutions, the Milli-Q water was first deoxygenated by pumping N_2 through the water for 10 to 14 h.

2.2. Microcartridges

Microcartridges for As speciation in waters were made by adding 0.4 g of Dowex® 1-X8 (anion exchanger, Richmond, USA) between two layers of glass wool in a 1 ml pipette tip. The glass wool secures the resin during use. Between 3 and 4 ml of the test solution was then added at the top of the microcartridges and the solution was pushed through the resin by attaching the 1 ml pipette tip to a 5 ml pipette and pressing the piston. Each microcartridge was preconditioned prior to its use with 2 ml of 0.2 mM $CaCl_2$. The commercial cartridges were provided by MetalSoft Center (Florida, USA, www.metalsoftcenter.com) and used accordingly to the product's specifications. The volume of filtered solution was reduced to 20 ml, instead of the prescribed 40 ml. The experiment with the (micro) cartridges was replicated 4 times for each solution. When passing an As solution over the microcartridge, As(V) is retained on the Dowex anion exchanger, while As(III) passes through without interaction. To release the retained As(V), 4 ml of a 0.2 M NaCl was passed over the microcartridge and As(V) was analysed. The As(V) concentration in samples was also calculated as the difference between total As concentration and As(III) concentration.

Total As concentrations were measured directly by ICP-OES (Perkin Elmer, Optima 3300 Dual View) at 188.981 nm. The limit of quantification of the axial plasma equipment is about 5 μg As l^{-1}.

2.3. DGT

Diffusive gels were prepared according to Zhang and Davison [17]. The FH-based binding gels were obtained by precipitating ferrihydrite on a diffusive gel layer according to Santner et al. [18]. Plastic DGT devices designed for soil deployment with a 2.52 cm^2 exposure window were used (DGT Research Ltd., Lancaster). A 0.13 mm thick cellulose nitrate filter (0.45 μm) was placed on top of the diffusive gel (thickness 0.6 mm) and binding layer. Each batch of gels featured two DGT blanks to measure background analyte concentrations. All DGT deployments (water and soil, see below) were performed in darkness at a constant temperature of 21 °C. After deployment, the devices were rinsed thoroughly with Milli-Q water and disassembled to retrieve the binding layer. The mass of As sorbed onto the binding gels was measured after elution of the FH-based gels in 1 ml 1 M HCl for 24 h. Luo et al. [10] reported a better elution of As from FH slurry gels with 1 M HNO_3 and H_2SO_4 than with 1 M HCl, but in our study we got a good recovery with HCl in our FH precipitate gels, which also works well for P determination in FH-gels [9,13]. The total As concentration in the eluate was measured by ICP-OES. A subsample (4 ml) of the original solution was passed over the microcartridge to speciate As, as described above. This additional step is required to calculate the diffusion coefficient of total As in the gel (see below, Eq. (3)).

The time-averaged DGT concentration (C_{DGT}) was calculated with following equation (Eq. 1) [17]:

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

where M (μg) is the mass of As in the gel, Δg the thickness of the diffusive layer, which includes both the diffusive gel and the membrane filter (0.073 cm), D ($cm^2\ s^{-1}$) the diffusion coefficient of As(III) or As(V) in the diffusive layer, A the exposed gel surface (2.54 cm^2) and t (s) the time of deployment.

We calculated the diffusion coefficient of As(III) and As(V) as reported by [19]. The measured As accumulation in the binding gel (either for As(III) or for As(V)) was plotted versus the deployment time (in minutes) and D was calculated with Eq. (2) using the slope of this relationship (μg min^{-1}):

$$D = \frac{\text{slope} \times \Delta g}{A \times C \times 60} \quad (2)$$

where C is the As concentration in solution (μg cm^{-3}). The '60' converts the time in minutes from the graph into seconds. Once the diffusive coefficients for As(III) and As(V) ($D_{As(III)}$ and $D_{As(V)}$, respectively) were obtained, the diffusion coefficient for mixed solutions, ($D_{As(III)+As(V)}$) was calculated as:

$$D_{As(III)+As(V)} = x \times D_{As(III)} + (1-x) \times D_{As(V)} \quad (3)$$

where x is the fraction of As(III) over total soluble As and $(1-x)$ the fraction of As(V) over the total soluble As. This fraction was measured in the synthetic/soil solution using the microcartridges.

