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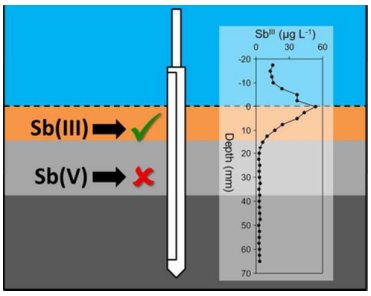
Environmental Impact Statement:

Antimony is a priority environmental contaminant, with the primary source being the mining and processing of antimony ore for industrial applications. Despite this, very little research on the behaviour and fate of antimony in the environment has been reported. To properly understand the processes controlling the movement of antimony through the environment, there is a need for tools to accurately measure the speciation of antimony, not just the total concentration. Here we report an *in situ*, passive sampling tool capable of measuring antimony speciation in surface waters and sediment porewaters. The application of this tool to investigating antimony speciation in the environment will provide new insights into the complex processes controlling its behaviour and fate.



A new *in situ* sampling method enables the selective measurement of Sb(III) in surface waters and sediment porewaters

In situ speciation of dissolved inorganic antimony in surface waters and sediment porewaters: development of a thiol-based diffusive gradients in thin films technique for Sb^{III}

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Abstract

Antimony is a priority environmental contaminant typically present as either the trivalent (Sb^{III}) or the pentavalent (Sb^{V}) oxidation state in aquatic systems. Both the toxicity and mobility of antimony are affected by its speciation, and thus the accurate measurement of antimony speciation is essential for investigating the behaviour of this contaminant in aquatic systems. Here we present a diffusive gradients in thin films (DGT) technique, which utilises a binding layer containing a thiol-based adsorbent (3-mercaptopropyl functionalised silica gel), for the selective measurement of Sb^{III} in surface waters and sediment porewaters. We also evaluated the Metsorb DGT technique, which has been previously reported to accurately measure Sb^{V}, for its ability to accumulate Sb^{III} and thus allow the measurement of total inorganic antimony. Both the mercapto-silica and Metsorb DGT techniques showed a high affinity for Sb^{III}, with uptake efficiencies >97%. Elution efficiencies of 86.9 ± 2.6% and 88.1 ± 1.2% were obtained for mercapto-silica and Metsorb, respectively, with 1 mol L^{-1} H_2O_2 in 1 mol L^{-1} NaOH. The accumulation of Sb^{III} by these DGT techniques was linear with time ($R^2 > 0.99$) and unaffected by pH (4.07 – 8.05), ionic strength (0.001 mol L^{-1} – 1.0 mol L^{-1} NaCl), bicarbonate (1 mmol L^{-1} – 15 mmol L^{-1}), and an artificial seawater matrix (pH 8.34; salinity 34.8). Finally, the mercapto-silica DGT technique was applied to measure porewater concentrations of Sb^{III} and As^{III} in a contaminated freshwater sediment at high resolution.

Introduction

Antimony is a metalloid widely exploited for industrial applications, with global mine production in 2013 estimated at 159,000 metric tons.[1] The extensive industrial use of antimony has resulted in it being listed as a priority pollutant by the United States Environmental Protection Agency.[2] Antimony is primarily used in flame retardants, lead alloys for lead-acid batteries, and the production of glass, ceramics, and plastics.[1] There have also been numerous reports of severe antimony contamination surrounding mining and processing facilities, and at shooting ranges (see Filella *et al.*[3] and Wilson *et al.*[4] for comprehensive reviews on antimony occurrence in the environment). Ultimately, inorganic contaminants like antimony are transported to aquatic systems, where they often accumulate in sediments and are subject to complex biogeochemical processes that determine their environmental behaviour and fate. The study of antimony biogeochemistry is complicated by the fact that it exists in different oxidation states; typically neutral $Sb(OH)_3$ (Sb^{III}) or oxyanionic $Sb(OH)_6^-$ (Sb^V), which can impact both its affinity for various solid-phases and its toxicity to biota.[5]

