Passive sampler measurements of inorganic arsenic species in environmental waters: A comparison between 3-mercapto-silica, ferrihydrite, Metsorb®, zinc ferrite, and zirconium dioxide binding gels

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ABSTRACT

The performances of five Diffusive Gradients in Thin Films (DGT) binding gels, namely 3-mercapto-functionalized silica (3MP), ferrihydrite (Fh), Metsorb®, zinc ferrite ($ZnFe_2O_4$), and Zirconium oxide (ZrO_2), were evaluated for in situ determination of As speciation in water and sediments. A combination of batch experiments at various pH (without addition of buffers) and in the presence of reduced species (Mn^{2+}, Fe^{2+} and HS^-),time-series experiments in oxic waters, and in situ deployment in anoxic river sediments has permitted to evaluate the potential interferences among the binding gels.

Firstly, the efficiency of each DGT binding gel dedicated to total As (i.e., Fh, Metsorb®, $ZnFe_2O_4$ and ZrO_2) or As(III) (i.e., 3MP) determination confirms that the determination of As species is possible in oxic freshwater and seawater over 96 h for a wide range of pH (5−9). Secondly, concerning the deployment in river sediment, high HCO_3^- concentrations have a little negative effect only on the DGT performances of the iron(III)-binding gels (i.e, Fh and $ZnFe_2O_4$). Thirdly, the presence of sulfides does not show any effect on the DGT uptake of As, but strongly affects the elution factor parameter. Discrepancies in elution between the different binding gels potentially result in precipitation of orpiment, especially in $1\,mol\,L^{-1}$ HNO_3. A correction of the classical elution factor derived from batch experiments was applied to provide more representative results.

Finally, this study shows the difficulties to determine As speciation in anoxic sediments, and suggests that corrections of the elution factor may be required as a function of the species present in the deployment matrices.

1. Introduction

DGT techniques appear to be an interesting alternative for studying As speciation in river sediments compared to traditional ex situ approaches consisting in extracting porewater samples in several steps under nitrogen atmosphere. Bennett and co-workers [1] commented on our previous works describing a new DGT method using a zinc ferrite ($ZnFe_2O_4$) binding gel for the determination of total arsenic (As) at low concentration in the sediments of the Marque River, northern France [2]. In that study, the DGT performances of the $ZnFe_2O_4$ binding gel were compared to that of the ferrihydrite (Fh) and Metsorb® binding gels. Bennett and co-workers [1] pointed out several issues in the analytical development and in the validation of the new $ZnFe_2O_4$-DGT method.

In this article, an improved methodology for the determination of As in natural waters is presented. The former experiments were repeated in more representative conditions to validate the DGT response of the binding gels to pH, and to determine whether pH buffers can be used for laboratory validation of the DGT technique. First, the evaluation of DGT response regarding to pH was performed in buffered solutions, as it has not been done yet in any study of DGT method development for As species determination [3–7]. We have explored the possibility to use different buffers at $0.1\,mol\,L^{-1}$ between pH 5 and 9, since it is difficult to maintain the pH of diluted $NaNO_3$ solution during several hours without an automatic pH titrator. In particular, the potential effect of a high content of the H_3BO_3 buffer (pH 7.5–9) on the DGT response is evaluated in batch experiments, as boric acid could inhibit the accumulation of inorganic As species on the Metsorb® binding gel [2].

Our previous results had also suggested that the Metsorb®-DGT was not suitable for measuring total As concentration in seawater. Investigations from time-series accumulation experiments are performed in more realistic matrixes to resolve the inconsistencies between our previous study [2] and prior research published in the field [4,8,9].

In addition, the reactivity of the main redox sensitive species, *i.e.*, Fe^{2+}, Mn^{2+} and HS^- with the binding gels has been evaluated in batch experiments, in order to highlight their potential reactions with each binding gel. We have also studied the possible interferences of the binding gels with carbonates, as Panther et al. [10] had observed that this species interfered more with the accumulation of phosphates [chemical analogue of As(V)]on the FeOOH binding gel than on the Metsorb®. As suggested by Bennett and co-workers [1], time-series accumulation experiments have now been performed to rule on the assumption that iron(III)-based binding gels are more susceptible to interference with carbonates, especially in sediment porewaters.

All the experiments allow for discussion on the difference of the DGT response compared to our previous study [2] between Metsorb® and iron(III) based-DGT methods (underestimation by over 50% of As concentration for the FeOOH and $ZnFe_2O_4$ binding gels) during 24 h of deployment in anoxic sediments of the Marque river. In addition, in the present study, the ZrO_2 binding gel has also been included in the experiments to allow for a more complete comparison between the existing binding gels for the determination of As.

2. Experimental section

2.1. Reagents, materials and solutions

Ultrapure water (Milli-Q) was produced by a Millipore apparatus with a 18.2 MΩ cm resistivity. The following ACS reagent- or analytical grade chemicals were purchased either from Sigma-Aldrich (Saint-Quentin Fallavier, France) or VWR (Fontenay-sous-Bois, France): $As_2^{III}O_3$, $Na_2HAs^VO_4.7H_2O$, H_3BO_3, KIO_3, NaOH, $NaNO_3$, $NaHCO_3$, $Fe^{II}SO_4·7H_2O$, $Fe^{II}Cl_2·4H_2O$ $Mn^{II}SO_4·H_2O$, $Na_2S·9H_2O$, $Fe^{III}(NO_3)_3·6H_2O$, $ZrOCl_2$, $ZnCl_2$, 2-(*N*-Morpholino)-EthaneSulfonic acid (MES), Metsorb® HMRP 50, 3-MercaptoPropyl functionalized silica (3MP), $(NH_4)_2S_2O_8$, acrylamide solution (20%, aqueous), *N*, *N*, *N'*, *N'*-TEtraMethylEthyleneDiamine solution (TEMED), 1,10-o-phenanthroline, *N, N*-dimethyl-p-phenylenediamine oxalate and ammonium phosphate dibasic. Optima grade nitric acid was purchased from Fisher Scientific (Illkirch, France). Prior to use, all DGT components and plastic containers used for the preparation and the storage of solutions were acid-cleaned in 1.5 mol L⁻¹ HNO₃ for at least 24 h, and rinsed thoroughly with ultrapure water.