2.4. Experiments with synthetic solutions

2.4.1. Microcartridges

In experiment 1.1, we assessed the recoveries of inorganic As species in three types of synthetic As solutions, (1) As(III) solutions: 200 and 1000 μg As(III) l^{-1}; (2) As(V) solutions: 200 and 1000 μg As(V) l^{-1}; (3) Mixed solutions containing 50% As(III) and 50% As(V) at a total concentration of 200 and 1000 μg As l^{-1}. For the last solution, we mixed half N_2-stripped (deoxygenated) water and half non-deoxygenated water. In all solutions the pH in the solutions was not fixed, but ranged 5–6.

Prior to filtering, a subsample of each solution was kept for analysis of total As concentration by ICP-OES. Subsequently, 20 ml were passed through the commercial cartridges and 3–4 ml through the self-made Dowex microcartridges. Only As(V) was retained on the Dowex. The As(III) concentration of the filtrate was analysed directly. Recovery of As(V) retained on the microcartridges was also assessed by eluting with 4 ml 0.2 M NaCl followed by analysis. We also tested whether the microcartridges are re-usable by doing four cycles of (i) filtering the sample, (ii) eluting As(V) with 0.2 M NaCl and (iii) conditioning the column with 0.2 mM $CaCl_2$. We used for this experiment the solutions of 1000 μg As l^{-1}, containing 50% As(III) and 50% As(V). The aliquot resulting from step (1) was measured for As(III).

2.4.2. DGT

In experiment 1.2, the linearity of As accumulation over time on the DGT binding layers was tested. The FH-DGT devices were immersed in solutions with 250 μg As l^{-1} (As(III) or As(V)) and retrived from the solution after a deployment of 5, 12 and 24 h. This experiment allowed the zero-sink properties of the binding layer over time to be confirmed. From these results the diffusion coefficients for both As(V) and As(III) could be estimated, as described earlier (Eq. 2). Even though there are several reported diffusion coefficients [15,16,20,21], we decided to calculate our own for a better accuracy.

In experiment 1.3, concentration effects were investigated. The uptake efficiency of the DGT units was tested by submerging the DGT assemblies for 12 h in solutions with an increasing As concentration (0, 50, 100, 250 and 500 μg As l^{-1}), with As present as either As(III) or As(V). The co-occurrence in solution of As(III) and As(V) was also investigated in mixed solutions containing a total of 100 and 250 μg As l^{-1}, with half of the As added as As(III) and the other half as As(V). To correct the diffusion coefficient and to estimate the ratio As(III) to As(V), synthetic solutions were sampled (20 ml). One aliquot (1 ml) was immediately measured by ICP-OES for total As, while a second aliquot was first passed through the microcartridges and the filtrate was analysed to obtain As(III) concentration.

The effect of competing ions was tested in experiment 1.4. The possible effect of ionic strength on DGT measurements were investigated by submerging DGT units for 12 h in solutions that were adjusted to 0.2, 2 and 20 mM NaCl. The solutions had an As concentration of 250 μg As l^{-1}, either as As(III) or as As(V). To determine the impact of phosphate, DGT measurements were performed in solutions of 250 μg As l^{-1} (either As(III) or As(V)) and a P concentration of 250 μg P-PO_4 l^{-1}.

2.5. Experiment with As-spiked soils

Plastic pots were filled with 150 g of air-dried soil collected in Teso, Kenya. The selected soil is a sandy Cambisol, characterized by a low pH (pH 5) and a relatively low content of Fe and Al oxides (respectively 190 and 340 mg/kg acid oxalate extractable content [13]), i.e., the anion adsorption retention capacity. This soil was selected for its low P-sorption, therefore we expected the soluble arsenic from the spike will not be intensively sorbed by the soil and we will be able to compare As in DGT with As in soil solution. This experiment was performed in triplicate. The soil spiked with As(III) was flooded 14 days before spiking, with 100 ml anoxic Milli-Q water and stored in a dark incubation room at 21 °C. After 14 days, the supernatant water was decanted. This pre-incubation ensured anoxic conditions in the soil before spiking with As(III). The soils spiked with As(V) were wetted with 100 ml of Milli-Q water and water was decanted after 5 h. Soils were spiked with, respectively As(III) or As(V) by mixing As solutions at the rate of 5 and 20 mg As(III or V) kg^{-1} and incubated for 24 h. The FH-DGT unit was subsequently softly pushed into the water saturated soil (30 g of soil) and deployed for 7 h at 21 °C. After deployment, the DGT sampler was removed and carefully rinsed with Milli-Q water to remove adhering soil particles before disassembling. The total As concentration on the binding gel was analysed after elution of the gels, as described before. A subsample of soil (50 g) was used for soil solution sampling by the double-chamber method (centrifugation at 4000 relative centrifugal force, 15 min). In an aliquot of the obtained soil solution total As concentration was measured, while another aliquot was used for passing through the microcartridges. The concentration of As(III) in the eluate was measured, and the concentration As(V) calculated from the difference between total As and As(III).