The most reliable way to determine antimony speciation in natural waters is by on-site or *in situ* separation of the species of interest. On-site approaches are limited to solid phase extraction (SPE) of the sample, typically with SPE cartridges through which the sample is passed.[6] Such methods have the advantage of avoiding sample preservation, storage, and transport, and can be done relatively quickly and inexpensively. Unfortunately, the methods that are available are not suitable for marine waters and require volumes of sample (typically millilitres) not often obtainable when extracting sediment porewater.[6] Passive *in situ* sampling methods for antimony speciation could provide the same benefits as on-site methods, with the additional advantage of integrating concentrations over the deployment time of the sampling device, thereby providing a more representative measurement of antimony concentrations in dynamic systems.[7]

Diffusive gradients in thin films (DGT) is an *in situ*, passive sampling technique that provides a time-weighted average analyte concentration in surface and interstitial waters (see Zhang and Davison[8] for a recent review on the application of DGT for measurements in water, sediment and soils).[9, 10] Solutes diffuse through a diffusive layer of known thickness, typically a polyacrylamide hydrogel overlain by a protective membrane, and are immobilised within a binding layer (often hydrogel-based) that contains a binding agent with high affinity for the analyte of interest. The analyte concentration in the bulk solution is calculated from the mass of analyte accumulated by the binding layer (determined after elution and analysis of the analyte), the deployment time, the area of sampler exposed to the bulk solution, the thickness of the diffusive layer, and the diffusion coefficient of the analyte in the diffusive layer.[10]

Numerous binding agents have been used in DGT to permit the measurement of a wide variety of analytes, including, for example: cationic trace metals,[11] oxyanionic metalloids,[12, 13] sulfide,[14] phosphate,[15, 16] and ammonium.[17] Additionally, the application of selective binding agents that only accumulate a specific analyte oxidation state, have expanded the DGT technique to allow the *in situ* measurement of chemical speciation. Recently, Fan *et al.*[18] described the application of a 3-mercaptopropyl functionalised silica-based DGT technique for measuring Sb^{III} in wastewater and freshwater, although this method was not tested in seawater and required a complicated elution procedure. Panther *et al.*[13] described a Metsorb DGT technique for measuring Sb^{V} in natural waters, although the ability of this technique to measure Sb^{III} was not tested. Bennett *et al.*[19] described the use of a binding layer containing 3-mercaptopropyl functionalised silica gel that selectively accumulated As^{III} in the presence of As^{V}. When combined with a DGT technique for measuring total inorganic arsenic, such as that described by Panther *et al.*[20] or Bennett *et al.*,[21] this approach allowed the quantification of As^{III} and As^{V} in surface waters and sediment porewaters.[22]

Here we present a diffusive gradients in thin films (DGT) technique for the selective *in situ* measurement of Sb^{III} in fresh and marine surface waters and sediment porewaters. The method utilizes a thiol-based binding layer (3-mercaptopropyl functionalized silica gel immobilized in a polyacrylamide gel matrix) with high selectivity for Sb^{III} over Sb^{V}. The existing Metsorb DGT technique that was previously evaluated for measuring Sb^{V},[13] was also tested for its ability to accurately measure Sb^{III}, which would allow this technique to be used to measure total inorganic antimony. The mercapto-silica and Metsorb DGT methods were tested at a range of pH, ionic strength, bicarbonate concentration, and in artificial seawater. Finally, the new mercapto-silica DGT method was applied to determining high-resolution porewater profiles of Sb^{III} and As^{III} in a contaminated freshwater sediment.

Experimental

Reagents, materials and solutions. All plasticware was washed in 5-10% HNO_3 or HCl and then thoroughly rinsed in deionized water (18.2 $M\Omega cm^{-1}$; Millipore) before use. All reagents were analytical reagent grade or better. Stock solutions (100 mg L^{-1}) of antimonite (Sb^{III}) and antimonate (Sb^{V}) were prepared by dissolution of potassium antimony(III) tartrate and potassium hexahydroxoantimonate(V), respectively, in deionized water. Stock solutions were stored at 4°C and diluted immediately before use. DGT sampler housings were purchased from DGT Research Ltd (http://www.dgtresearch.com). 3-mercaptopropyl functionalised silica gel (SiliaMetS Thiol) was purchased from Silicycle (Quebec, Canada), and Metsorb HMRP (50 μm powder) was obtained from Graver Technologies (Delaware, United States of America).