An Agarose-PolyAcrylamide (APA) hydrogel consisting of 15% acrylamide (Bio-Rad) and 0.3% agarose derived cross linker (DGT Research Ltd.) was selected as the diffusive gel in each DGT experiments [11]. The diffusive gels were made using either 500 or 800 μm-thick Teflon plastic spacers. After complete polymerization, the diffusive gels were rinsed 3 times into ultrapure water, then stored in a 10⁻² mol L⁻¹ NaNO₃ solution (24 h). The thickness of the diffusive gels was controlled after complete hydration using an optical microscope. Depending on the Teflon spacer thickness, the final thickness of the diffusive gels was 800 or 1100 μm. The 3MP, Metsorb®, and $ZnFe_2O_4$ binding gels were prepared by casting adsorbents in the APA hydrogel as previously described in [2]. The binding gels were stored in a 10⁻² mol L⁻¹ NaNO₃. The Fh and ZrO_2 binding gels were obtained by the precipitation method in APA hydrogel (800 μm-thick) [9,12]: the APA hydrogels were placed in a 0.1 mol L⁻¹solution of either Fe(NO₃)₃ or ZrOCl₂ for at least 2 h. Once the equilibrium was reached, the gels were quickly rinsed with ultrapure water in order to remove the excess of reagents, and then placed in a0.05 mol L⁻¹ MES buffer at pH 6.7 in order to precipitate either Fh or ZrO_2in the APA hydrogel. The binding gels were removed from the buffer solution after 30 min of contact, rinsed with ultrapure water (at least 4 times), and stored in a 10⁻² mol L⁻¹

NaNO₃ solution. The storage of the diffusive and binding gels was limited to three weeks before assembling the DGT units. The piston-type DGT units with a sampling area of 3.14 cm² (DGT Research Ltd) were mounted by assembling a binding gel layer (800 μm-thick), a diffusive gel layer (800 or 1100 μm-thick), and a cellulose acetate filter (Sartorius Biolab, 0.45 μm in pore size and 130 μm-thick).

2.2. Analytical procedures

The total concentrations of As were determined by Inductively Coupled Plasma –Mass Spectrometry (ICP-MS Varian 820MS). The spectrometer was calibrated using standard solutions prepared in 0.15 mol L⁻¹ HNO₃ using the same matrixes of eluent as for the binding gels in order to consider potential matrix effects on the signal. Analyses were performed using the collision reaction interface mode with hydrogen as additional gas (100 mL min⁻¹ at the skimmer cone) [13]. The quantification limits for As range from 0.05 μg L⁻¹ to 0.2 μg L⁻¹, depending on the matrix composition.

Elemental concentrations (B, Fe and Mn) in the samples were determined by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES, Varian Vista Pro, axial view) using standard solutions prepared in 0.15 mol L⁻¹ HNO₃. The concentration of ferrous ion (Fe^{2+}) was obtained by the colorimetric 1,10-o-phenanthroline method at 510 nm, and the sulfide concentration by the colorimetric methylene blue method at 660 nm [14]. Colorimetric measurements were done using a double-beam spectrophotometer (Cary 100, Varian) with quartz cells of 1 cm in path length. The S(-II) stock solution was prepared under nitrogen atmosphere from Na₂S·9H₂O and titrated by potentiometry with a Cd^{2+} standard solution (0.1–1 g L⁻¹), using a sulfide ion-selective electrode (Orion) and a Hg/Hg₂SO₄ reference electrode [15].

2.3. Laboratory evaluation of the DGT performances

The evaluation of DGT performances was assessed in both oxic environmental waters and anoxic river sediments. The general experimental setup and calculations are first described in this section. In addition, the accumulation performance of the five binding gels during time-series experiments (natural matrix and carbonate solution), batch experiments (pH), and deployment in anoxic sediment will be displayed.

2.3.1. Experimental set up and calculations

Except for the DGT experiments in anoxic sediments, triplicate DGT units were deployed in each experiment and were removed from the well-mixed solutions at incremental time intervals. The temperature and pH were recorded throughout the experiments. Prior to the retrieval of the DGT units, grab samples were taken, filtered at 0.45 μm on acetate cellulose filter, acidified at 0.15 mol L⁻¹ HNO₃, and stored at 4 °C before analysis. The mean value of temperature, pH and total As concentration is provided in the figures, as the standard deviation of the replicate experiments. After the DGT deployment, each binding gel was eluted in 2 mL of eluent solution for 24 h before chemical analyses. Eluent solution composition was 1 mol L⁻¹ HNO₃ for the Fh and $ZnFe_2O_4$ binding gels, 1 mol L⁻¹ HNO₃ and 10⁻² mol L⁻¹KIO₃ for the 3MP binding gel, and 1 mol L⁻¹ NaOH for the Metsorb® and ZrO_2 binding gels. Prior to analyses, the eluent solutions were diluted 10-fold in 0.15 mol L⁻¹ HNO₃.

The accumulated mass of As species by each binding gel (M_{DGT}^{As}, ng) were calculated using Eq. (1).

$$M_{DGT}^{As} = \frac{C_e^{As} \times (V_{binding\ gel} + V_{eluent})}{EF} \tag{1}$$

where C_e^{As} is the eluted concentration of As in the elution solution (μg L⁻¹), V_{gel} the volume of the AMP binding gel (mL), V_{eluent} the volume of eluent solution (mL) and EF the specific eluent factor (86% for 3MP [4],

100% for the iron(III)-based binding gels [2], 78% for Metsorb® [3] and 88% for ZrO_2 [16]). Average eluent factors of As(III) and As(V) were used to calculate the total As mass obtained by Metsorb® and ZrO_2 binding gels.

To evaluate the experimental DGT performances, the theoretical mass of As(III) ($M_{Predited}^{As(III)}$, ng) and total As ($M_{Predited}^{total\ As}$, ng) were calculated using the following equations [17], respectively.

$$M_{Predited}^{As(III)} = C_{solution}^{As(III)} \times D_{g+f}^{As(III)} \times A \times t/\Delta g \tag{2}$$

$$M_{Predited}^{total\ As} = M_{Predited}^{As(III)} + C_{solution}^{As(V)} \times D_{g+f}^{As(V)} \times A \times t/\Delta g \tag{3}$$

Where $C_{solution}^{As(III)}$ is the concentration of As(III) in the deployment solution (µg L^{-1}), $D_{g+f}^{As(III)}$ / $D_{g+f}^{As(V)}$ the effective diffusion coefficient of As (III) / As(V) in the diffusive gel and filter corrected from the temperature of the deployment solution (7.2 10^{-6} ± 7 10^{-7} and 4.2 10^{-6} ± 6 10^{-7} cm^2 s^{-1} for As(III) and As(V) at 25 °C, respectively [2]), A is the exposure area of the binding gel (3.14 cm^2), t is the deployment time (s) and Δg is the thickness of both the diffusive gel and the filter membrane (see further in figure captions). For seawater deployments, a value of $0.9 \times D$ was used [7,16].

2.3.2. Effects of pH and buffer solutions

To compare the accumulation efficiency of each binding gel as a function of pH, 15 DGT samplers were simultaneously deployed for 24 h in 4 L of 10^{-2} mol L^{-1} NaNO$_3$ spiked with either As(III) or As(V) at 50 µg L^{-1}. A pH titrator (Metrohm, model 736 GP Titrino), equiped with a NaOH stock solution (10^{-3} - 10^{-4} mol L^{-1}) and using a combined glass electrode and a Ag/AgCl [KCl] = 3 M reference electrode (Metrohm) was used to control and adjust the pH of the deployment solutions ranging from 5 to 9.