3. Results

3.1. Comparison of self-made and commercial cartridges to separate As species (experiment 1.1)

As(III) passes through the self-made microcartridges containing Dowex® without significant retention on the anion exchanger. On average 96% to 97% of the added As(III) was recovered in the eluate, even when mixed solutions were tested (Table 1). Afterwards, As(V) was eluted from the microcartridges, with the

Table 1
Total As concentration measured in solution (by ICP-OES) and the nominal As(III) and As(V) concentrations based on added As. Comparison of As speciation with self-made Dowex®-based microcartridges (using 3–4 ml of solution) and commercial cartridges from MetalSoft Center (using 20–25 ml). The recoveries are expressed as % of the total As and As(V) was calculated as the difference between total As and As(III). Standard deviation are given in brackets ($n=3$).

Solution	As species	Nominal			Self-made microcartridges				Commercial cartridges			
		Total As (μg l^{-1})	As(III) (μg l^{-1})	As(V) (μg l^{-1})	As(III) (μg l^{-1})	As(V) (μg l^{-1})	As(III) (%)	As(V) (%)	As(III) (μg l^{-1})	As(V) (μg l^{-1})	As(III) (%)	As(V) (%)
1	As(III)	174 (3)	174	0	169 (2)	5 (2)	97	3	193 (2)	n.d.	111	0
		891 (12)	891	0	851 (21)	40 (15)	96	4	965 (11)	n.d.	108	0
2	As(V)	190 (3)	0	190	n.d.	190 (3)	0	100	10 (8)	181 (6)	5	95
		1006 (3)	0	1006	n.d.	1006 (3)	0	100	18 (16)	987 (19)	2	98
3	As(III) and As(V)	180 (5)	83	97	83 (4)	97 (5)	46	54	95 (3)	85 (8)	53	47
		923 (6)	406	517	431 (13)	492 (12)	47	53	491(3)	431 (8)	53	47

recoveries of As(V) being between 75% and 90% of the added As (data not shown). The use of commercial microcartridges resulted in a overestimation of As(III) by 10% to 20%. Re-use of microcartridges was also successful. Even after four cycles of filtering, eluting and regenerating the As(III) concentration measured remained constant (Table SM1), with recoveries of 91–105%.

3.2. Performance of the FH-layer for assessing As in solutions (experiment 1.2 and 1.3)

To test whether the proposed binding layers are effective zero sinks for As, the mass of As accumulated on the gel during DGT deployment was assessed for increasing deployment times (Fig. 1, experiment 1.2). The mass of accumulated As increased linearly in time. This holds for both As species and both FH-based binding gel. These results show that the zero sink sustained at least up to an accumulated mass of 5.1 μg As(V) and 7.7 μg As(III) for FH gels. The consistent larger uptake of As(III) than that of As(V) is due to differences in diffusion rates of both species through the gel. The diffusive coefficients of each As species can be calculated from the slope of the fitting line in Fig. SM1, supplementary material. The slopes were 5.47×10^{-3} μg As(III) min^{-1} and 3.39×10^{-3} μg As(V) min^{-1}. The diffusive coefficients were $1.01(\pm 0.02) \times 10^{-5}$ cm^2 s^{-1} for As(III) and $6.28\ (\pm 0.32) \times 10^{-6}$ cm^2 s^{-1} for As(V), at 21 °C.

Fig. 2 shows the linear increase of accumulated As at increasing As concentrations after 12 h of deployment (experiment 1.3).