Antimony analysis. Antimony (m/z 121) was measured by inductively coupled plasma – mass spectrometry (ICP-MS; Agilent 7900). The instrument was equipped with an octopole collision/reaction cell, which was operated in helium collision mode to reduce potential polyatomic

interferences. All solutions for analysis were prepared in 2% (v/v) ultrapure HNO_3 (sub-boiling distilled). External calibration solutions and quality control solutions were prepared from separate commercially available standard solutions (High Purity Standards). A certified reference material (Riverine Water, SLRS-5; National Research Council Canada) was analysed in each analytical run and had an average recovery of 102.1 ± 6.0 % (n = 9). The stability of inorganic antimony species in the experimental solutions was monitored using a solid phase extraction (SPE) procedure followed by ICP-MS analysis, as described previously,[6] Speciation changes were negligible over the experimental durations used in this study. Samples taken for speciation analysis were processed immediately, to avoid possible speciation changes due to storage.

DGT samplers. DGT samplers with binding layers containing either 3-mercaptopropyl functionalized silica gel (mercapto-silica) or Metsorb were prepared as described previously.[19, 21] The diffusive layers of the samplers consisted of a polyacrylamide hydrogel, prepared as described previously,[19, 21] and a protective 0.45 μm pore-size cellulose nitrate (Merck Millipore Ltd.) or polysulfone (Pall Corp.) filter membrane, with a total thickness of 0.088 ± 0.04 cm. Samplers were stored in sealed polyethylene bags at 4°C prior to use. Following retrieval of DGT samplers from deployment solutions they were thoroughly rinsed in deionised water and stored at 4°C prior to elution. DGT binding gels were eluted in 1 mL of 1 mol L^{-1} H_2O_2 / 1 mol L^{-1} NaOH for at least 24 hours, before being diluted 20-fold in 2% HNO_3 for ICP-MS analysis, except where stated otherwise.

Uptake and elution. Mercapto-silica and Metsorb binding gel discs were exposed in triplicate to known volumes of 100 μg L^{-1} Sb^{III} (pH 6, 0.01 mol L^{-1} NaCl) for at least 12 hours. Samples of the solution before and after exposure of the binding gel discs were collected for ICP-MS analysis to determine the mass of antimony accumulated by the binding gels. Elution of antimony from the binding gels was tested by exposing them to 1 mL of one of the following solutions for at least 24 h: 0.1 mol L^{-}

[1] KIO_3 / 1 mol L^{-1} HNO_3 / 1 mol L^{-1} HCl; or 1 mol L^{-1} H_2O_2 / 1 mol L^{-1} NaOH. Eluents were diluted and analysed by ICP-MS to determine the efficiency of elution procedures.

Accumulation over time. To determine if the accumulation of Sb^{III} by Mercapto-silica and Metsorb DGT samplers was linear, three sets of triplicate samplers were exposed to a well-stirred solution containing 100 µg L^{-1} Sb^{III} in 0.01 mol L^{-1} NaCl (buffered at pH 7.79 ± 0.05 with 5.0 x 10^{-4} mol L^{-1} $NaHCO_3$) for 10, 18, and 26 hours. A similar experiment was done to determine if Sb^{V} was accumulated by mercapto-silica DGT, where a single set of triplicate samplers was exposed to a well-stirred solution of 100 µg L^{-1} Sb^{V} in 0.01 mol L^{-1} NaCl (buffered at pH 7.90 ± 0.02 with 5.0 x 10^{-4} mol L^{-1} $NaHCO_3$) for 26 hours. The average temperature of the experimental solutions was 24.8 ± 0.4°C. Samples of the solution were taken at the beginning of the experiment, and each time DGT samplers were removed, for ICP-MS analysis of total antimony and for antimony speciation analysis by SPE-ICP-MS.