2.3.3. Time-series experiments in oxic waters

To determine the performance of each binding gel in oxic fresh and sea waters, 60 DGT samplers were simultaneously deployed up to 4 days (96 h) in a 20 L reactor spiked with As(III) and As(V) at concentrations of about 20 and 10 µg L^{-1}, respectively. Freshwater (pH 8.2, conductivity 400 µS cm^{-1}) was collected in the Lys River (northern France) in October 2016. Physico-chemical composition is presented in Supporting information (Table S1). Synthetic seawater (pH 8.2, salinity 34.6) was prepared according to Grashoff et al. [18], with the composition listed in Table S2. For each type of binding gel, triplicate DGT samplers were removed after 24, 48, 72 and 96 h of experiment. For samplers deployed in seawater, each binding gel was rinsed in 5 mL of ultrapure water for 1 h to remove unbound salts [10].

2.3.4. Deployment in anoxic sediment

This experiment was performed in order to compare the accumulation performances of the binding gels in anoxic environment, and to eventually select the best combination of binding gels to evaluate the redox speciation of As in such conditions. For this purpose, three sediment cores were collected in the Marque river (northern France) in March 2017 using a manual corer equipped with a Perspex® tube (35 cm in length, 15 cm i.d.). The first core was sliced every 1–2 cm for the determination of total dissolved As content as a function of depth. The cutting operation was done under nitrogen atmosphere in a glove box. Each sediment slice was centrifuged using a X-340 Prolabo centrifuge (rotation radius: 20 cm) during 20 min at 2500 rpm in order to extract the porewaters. The samples were subsequently filtered at 0.45 µm under nitrogen atmosphere. The second core was used for the measurement of the redox potential every cm in a Perspex® tube with holes. Measurements were performed using a platinum electrode (Mettler Toledo) combined with an Ag/AgCl ([KCl] = 3 M) reference electrode, with a potential equal to 0.22 V versus the Standard Hydrogen Electrode (SHE). The third core was placed in a thermostatic chamber at 13.5 °C (field temperature) and then used for the simultaneous

deployment of 5 DGT probes for 24 h (one for each type of binding gel). Each binding gel was finally sliced every 1 cm to measure the evolution of As(III) or total As as a function of depth.

2.3.5. Time-series experiment in carbonate solution

To examine the effect of the high carbonate concentration in sediment pore waters, 45 DGT samplers were simultaneously deployed up to 3 days in 20 L of a 10^{-2} mol L^{-1} NaNO$_3$ and NaHCO$_3$ solution spiked with As(III) and As(V) at concentrations of about 25 and 20 µg L^{-1}, respectively. For each type of binding gel, triplicate DGT samplers were removed after 24, 48 and 72 h.

2.4. Batch experiments with binding gel discs

Several batch experiments were dedicated to highlight the possible interaction of the five binding gels with some diagenetic products (*i.e.*, Fe^{2+}, Mn^{2+} and S^{2-}) and boric species.

2.4.1. Selectivity of binding gels for non-As species

Uptake efficiency was measured by immerging binding gel discs in 20 mL of a 10^{-2} mol L^{-1} NaNO$_3$ solution spiked with either Fe^{2+}, Mn^{2+} or S^{2-} at a concentration of 1 mg L^{-1} (typical concentrations in the sediment of the Marque river), and shaken at room temperature. Batch experiments for reduced dissolved species were performed under nitrogen atmosphere. The amount of analyte adsorbed to the binding gel (%) is calculated from the initial mass of dissolved species in the deployment solution (M$_i$, µg), and the mass of dissolved species remaining in solution after the experiment (M$_f$, µg).

$$Adsorption = \frac{M_i - M_f}{M_i} \tag{4}$$

In addition, investigations of the possible interactions with H$_3$BO$_3$ were performed under similar experimental conditions than for the reduced species (except operations under nitrogen atmosphere). These batch experiments are performed to confirm whether or not the use of borate buffer could potentially reduce the accumulation performances of the binding gels as suggested in the comments of Bennett and co-workers [1].

2.4.2. Impact of sulfides on the elution factor

Successive batch experiments were performed under nitrogen atmosphere to identify the potential impact of sulfides on the elution of inorganic As species from binding gels. Firstly, the binding gel discs were loaded with 400 ng of As(III) or As(V) (experimental conditions: 20 mL of 10^{-2} mol L^{-1} NaNO$_3$; [As(III)] = [As(V)] = 20 µg L^{-1}; 24 h of deployment). Then, the discs were immersed for 24 h in 10 mL of 10^{-2} mol L^{-1} NaNO$_3$ and 1 mg L^{-1} S^{2-}. Finally, the elution procedure was done for each binding gel disk (see Section 2.3.1).

In addition, to better understand the impact of sulfides on the elution of As species from binding gels, the geochemical software PHREEQC v3 (https://www.usgs.gov/software/phreeqc) was used to calculate the speciation of As in the elution solutions, using the thermodynamic database ThermoChimie v9b0 developed at Andra (http://www.thermochimie-tdb.com/) [19,20]. Input data were the concentrations of As, HS$^-$, Na$^+$, NO$_3^-$ and pH in the elution solutions. Redox reactions between As(V) and HS$^-$ were considered. Minerals were not considered in these thermodynamic calculations. The output files provide the predicted speciation of each component in the deployment waters and the saturation index (SI) with respect to any mineral phase. Hence, porewaters can be considered as supersaturated with respect to a mineral when SI > 1, at equilibrium when SI = 1 and undersaturated when SI < 1.
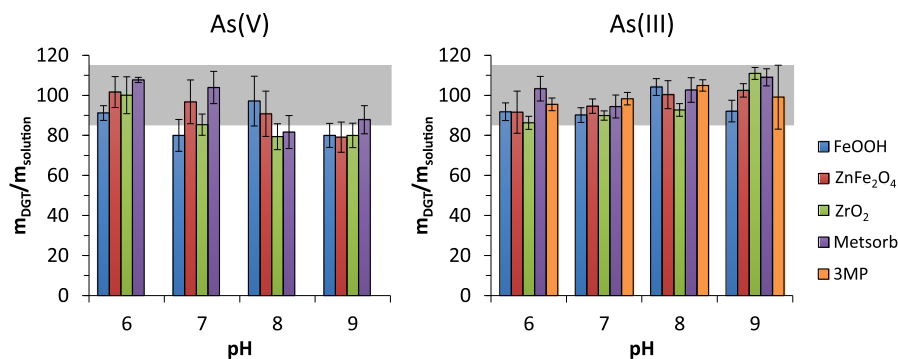
Fig. 1. Effect of pH on the accumulation performance of As(III) or As(V)for the different binding gels. Experimental conditions: $[NaNO_3] = 10^{-2}$ M; $[As(III)] = [As(V)] = 50\,\mu g\,L^{-1}$; 24 h of deployment.