The accuracy of the DGT measurement was assessed by calculating the recovery, i.e., the ratio of C_{DGT} measured concentration over the As concentration measured in the solution (Fig. 3). FH-based gels are highly efficient for binding As(III) or As(V) in all types of solutions (pure As(III) or As(V) solutions and mixtures) with recoveries close to 1 (between 0.9 and 1.1). Measurements were also highly reproducible with coefficients of variance of 3–14%. The different background concentrations of NaCl in the solutions did not affect As(III) or As(V) retention in the FH-based binding layer (Fig. 4, experiment 1.4). The recovery was

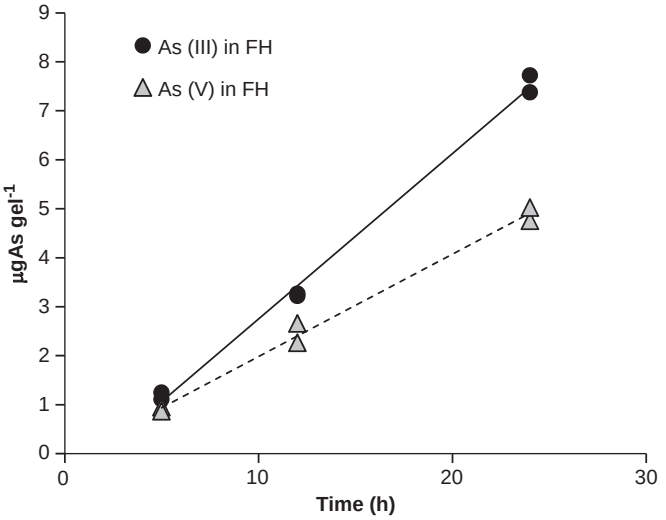

Fig. 1. Progressive accumulation of As(III) (black circles) and As(V) (grey triangles) on the ferrihydrite (FH) binding layer measured in a solution with 250 μg As l^{-1}.

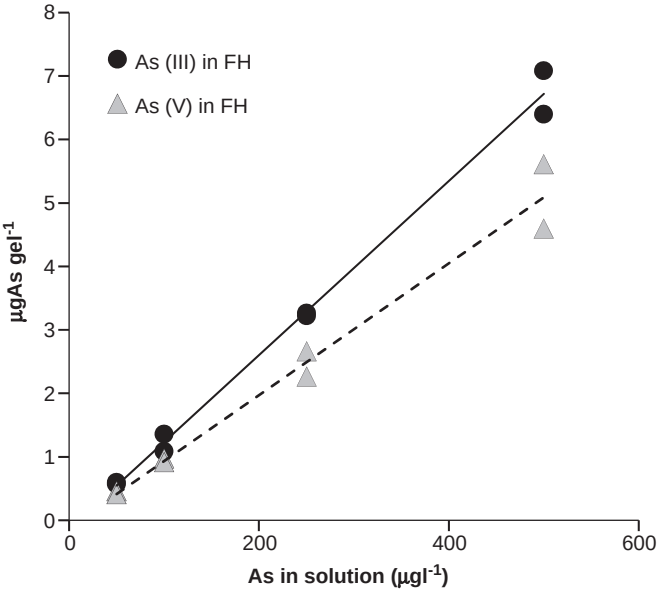

Fig. 2. Mass of As(III) (black circles) and As(V) (grey triangles) accumulated at increasing As concentrations. DGT units were deployed for 12 h.

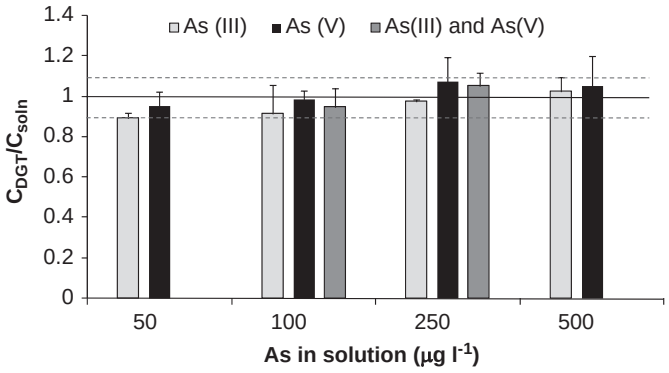

Fig. 3. The C_{DGT}/C_{soln} ratio at different concentrations (in μg l^{-1}) of As(III), As(V) or a mixture of both species in synthetic solutions. Error bars represent the standard deviation ($n=2$). Horizontal lines illustrate the acceptable range: 0.9–1.0 (dotted lines), while 1 (continuous line) means 100% recovery.