Effect of pH, ionic strength, bicarbonate concentration, and artificial seawater. The performance of mercapto-silica and Metsorb DGT were assessed for measuring Sb^{III} over a range of pH, ionic strengths, bicarbonate concentrations, and in artificial seawater. DGT samplers of each type were deployed in triplicate in well-stirred solutions containing 100 µg L^{-1} Sb^{III} for 24 – 26 hours (exact time recorded). Solutions of different pH were prepared in 0.01 mol L^{-1} NaCl through the addition of HCl (for pH < 6) or by buffering with 5.0 x 10^{-4} mol L^{-1} $NaHCO_3$ (for pH > 7). Solutions of different ionic strength were prepared with NaCl at 0.001, 0.01, 0.1, and 1.0 mol L^{-1} (buffered at pH 7.82 ± 0.12 with 5.0 x 10^{-4} mol L^{-1} $NaHCO_3$). Solutions of different bicarbonate concentration were prepared in 0.01 mol L^{-1} NaCl with $NaHCO_3$ at 0.001, 0.005, 0.01 and 0.015 mol L^{-1}. Due to the buffering of solution pH by $NaHCO_3$, the pH of each solution was slightly different: pH 8.20 ± 0.03 for 0.001 mol L^{-1} $NaHCO_3$; pH 8.65 ± 0.22 for 0.005 mol L^{-1} $NaHCO_3$; pH 8.81 ± 0.18 for 0.010 mol L^{-1} $NaHCO_3$; and

pH 8.79 ± 0.18 for 0.015 mol L^{-1} $NaHCO_3$. Artificial seawater was prepared as described by Grasshoff *et al.*,[23] and had a pH of 8.34 ± 0.01 and a salinity of 34.8.

Capacity. The linear accumulation capacity of mercapto-silica DGT and Metsorb DGT samplers was determined by exposing ten samplers of each type to a well-stirred solution of 22 mg L^{-1} Sb^{III} and removing one sampler of each type every 30 minutes. The mass accumulated by each sampler was compared to the theoretical mass calculated from the diffusion coefficient of Sb^{III}, the deployment time, the area of sampler exposed to solution and the diffusive layer thickness (as per the DGT equation).[10] Deviation of the measured mass from the theoretical mass indicates that the linear accumulation capacity has been exceeded, and the sampler is no longer accumulating Sb^{III} quantitatively.

High-resolution, porewater measurements of Sb^{III} and As^{III} with mercapto-silica DGT. Sediment was collected from an antimony and arsenic contaminated wetland in Urunga, New South Wales, Australia (30°30'12.4"S 153°00'46.1"E), and transported to the laboratory. The sediment was sieved to < 1 mm and homogenised, before being placed into a large Perspex mesocosm and allowed to stabilise for at least one month in a constant temperature room at 21 ± 0.2°C. The overlying water of the mesocosm was constantly sparged with air to ensure oxic conditions. A DGT sediment sampler containing a mercapto-silica binding layer for the selective measurement of Sb^{III} and As^{III} was prepared with a diffusive layer consisting of a 0.08 cm-thick bisacrylamide-crosslinked polyacrylamide hydrogel covered with a 0.01 cm-thick 0.45 μm-poresize cellulose nitrate filter membrane. The sampler was deoxygenated in 0.01 mol L^{-1} $NaNO_3$ sparged with nitrogen gas for at least 2 hours prior to deployment. The sampler was deployed in the sediment for 24 hours, after which time it was removed, thoroughly rinsed with deionised water, and stored at 4°C prior to processing and analysis. The mercapto-silica binding gel was cut from the DGT sampler and washed for at least 1 hour in 50 mL of deionised water to remove unbound solutes, before being laterally sliced at 2.5 mm intervals and each

slice eluted in 0.5 mL of 0.01 mol L^{-1} KIO_3 / 1 mol L^{-1} HNO_3 / 1 mol L^{-1} HCl for 24 hours. A sub-sample of each eluent was diluted 20-fold in 2% HNO_3 prior to analysis by ICP-MS. A blank DGT sampler was processed in the same way to determine the limit of detection (3σ).