3. Results and discussion

3.1. Laboratory evaluation of DGT performances

3.1.1. Effects of pH

The pH effects of deployment solution were studied in 10^{-2} mol L^{-1} NaNO$_3$ solution over 24 h. Results are displayed in Fig. 1. The accumulation performances of the binding gels are in the range 85–117% and 86–113% for As(V) and As(III), respectively. The DGT measurements were consequently quantitative assuming $\pm$ 15% of error [21]. Moreover, the binding gels dedicated to total As determination have the same accumulation performances in the pH range 5–9. Measuring the redox speciation of As was possible in 10^{-2} mol L^{-1}NaNO$_3$ solution by combining a DGT sampler with the 3MP binding gel for the determination of As(III), with one of the four other sampler with either the Fh, Metsorb®, ZnFe$_2$O$_4$ or ZrO$_2$ binding gel for the total determination of As. These accumulation performances are in good agreement with previous laboratory validation experiments performed in diluted NaNO$_3$ solution using DGT samplers containing 3MP (3.5–8.5) [4], Fh (3−8) [6,22,23], Metsorb® (3.5–8.5) [3], or ZrO$_2$ binding gel (2−9) [7,24]. In our previous work [2], similar results were obtained using buffered solutions for 3MP (5−9), Fh (5−8), Metsorb® (5−8) and ZnFe$_2$O$_4$ (5−9) binding gels. It is now clarified that the use of buffer solutions in our previous study [2] (*i.e.*, sodium acetate, sodium 2-(*N*-morpholino)-ethanesulfonate (MES), sodium 4-(2-hydroxyethyl)-1-piper-azineethanesulfonate (HEPES), and boric acid salts) does not impact the accumulation performances of the 3MP, Fh, Metsorb®or ZnFe$_2$O$_4$ binding gels. Then, the use of buffer solutions is possible in the absence of pH titrator in the lab. HEPES and MES are non-complexing agents [25,26], which have already been used as pH buffers in sorption experiments of inorganic As species by iron(III) or titanium(IV) minerals [27–31], or complexation experiments between inorganic As species and dissolved humic acids [32]. Acetate buffer have been also employed as a mobile phase in ion chromatography to separate inorganic As species [33]. Batch experiments were performed to control that no interaction of the binding gels with borate species was detected (Fig. 2). Dissolved borate species does not accumulate in the binding gels, with 100% of recovery in the deployment solutions. The presence of dissolved borate species in the deployment solutions should not interfere with As(III) in the 3MP binding gel, or with inorganic As species in the Fh, Metsorb®, ZnFe$_2$O$_4$ and ZrO$_2$ binding gels. It is now clearly confirmed that the use of borate buffer in our previous work [2] did not alter the performance tests of the binding gel.

Adsorbents encapsulated in APA hydrogel are considered amphoteric with the existence of a specific point of zero charge (PZC): Metsorb® (5.9) > ZrO$_2$ (6.5) > Fh (7.5) > ZnFe$_2$O$_4$ (8.1) [2,34,35]. The surface charge of these adsorbents may consequently vary according to the pH of the deployment solution. For instance, the surface of hydroxyl groups is negatively charged for a pH above pH$_{PZC}$, and is
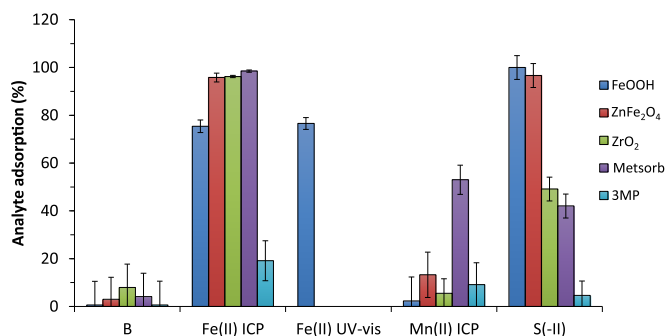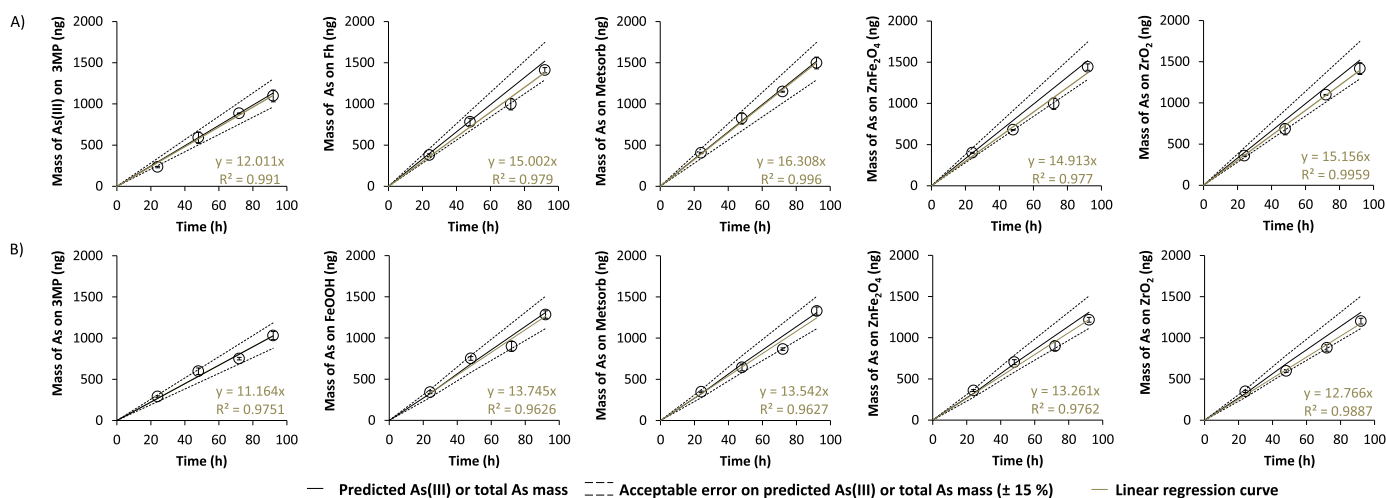

Fig. 2. Investigation of the interactions between the binding gels and H$_3$BO$_3$, Fe^{2+}, Mn^{2+} or S^{2-}. Experimental conditions: $[NaNO_3] = 10^{-2}$ M; $[H_3BO_3] = [Fe^{2+}] = [Mn^{2+}] = [S^{2-}] = 1$ mg L^{-1}; 24 h of deployment; $\Delta g = 930\,\mu m$. The experimental pH was set free during the batch experiments. pH values measured are the following: pH$_{boric\ acid}$ = 7.9 $\pm$ 0.1, pH$_{Fe(II)}$ = 6.9 $\pm$ 0.1; pH$_{Mn(II)}$ = 6.9 $\pm$ 0.1 and pH$_{S(-II)}$ = 8.9 $\pm$ 0.1.

positively charged for a pH is below pH$_{PZC}$. From an electrostatic point of view, the sorption processes of As(III) are more complex because H$_3$As^{+III}O$_3$, which is the main species at pH 6–9, is electrically neutral. The complexation between the anionic As(V) species (H$_2$AsO$_4^-$, HAsO$_4^{2-}$) and the negative surface sites of the adsorbent is theoretically not favourable for pH$_{solution}$ > pH$_{PZC}$ due to the charge repulsion. This suggests that the chemical potential prevails over the electrical potential in sorption processes for Fh, Metsorb® and ZnFe$_2$O$_4$. This hypothesis is reinforced by X-ray absorption experiments showing inner-sphere complexation of inorganic As species with iron(III), titanium or zirconium-based materials [36–40].