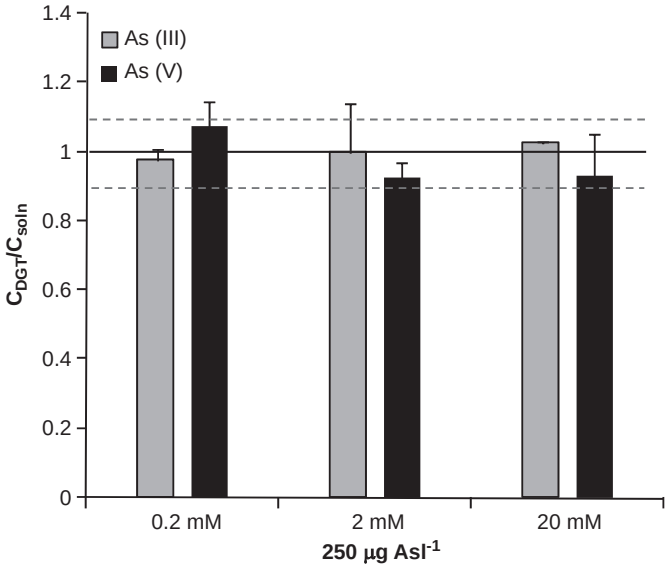

Fig. 4. The C_{DGT}/C_{soln} ratio as affected by different ionic strengths (0.2, 2 and 20 mM NaCl) in synthetic solutions containing 250 μg l^{-1} of either As(III) or As(V). Error bars represent the standard deviation ($n=2$). Horizontal lines illustrate the acceptable range: 0.9–1.0 (dotted lines), while 1 (continuous line) means 100% recovery.

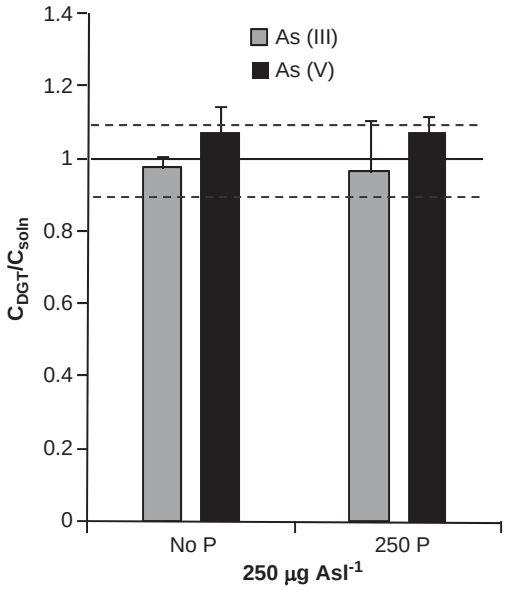

Fig. 5. The C_{DGT}/C_{soln} ratio as affected by different concentrations of PO_4-P (0 and 250 µg P l^{-1}) in synthetic solutions containing 250 µg l^{-1} of either As(III) or As(V). Error bars represent the standard deviation ($n=2$). Horizontal lines illustrate the acceptable range: 0.9–1.0 (dotted lines), while 1 (continuous line) means 100% recovery.