Results and Discussion

Uptake and elution. Uptake efficiencies of Sb^{III} by mercapto-silica and Metsorb binding gels were 99.5% and 97.9%, respectively, which provided initial verification that these binding gels had a high affinity for Sb^{III} and were suitable for further testing. Elution of Sb^{III} from Metsorb was done using 1 mol L^{-1} H_2O_2 / 1 mol L^{-1} NaOH, as previously described for the elution of Sb^{V} from Metsorb binding gels,[13] and resulted in an Sb^{III} elution efficiency of 88.1 ± 1.2%. The elution of Sb^{III} from mercapto-silica binding gels was tested with 0.1 mol L^{-1} KIO_3 / 1 mol L^{-1} HNO_3 / 1 mol L^{-1} HCl (which is similar to the procedure previously reported for the elution of As^{III} from the same binding layer[19]); and 1 mol L^{-1} H_2O_2 / 1 mol L^{-1} NaOH, which resulted in elution efficiencies of 62.6 ± 1.4% and 86.9 ± 2.6%, respectively. The comparatively high elution efficiency obtained with 1 mol L^{-1} H_2O_2 / 1 mol L^{-1} NaOH may be due to the oxidation of the thiol functional groups on the mercapto-silica under these conditions. These elution procedures are much simpler than that reported by Fan *et al.*[18] for the same binding gel, which required microwave-assisted extraction in concentrated HNO_3, HCl, and HF. Subsequent elution of Sb^{III} from DGT binding layers in this study was done with 1 mol L^{-1} H_2O_2 / 1 mol L^{-1} NaOH, except where otherwise stated. Depending on the analytical equipment being used for the quantification of antimony in the eluent solutions, it may be more appropriate to use the 0.1 mol L^{-1} KIO_3 / 1 mol L^{-1} HNO_3 / 1 mol L^{-1} HCl eluent solution to minimise the dilution required before analysis. The Agilent 7900 ICP-MS used in this study was tuned to have a robust plasma (i.e. CeO:Ce < 0.2%) that was capable of analysing 1 mol L^{-1} H_2O_2 / 1 mol L^{-1} NaOH eluent solutions after only a 10 or 20-fold dilution, with negligible ionisation suppression due to high sodium ion concentrations.

Accumulation over time. The accumulation of Sb^{III} by mercapto-silica DGT and Metsorb DGT was tested by deploying samplers of each type in triplicate for 10, 18, and 26 hours. Unfortunately, the instability of Sb^{III} in laboratory solutions prevented longer deployment times. Linear regression of the mass of Sb^{III} accumulated by the samplers over time confirmed that the uptake process was linear, with R^2 values of 0.999 and 0.991 for mercapto-silica DGT and Metsorb DGT, respectively (Figure S1). Effective diffusion coefficients were calculated as described previously[19] from the slope of the regression line, the ICP-MS-measured concentration of antimony in the deployment solution, the thickness of the diffusive layer, and the area of the sampler exposed to the solution. The effective diffusion coefficients of Sb^{III} estimated from the mercapto-silica DGT and Metsorb DGT data were 9.42×10^{-6} cm^2 s^{-1} and 8.23×10^{-6} cm^2 s^{-1} at 25°C, respectively. These values are similar to the diffusion coefficient previously reported for As^{III} (9.04×10^{-6} cm^2 s^{-1}), which is a similar neutral oxyanion.[19] The diffusion coefficient of Sb^{III} reported by Fan *et al.*[18] is only 32% of the value determined in this study. This discrepancy is unlikely to be due to the difference in binding layer materials, as suggested by Fan *et al.*,[18] because the polyethersulfone membrane used in their study has been used as a component of DGT diffusive layers previously without retarding diffusion to such a large extent.[24] To ensure accurate results, we recommend that laboratories independently determine diffusion coefficients with their specific DGT configuration.