3.1.2. Time-series experiments in oxic waters

The DGT performances of the binding gels were compared during 4 days in natural freshwater and synthetic seawater containing As(III) and As(V). Long deployment times are often adequate to reveal possible interferences, especially in seawater, and 4 days is a typical deployment time for *in situ* investigations. The mass of As(III) and total As in the DGT samplers was monitored over time, and compared to the theoretical values (black line in Fig. 3, obtained from Eqs. (2) and (3)). A linear accumulation of As(III) by the 3MP-DGT samplers was observed over time both in freshwater and seawater ($R^2 > 0.96$). The concentration of As(III) recovered from the 3MP-DGT samplers reached 93.8 $\pm$ 8.6 and 103 $\pm$ 7.0% (mean $\pm$ standard deviation) of the initial As(III) concentration in freshwater and seawater, respectively. Similar trends were observed with the other DGT samplers for total As, with a linear accumulation over time ($R^2 > 0.96$). The concentration of total As recovered from the other DGT samplers was very close both in freshwater: 92.3 $\pm$ 6.0% for Fh, 100 $\pm$ 2.8% for Metsorb®, 91.3 $\pm$ 6.9% for ZnFe$_2$O$_4$, and 90.0 $\pm$ 2.8% for ZrO$_2$, and

Fig. 3. Results of time-series experiments performed in: (A) natural freshwater ($[As]_{ICP-MS}$ = 36.0 ± 1.3 µg L^{-1}; $[As(III)]_{DGT}$ = 18 ± 2.7 µg L^{-1}; $[As(V)]_{DGT}$ = 13.0 ± 2.0 µg L^{-1}; pH 7.9 ± 0.4; T = 16 ± 2 °C; Δg = 930 µm); and (B) synthetic seawater ($[As]_{ICP-MS}$ = 31 ± 2.4 µg L^{-1}; $[As(III)]_{DGT}$ = 21.6 ± 3.2 µg L^{-1}; $[As(V)]_{DGT}$ = 9.4 ± 1.4 µg L^{-1}; pH 7.8 ± 0.4; T = 16 ± 2 °C; Δg = 930 µm).
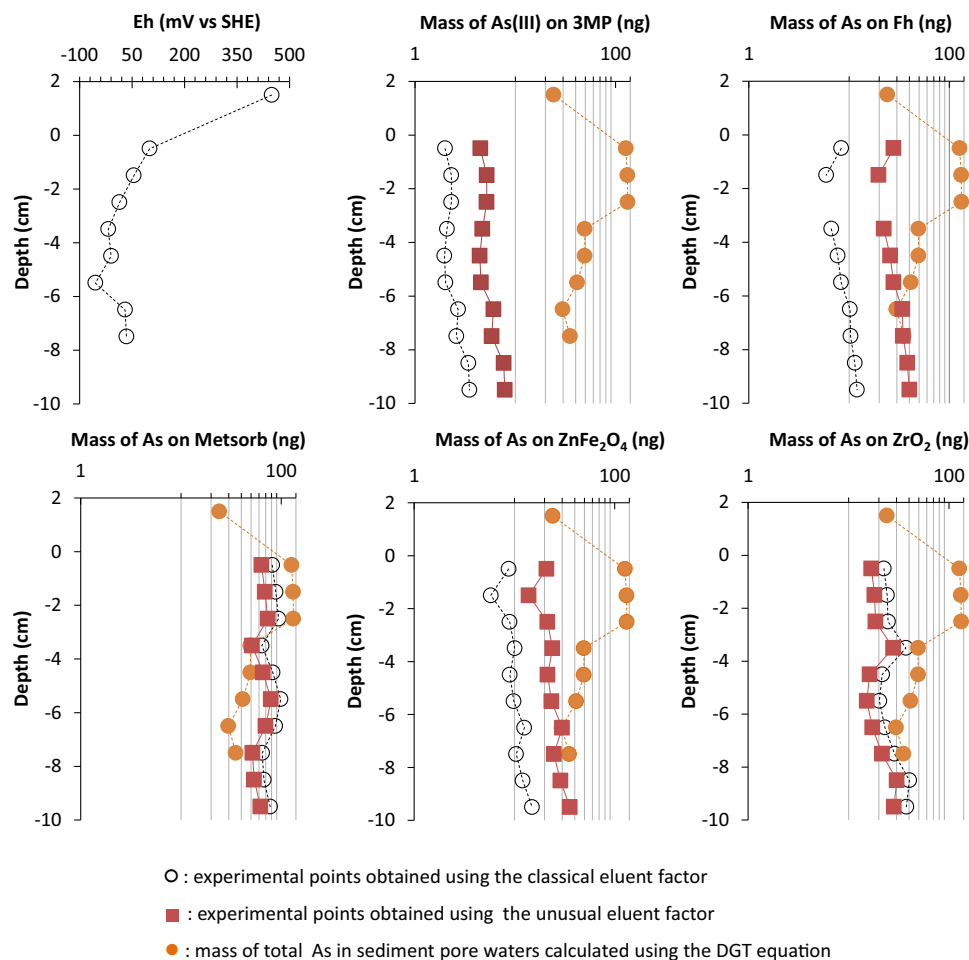
in seawater: 100.3 ± 8.3% for Fh, 96.8 ± 8.5% for Metsorb®, 98.6 ± 8.9% for ZnFe$_2$O$_4$, and 93.2 ± 8.8% for ZrO$_2$. Assuming 15% of error on the predicted As(III) or total As mass accumulated by the DGT samplers (see the dashed lines in Fig. 3), the five DGT methods tested are shown to be quantitative both in freshwater and seawater over 4 days of experiment. Moreover, the DGT response of each binding gel was not impacted by either the ionic strength or the composition of the deployment solution. As the saturation of the binding gels was not reached during these time-series experiments [decreasing accumulation of As(III) or total As], the maximal deployment time cannot be determined in these conditions.