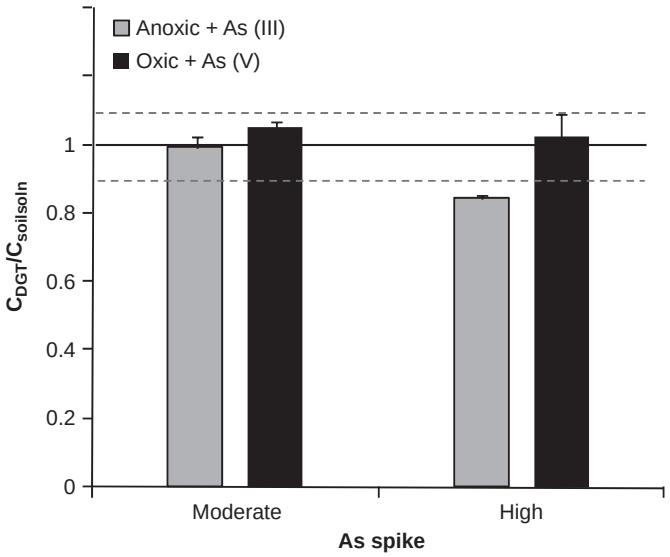

Fig. 6. The C_{DGT}/C_{soln} ratio in freshly spiked soils: moderate (at a rate of 5 mg As kg^{-1}) and high As-spikes (20 mg kg^{-1}) with either As(III) or As(V). Error bars represent the standard deviation ($n=2$). Horizontal lines illustrate the acceptable range: 0.9–1.0 (dotted lines), while 1 (continuous line) means 100% recovery of the corresponding dissolved As species. The spiking resulted in the following concentrations of As in soil solution (in parenthesis the percentage of As(III)): 350 µg As l^{-1} (78% as As(III)) in moderate As(III); 1573 µg As l^{-1} (89% as As(III)) in high As(III); 471 µg As l^{-1} (3% As(III)) in moderate As(V); 1503 µg As l^{-1} in high As(V).

found not to change significantly in the range 0.2–20 mM NaCl, with recoveries between 0.9 and 1.1 and with acceptable repeatability ($<14\%$). Fig. 5 shows the influence of PO_4 on As measurements by FH-based DGT. The presence of PO_4 did not significantly influence the recovery on the FH-gel, for both As species in the binding layer.

3.3. Performance of DGT in freshly As-spiked soils (experiment 2)

The speciation of As in the soil solution, using microcartridges, revealed that 78–86% of soluble As in anoxic soils was As(III), while under aerobic conditions $>95\%$ was found to be As(V). Independent of the inorganic As species in the soil, the ratios of C_{DGT} to As concentration in soil solution were 0.85–1.04 (Fig. 6), with a coefficient of variance $<7\%$.

4. Discussion

4.1. Speciation of As by microcartridges

Since both self-made and commercial (micro-)cartridges were based on an anion exchanger, it was expected that As(III) would be poorly retained in the cartridge because As(III) is predominantly present in solutions in the fully protonated form (as H_3AsO_3), while As(V) is retained on the anion-exchanger because it is usually present in solutions in the deprotonated form at $pH>3$ ($H_2AsO_4^-$ and $HAsO_4^{2-}$) [22]. Results confirm that with both microcartridges, containing Dowex®, the fraction of As(III) measured in the filtrate is in good agreement with the added As(III) concentration, and thus negligible amounts of As(III) were retained on the cartridges. With the commercial cartridges, the As(III) concentration was slightly overestimated (5–10%). This overestimation may be related to the smaller volume tested, i.e., 20 ml in contrast to the recommended volume of 50 ml.

Under field conditions, soil solution can be sampled either with Rhizon samplers [23], or by pore water extraction by centrifugation. The Rhizon samplers only provide 5–10 ml per sampler per extraction. Also with the pore water extraction by centrifugation, it is difficult to obtain sufficient volume of pore water, i.e., in order to obtain 50 ml soil solution, a minimum of 200 g of water saturated soil is needed. Our results show that even when only 4 ml solution is passed over the self-made microcartridge, As(III) can accurately be separated from As(V). We can conclude that our microcartridges are useful for small volumes; this technique can be applied in the field in combination with Rhizon samplers and limits changes of As speciation during transport or storage [24]. An additional advantage is the low production cost for the proposed micro-cartridges. The self-made cartridges will cost approximately 0.2 to 0.3 Euro per piece. Arsenic speciation in soil solution is frequently analysed by HPLC–ICP-MS or HPLC–AFS, but still such analyses are expensive because of the high cost of instruments and of operation (reagents, gases, etc). Therefore the microcartridges are a cheap alternative for As speciation.

4.2. Measurement of As in solutions and soils using FH-DGT

The calculated diffusion coefficients of As(III) and As(V) in the diffusive gels are in agreement with previously reported ones: our $D_{As(III)}=1.01\times10^{-5}$ was slightly larger than those found earlier, i.e., $5.9-9.8\times10^{-6}$ cm^2 s^{-1}, while $D_{As(V)}=6.28\times10^{-6}$ cm^2 s^{-1} is within the range, i.e., $4.9-6.8\times10^{-6}$ cm^2 s^{-1} [15,16,20,21]. The As(V) is mostly present in its deprotonated form, which makes it more likely to react with the diffusive gel compared to the neutral As(III). The diffusion coefficient for As(V) in the gel is very similar to that of phosphate: $5.42-6.05\times10^{-6}$ at 21 °C [25]. This is not surprising given that both anions have similar chemical properties.