The accumulation of Sb^{V} by mercapto-silica DGT was also tested over 26 hours, and was found to be negligible (mass of Sb^{V} accumulated was ~2% of the mass of Sb^{III} accumulated over the same time) (Figure S1). This provides initial verification that mercapto-silica DGT can be used to selectively measure Sb^{III} in the presence of Sb^{V}, thus providing speciation information. Furthermore, previous research by Panther *et al.*[13] has demonstrated that Metsorb DGT quantitatively measures Sb^{V}, which in association with this work demonstrating its ability to measure Sb^{III}, confirms that Metsorb DGT can be used to measure total inorganic antimony (Sb^{III} + Sb^{V}). The simultaneous application of both mercapto-

silica DGT, for selectively measuring Sb^{III}; and Metsorb DGT, for measuring both Sb^{III} and Sb^{V}, will allow the determination of inorganic antimony speciation in natural waters. Such an approach to *in situ* speciation using DGT has been described in detail previously for inorganic arsenic.[19, 25]

Effect of pH, ionic strength, bicarbonate concentration, and artificial seawater. The performance of mercapto-silica DGT and Metsorb DGT under various solution conditions is summarised in Table 1. Both mercapto-silica DGT and Metsorb DGT show acceptable performance under all tested conditions, indicating that these techniques can be deployed in a variety of natural water types with confidence. Importantly, this is the first time that a thiol-based DGT technique has been tested for its ability to measure Sb^{III} in a seawater matrix and in the high concentrations of bicarbonate often found in sediment porewaters due to the microbial metabolism of organic matter. Previous work by Panther *et al.*[26] demonstrated the importance of considering bicarbonate as an interference, particularly for the measurement of oxyanionic species by DGT techniques with metal oxide-based binding gels.

Table 1. Effect of pH, ionic strength, bicarbonate concentration, and artificial seawater on the measurement of Sb^{III} by mercapto-silica DGT (C_{MSIL}) and Metsorb DGT (C_{MET}). The concentration of antimony in solution (C_{SOLN}) was measured by ICP-MS.

Parameter		C_{MSIL}:C_{SOLN}	C_{MET}:C_{SOLN}
pH	4.07	0.99 ± 0.10	1.17 ± 0.08
	6.15	1.06 ± 0.04	1.09 ± 0.05
	8.05	0.98 ± 0.04	1.06 ± 0.04
Art. seawater (pH 8.35)		0.93 ± 0.13	0.99 ± 0.03
Ionic strength	0.001 mol L^{-1}	1.05 ± 0.03	1.14 ± 0.05
	0.01 mol L^{-1}	1.00 ± 0.07	1.10 ± 0.05

(as NaCl)	0.1 mol L^{-1}	0.98 ± 0.01	1.14 ± 0.03
	1.0 mol L^{-1}	0.95 ± 0.01	1.05 ± 0.09
$[HCO_3^-]$	1 mmol L^{-1}	1.08 ± 0.06	1.09 ± 0.08
	5 mmol L^{-1}	1.04 ± 0.08	1.14 ± 0.11
	10 mmol L^{-1}	1.15 ± 0.02	1.04 ± 0.10
	15 mmol L^{-1}	1.12 ± 0.05	1.03 ± 0.05

As the purpose of the mercapto-silica DGT technique is to selectively measure Sb^{III}, unlike Metsorb DGT that is designed to measure total inorganic antimony (Sb^{III} + Sb^{V}), the effect of pH on the accumulation of Sb^{V} by mercapto-silica DGT was tested to ensure that this technique remained selective for Sb^{III} over a range of environmentally relevant pH (Figure 1).