For total As, numerous studies have shown that the DGT performances of the 3MP, Fh, Metsorb®, and/or ZrO$_2$ binding gels were comparable in laboratory over 40 – 120 h of deployment in freshwater [3,9,12,41,42], similarly to what has been observed in the present study. On the contrary, in seawater, several inconsistencies between experimental studies have been noticed. In Panther et al. [41], Price et al. [9], quantitative and comparable DGT measurements were obtained using the Fh and Metsorb® binding gels up to 40–96 h of deployment time. Similar results were obtained in this study. However, Bennett et al. [4] have observed non quantitative DGT quantification using the Fh binding gel after 72 h (C_{DGT} / $C_{solution}$ < 85%), contrary to the 3MP and/or Metsorb® binding gel. Comparing the performances of three DGT binding gels, Sun et al. [7] concluded that the maximal deployment time for quantitative measurement was: 96 h for ZrO$_2$ > 48 h for Metsorb® > 24 h for Fh. The lower Fh- and Metsorb®-DGT performances were explained by either a difference in the sorption capacity and/or interference with carbonates as suggested by Panther et al. [10]. Indeed, during time-series experiments, Panther and co-workers highlighted that the accumulation of PO$_4^{3-}$ [a chemical analogue of As(V)] by the Fh-DGT samplers was impacted by the carbonate concentration level. Zhang et al. [43] have alerted upon uncontrolled Fh preparation, which can produce a mixture of Fh, goethite (Goe) and hematite (Hem), with a progressive conversion of Fh into Goe during the binding gel storage. In addition, the stability of the Fh binding gel in DGT unit could be also altered over time by the physico-chemical composition of deployment solution. Indeed, numerous factors could act on the Fh transformation into Goe and Hem such as pH, temperature, dissolved organic matter, or dissolved species, *e.g.*, silicates, PO$_4^{3-}$, NO$_3^-$, Cl$^-$, SO$_4^{2-}$ Fe^{2+} or Mn^{2+} [44–51]. If Fh transformation has occurred during experiments, a lower Fh-DGT response due to lower Goe and Hem affinity for As species would be expected, similarly to carbonate interferences [52–55].

3.1.3. Deployment in anoxic sediment

The accumulation performance of the binding gels was compared as a function of depth in the sediment of the Marque River, similarly to our previous study [2]. More information about the physico-chemical properties of the sediment is available in [56,57]. The recorded potential redox profiles are typical of those encountered during early diagenetic processes (Fig. 4). A loss of more than 450 mV is observed between the overlying water and the sediment, suggesting oxidant consumption by bacteria. In particular, reduction of iron(III) and manganese (IV) (oxy)hydroxides is expected to release some adsorbed and/or co-precipitated arsenic species. This predictable behaviour was discussed in our previous study [57], where we demonstrated that the correlation between As and Fe and As and Mn concentrations in porewaters were not relevant in sediments. Conversely, the link between As and the production of sulfides was established. Moreover, it is also important to remind that DGT probes deployed in sediments give information on the labile As fluxes (including species in porewaters and species weakly adsorbed on particles). Therefore, it is not surprising to observe presently different profiles of total As in porewaters and labile As measured with the DGT technique. Additional deployments of DGT probes with different diffusive gel thicknesses may bring a new insight into the rate of renewal of As in porewaters close to the probe.

The average mass of As accumulated decreased as follows: 80.4 ± 12.9 ng for Metsorb® > > 28.6 ± 7.7 ng for ZrO$_2$ > 10.4 ± 2.6 ng for ZnFe$_2$O$_4$ ~ 9.1 ± 2.2 ng for Fh > 2.5 ± 0.6 ng for 3MP. The As mass retrieved from the DGT samplers containing the 3MP, Fh, ZnFe$_2$O$_4$ or ZrO$_2$ binding gels is generally lower than those measured in porewaters. Conversely, the trend is opposite below 4 cm for the Metsorb® - DGT samplers, and might be linked to spatial heterogeneities. It can be observed from the DGT measurements that As(III) is a minor As species in the sediment of the Marque River. As opposed to time-series experiments performed in oxic waters (Section 3.1.3), the measurement of total As seems dependent of the binding gel used. The chemical reactivity of the iron(III)-based binding gels look the same due to similar DGT response, contrary to the Metsorb® and ZrO$_2$ binding gels. Their performance could be more sensitive to the high concentration level of carbonates recorded in the sediment pore waters of the Marque river (~10 mmol L^{-1}). This hypothesis is tested in the laboratory and will be detailed in the next section (Section 3.1.4). The presence of other diagenetic species could also reduce the accumulation performance of the iron(III)-based binding gels. In light of this assumption, batch experiments were performed to test the accumulation performance of the binding gels in the presence of Fe^{2+}, Mn^{2+} and HS$^-$; the results will be presented in Section 3.2.1.

Fig. 4. Depth profiles of redox potential (E_h) and mass of As(III), total As accumulated by different DGT samplers from sediment cores sampled in the Marque River in 2017 (24 h of deployment time; $\Delta g = 1230\,\mu m$; T = $13.5 \pm 0.1\,°C$). Data are also available in Table S3.

3.1.4. Time-series experiments in carbonate solution

Time-series experiments were performed to investigate a potential effect of a high carbonate concentration (10 mmol L^{-1}, a value higher than in the tested oxic waters) on the DGT uptake. A linear accumulation of As by the DGT samplers was observed over 72 h whatever the binding gel used (R^2 > 0.93; Fig. 5). The amount of As species recovered are: 96.8 ± 5.9% for 3MP, 82.6 ± 6.7% for Fh, 106.4 ± 1.9 for Metsorb®, 84.4 ± 4.1% for ZnFe$_2$O$_4$, and 97.8 ± 11.9% for ZrO$_2$. However, the maximum deployment time for a quantitative measurement of total As was only 48 h for the iron(III)-binding gels (M$_{DGT}$ / M$_{predited}$ < 85%) assuming ± 15% of error on predicted As mass, whereas quantitative measurements were possible over 72 h for the others binding gels. Although the presence of carbonates has a small negative effect on the As uptake by the iron(III)-binding gels, it does not explain why their DGT response differs from the other binding gels during 24 h of deployment in the anoxic sediment of the Marque river (Fig. 4). Further investigations testing the effects of other diagenetic species (Fe^{2+}, Mn^{2+} and HS$^-$) are presented below to better understand these differences.

3.2. Batch experiment with binding gel discs

3.2.1. Selectivity of the binding gels for other species

Results show that the 3MP binding gel accumulates 20% Fe^{2+}, and does not react with either Mn^{2+} or HS$^-$ (Fig. 2). Note that redox speciation of dissolved iron was not impacted during batch experiments as shown Fig. 2. Fe^{2+} could be considered as a minor competing species with As (III), Hg^{2+} [58], CH$_3$Hg$^+$ [59–61] and Sb(III) [21] during the deployment