C_{DGT} concentrations for As measured using FH-DGT were in good agreement with the true solution As concentrations. Measured C_{DGT} using a FH-DGT, show that measured As concentrations were in good agreement with the true solution As. This outcome is independent of the inorganic species and their

combinations. The good recoveries and low variability between measurements demonstrated the applicability of FH-DGT assemblies for As assessment in waters. Similarly, [16] reported that As concentrations could be reliably measured by FH-DGT in synthetic solutions with a background concentration of 0.02 M NaCl. The performance of FH-based binding gels was unaffected by increasing ionic strength, with accurate measurements for solutions having a background concentration up to 20 mM NaCl. The ionic strength tested (0–20 mM NaCl) is comparable to EC in saturated soils of 1–10 dS m^{-1} [26], which is equivalent to a moderate ionic strength in saline soils solutions. Likewise, the As measurements with FH-DGT were unaffected by the presence of P at concentrations close to the typical concentration in soil solutions of 10 μM [12]. Complementary to the current work, As accumulation in FH-based DGT was previously found to be stable under pH 3–10, the common range for soil pH [10]. These results obtained in synthetic solutions demonstrate the potential and robustness of DGT to assess As in common soils.

Our study shows that C_{DGT} measured using FH-based binding gels is similar to As concentrations measured in pore water in soils with different watering management. Prior to DGT measurements on soils, the As speciation must be measured in soil solution to correct the diffusion coefficient with the fraction of soluble As(V) and As(III). This additional measurement is a drawback inherent to the method but is required for accuracy since As(III) has about 60% higher mobility in the gel than As(V) (Eq. (2)). Arsenic speciation of the original solution cannot be analysed directly by the As speciation in FH-DGT eluents because FH has been shown to promote As(III) oxidation [27] and, therefore, that could overestimate As(V). The correspondence between C_{DGT} and soil solution concentration found here is likely related to the soil properties used here and this correspondence should not always be found. In soil samples, depletion of soluble As near the diffusive layer surface is expected in contrast to well-stirred synthetic solutions. The ratio of the time averaged As concentration near the DGT (i.e., C_{DGT}) to the bulk soil solution As concentration depends on the deployment time, the extent and rate of buffering by the solid phase and on the rate of diffusion, e.g., depending on the porosity of the soil [28].The sandy soil and the relatively short contact times (7 h) likely explain the weak depletion. The concentrations of soluble As in our spiked soils (0.3–1.5 mg As l^{-1}) were higher than what is expected in soil solutions, approximately <1 mg As l^{-1} [23]. The deployment time (7 h) used in this study was suitable for this heavily spiked soils because (i) enough As will have accumulated onto the FH binding gel for reliable measurement, and (ii) the total amount of As bound on the gel should be below the capacity of the FH gel, thus avoiding saturation. In soils with lower As concentration in solution or at lower temperatures (lower diffusion rates), longer deployment times are needed for which the depletion might be more pronounced. However, similar scenarios may occur during plant uptake of As, therefore DGT might mimic plant uptake [12].

Our results from different experiments strongly support the use of Dowex microcartridges to assess As in soil solutions and precipitated FH-based diffusive gels. This precipitated FH gel shows a high homogeneity and is a promising technique for 2-D mapping of As in soils, as it was done for P [29], which may assist unravelling As biogeochemistry in plant rhizosphere (e.g., in paddy soils).

In the present study, we did not study the ability to use FH-DGT to assess organic As. So far nobody has studied the organic As accumulation in FH-DGT. Recently, [20] reported the effective sorption of the most abundant organic species in soils, namely dimethylarsinate (DMAA) and monomethylarsonate (MMAA), both with similar coefficient of diffusion as for As(V). Although organic species in soils are usually less abundant than inorganic species, they can occur at high percentages in some specific sites. The microcartridges used in our study are not able to separate organic species. Organic As species will pass through the cartridges like As(III). However in most soils, inorganic As species are predominant [3,30,31].

5. Conclusions

The results confirmed the suitability of FH-based DGT for the measurement of inorganic As species in both synthetic solutions, with ionic strengths up to 20 mM and high concentration of soluble P, and in soils. The self-made microcartriges are a valid option to speciate small volumes of inorganic As in soil solution. Future research may test the suitability of this technique to assess As in soils/soil solutions under field conditions and determine whether DGT assessment of As matches with availability in soils.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.11.007.

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