of the 3MP DGT samplers in anoxic environment. Conversely, the other binding gels strongly accumulate Fe^{2+} (75–98%). Mn^{2+} was shown to only adsorb on the Metsorb® binding gel (47%) (Fig. 2). A total uptake of HS$^-$ was observed in contact with the iron(III)-based binding gels (Fig. 2), without any related increase of the Fe^{2+} concentration in the deployment solutions (< 50 µg L^{-1}). It is difficult to evaluate the reduction of iron (III)-based adsorbents by HS$^-$. If the reduction was effective, it is possible that Fe^{2+} produced could be adsorbed at the surface of the remaining iron(III)-based adsorbents [62]. No acidic volatile sufilde determination was done to ensure that amorphous Fe^{II}S could be formed during the batch experiments. The Metsorb® and ZrO$_2$ binding gels partially accumulate HS$^-$ (~ 50%). The interactions of these reduced species could modify the reactivity of the initial adsorbent encapsulated in the APA hydrogel over time, and consequently, their sorption could reduce the number of surface sites available for the accumulation of As species. Surface precipitates involving CO$_3^{2-}$ [63], PO$_4^{3-}$ [64] or HS$^-$ [65] could also form. As for the Fh binding gel, interaction with Fe^{2+} could result from the transformation of Fh into Goe and Hem over time [66–69]. Changes in mineral composition could lead to a decrease in the uptake of As by the Fh binding gel during DGT deployment in the sediment of the Marque River (Fig. 4). Reduction of iron(III)-adsorbents by sulfides could also lead to As remobilization, thus impacting the uptake of As species by the DGT samplers. This assumption is tested in the following section (section 3.2.2).

3.2.2. Impact of sulfides on the elution factor

The exposition of the binding gels to HS$^-$ for 24 h did not show any remobilization of As(III) or As(V) from the binding gels in the
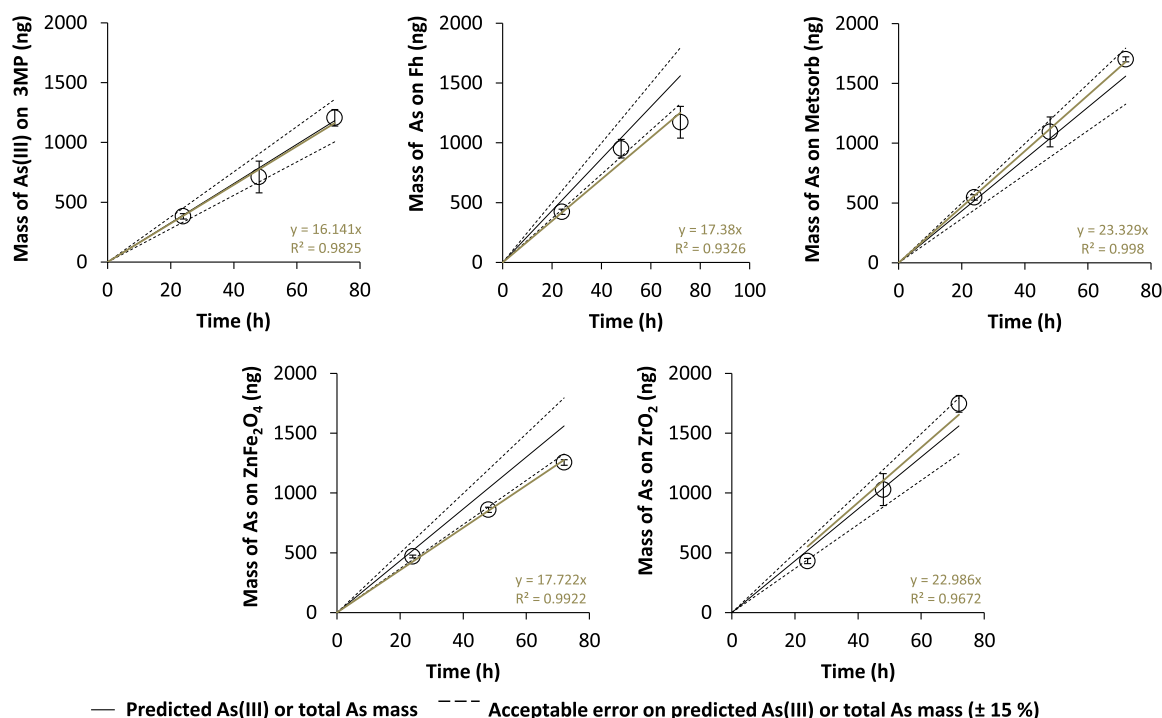
— Predicted As(III) or total As mass   _ _ _ Acceptable error on predicted As(III) or total As mass (± 15 %)

Fig. 5. Results of time-series experiments performed in 10^{-2} mol L^{-1} NaNO$_3$ and 10 mmol L^{-1} NaHCO$_3$. ([As]$_{ICP-MS}$ = 44.0 ± 2.3 µg L^{-1}; [As(III)]$_{DGT}$ = 26.2 ± 3.9 µg L^{-1}; [As(V)]$_{DGT}$ = 17.8 ± 2.7 µg L^{-1}; pH 8.7 ± 0.3; T = 20 ± 2 °C; Δg = 1230 µm).

deployment solutions (Fig. 5). These results suggest that the presence of sulfides in solution does not affect the DGT uptake whatever the binding gel used. For the iron(III)-based binding gels, the amount of Fe^{2+} in the deployment solutions was very low (1.9–23 µg L^{-1}). After the experiments, the binding gels were placed in the eluent solutions to elute As species. The elution efficiency of As strongly depends on the eluent composition (Fig. 5): 25.6–39.4% for Fh using 1 mol L^{-1} HNO$_3$, 48.9–67% for ZnFe$_2$O$_4$ using 1 mol L^{-1} HNO$_3$, 62.6% for 3MP binding gel using 1 mol L^{-1} HNO$_3$ and 10^{-2} mol L^{-1} KIO$_3$, and 94–117% for Metsorb® and ZrO$_2$ binding gels using 1 mol L^{-1} NaOH. The elution efficiencies are different from conventional values obtained without sulfide contact, *i.e.*, 85.6 ± 1.7% for 3MP [4], 100% for iron(III)-based binding gels [2], 75.2–81.2% for Metsorb® [3], 88.4–86.9% for ZrO$_2$ [7], with an elution efficiency of As reduced in HNO$_3$ and total in NaOH. Our experimental results clearly show that the exposition of the binding gels to HS⁻ modifies the efficiency of the elution procedure, with suspicion that formation of orpiment (As$_2^{III}$S$_3$) occurred during the elution. From thermodynamic calculations, this mineral phase should only dissolve for elution in basic solutions (SI$_{NaOH}$ = −110.8 for Metsorb and ZrO$_2$ binding gels; SI$_{HNO3}$ = −12.7 for Fh and ZnFe$_2$O$_4$ binding gels), which agrees with Floroiu et al. [70], who showed that an increase in pH would promote the dissolution of As$_2^{III}$S$_3$. Addition of KIO$_3$ permits to oxidize the thiol group of the 3MP adsorbent, leading to a release of As in the eluent solution, and eventually of As$_2$S$_3$, thus improving the extraction yield (loss of 26%) compared to the elution procedure of the Fh and ZnFe$_2$O$_4$ binding gels (loss of 33–75%). Note that elution factors lower than 85% are not acceptable for analytical applications [71]. An alternative elution method should be found to better extract As species from the 3MP and iron(III)-based binding gels (eventually 1 mol L^{-1} NaOH [22]).

Consequently, conventional eluent factors should not be used to retrieve the concentration of As species from DGT samplers during deployment in anoxic environments. Instead, the mass of As species accumulated in the binding gels of the DGT deployed in the sediment of the Marque River was re-calculated using the mean values of the unconventional eluent factors of As(III) and As(V) obtained from batch

experiments in the presence of sulfides. Results are presented in Fig. 4. The average mass of As accumulated in the sediment core decreased as follows: 64.0 ± 10.0 ng for Metsorb® > 30.3 ± 7.5 ng for Fh ∼ 24.8 ± 6.2 ng for ZnFe$_2$O$_4$ > 21.5 ± 5.8 ng for ZrO$_2$ > 5.6 ± 1.3 ng for 3MP. Speciation remains unchanged with As(III) as a minor As species. The accumulation capacities of the iron(III)-based binding gels are globally comparable to the ZrO$_2$ binding gel, but remain lower than those of the Metsorb® binding gel, which presented the best performance in 2017.

In comparison with [2], we found a good agreement between As(V) mass accumulated by the ZnFe$_2$O$_4$- and Fh- DGT samplers, with differences less than 10%. The Metsorb® binding gel did not stand out from the iron(III)-based binding gels in the previous study [2]. However, in this study, the amount of total As accumulated Metsorb® binding gel is higher compared to the other binding gels (by over 50% in some case). The As(V) concentrations were similarly re-calculated using the unconventional eluent factor. Results are displayed in Table S4. The DGT depth-profiles measured with the Metsorb® and iron(III)-based binding gels were more similar, with differences of < 30% (except for the Metsorb binding gel at − 2.80 cm). The DGT performances of the Metsorb® binding gel are not better than the ZnFe$_2$O$_4$ and Fh ones in [2], as opposed to results obtained in 2017 in the same river sediments. The better accumulation of Metsorb® observed could be eventually linked to spatial heterogeneity within the sediment core. Regarding the results of these two studies, it is however difficult to draw conclusions on the efficiency of the binding gels in these anoxic conditions. Finally, the elution efficiency might be important factor to explain the large discrepancy between results (except for Metsorb® in the present study) when the conventional eluent factor is used for DGT calculations. Carbonates interferences should not impact the DGT uptake whatever the binding gels for 24 h of deployment (Section 3.1.4) in the sediments of the Marque River. Since no isotopic tracer exists for As, an elemental tracer could eventually be defined and used just before the elution procedure in order to account for the changes in elution efficiency, thus improving the robustness of As determination whatever the DGT gel used. Fig. 6
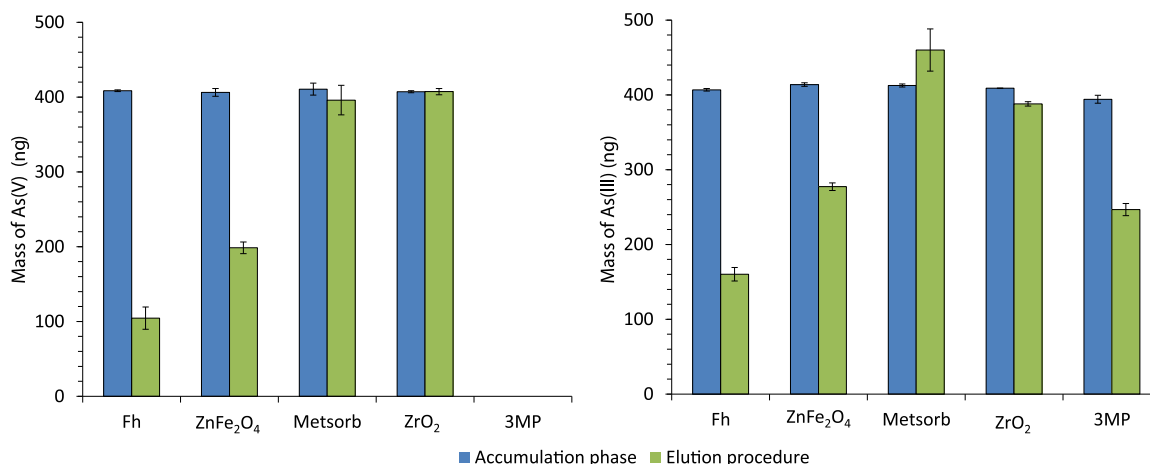
Fig. 6. Accumulation of inorganic As species by the different binding gels, and elution after sulfide exposition of the As-loaded binding gels.

4. Conclusions

In this work, the DGT performances of the 3MP, Fh, Metsorb®, ZnFe$_2$O$_4$, and ZrO$_2$ binding gels have been tested to measure As species concentration at trace level in environmental waters. A study combining batch experiments in the presence of reduced species, time-series experiments in oxic waters (both freshwater and seawater) and deployment in anoxic river sediments was performed in order to highlight the potential limitations of the binding gels. The results show that the DGT measurements were not impacted by pH buffers in the range pH 5–9 whatever the binding gel used. In both oxic freshwater and seawater, the DGT deployment was possible up to 96 h, with a good DGT response whatever the binding gel used. It is therefore conceivable to determine the redox speciation in oxic environmental waters by deploying DGT samplers with the 3MP binding gel for the determination of As(III) and the other DGT samplers, *i.e.*, Fh, Metsorb®, ZnFe$_2$O$_4$ and ZrO$_2$, for the determination of total As.

In anoxic sediments, however, *in situ* determination of As speciation remains a challenge regarding the composition of porewaters. DGT samplers with Fh and ZnFe$_2$O$_4$ binding gels should be deployed for a maximum of 48 h in high carbonate concentration waters (10 mmol L^{-1}). Interactions between reduced species (Fe^{2+}, Mn^{2+} or HS$^-$) and the binding gels have also been identified in batch experiments. The sorption of Fe^{2+} was not negligible in the Metsorb®, ZrO$_2$ and iron(III)-based binding gels. It could be also possible that the initial reactivity of these binding gels is modified with time.

We have also demonstrated that sulfides impact the efficiency of the elution procedures. The conventional eluent factors are consequently not adapted to calculate the mass of As species accumulated in the binding gels. The formation of orpiment during elution could explain the low recovery of As, since its solubility depends on pH. In that case, elution in a basic eluent (1 mol L^{-1} NaOH) would be more adapted for the determination of total As. Elution is shown to be a critical point for which attention should be paid in order to correctly evaluate the redox speciation of As in sulfidic environments. Using unconventional eluent factors to correct for the interaction with sulfides improve the determination of As(III) for the 3MP binding gel and of total As for the Fh and ZnFe$_2$O$_4$ binding gels. Elemental tracer could be eventually used just before the elution procedure to account for the changes in elution efficiency, with the aim of improving the robustness of As species determination whatever the DGT gel used. Further studies would be required before selecting a specific binding gel for the determination of total As in anoxic sediments through inter-comparison exercises.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2019.01.127.

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