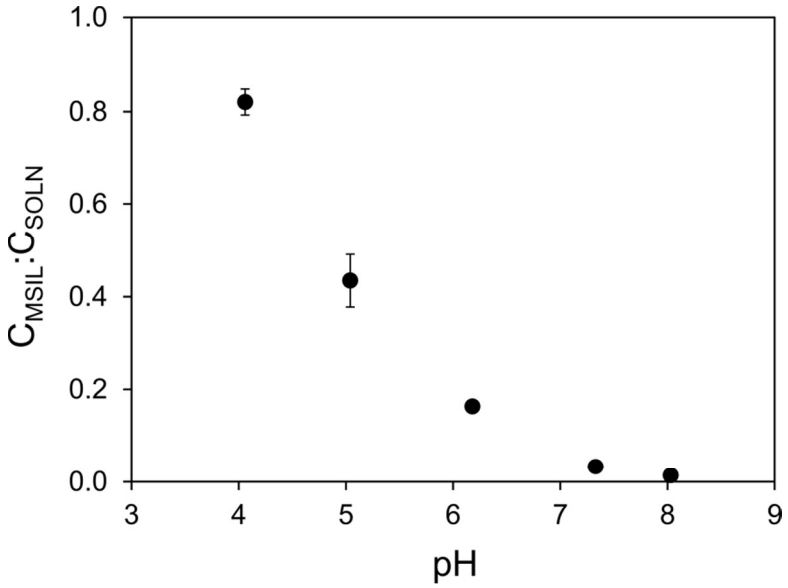


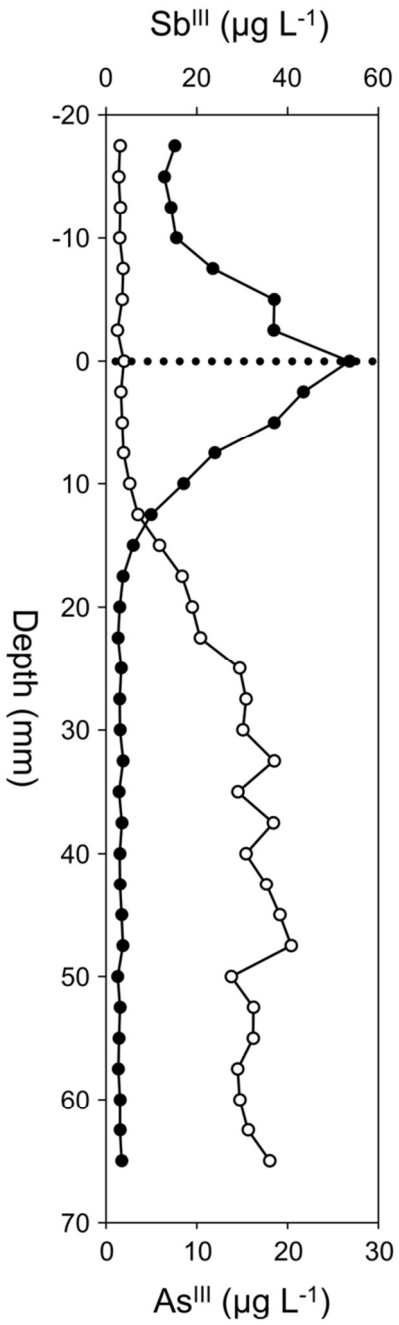
Figure 1. Effect of solution pH on the accumulation of Sb^{V} by mercapto-silica DGT as shown by the ratio of the concentration measured by mercapto-silica DGT (C_{MSIL}) to the concentration measured in solution by ICP-MS (C_{SOLN}). Error bars represent ± 1 standard deviation from the mean (n=3).

The solution pH had a strong effect on the accumulation of Sb^{V} by mercapto-silica DGT. At pH 4.06 the accumulation of Sb^{V} is close to quantitative, as indicated by a C_{MSIL}:C_{SOLN} value of 0.82. The ratio decreased at pH 5.04 to 0.43, and at pH 6.18 it was only 0.16. Above pH 7, the accumulation of Sb^{V} by mercapto-silica DGT was negligible (C_{MSIL}:C_{SOLN} < 0.03). The most likely explanation for the accumulation of Sb^{V} by mercapto-silica at lower pH is the reduction of Sb^{V} to Sb^{III} by the thiol functional groups, a phenomena observed previously in antimonial drug compounds,[27] followed by adsorption of Sb^{III} to the mercapto-silica. At pH 4.06, the rate of the reduction reaction appears to be sufficiently rapid to facilitate adsorption of Sb to the mercapto-silica without the accumulation of antimony at the interface of the binding and diffusive layers. As the pH increases, the rate of the reduction reaction may not be sufficiently rapid to allow adsorption of the antimony as it diffuses into the sampler, causing the concentration at the interface of the binding and diffusive layers to increase, which retards further diffusion of Sb^{III} from the bulk solution and results in the accumulation departing from the linear theoretical response.[10] We recommend that Sb^{III} concentrations measured with the mercapto-silica DGT technique be interpreted with caution when deployed in natural waters below pH 6.5, as there may be a confounding effect of Sb^{V} adsorption at lower pH. Future work should examine if this effect is observed in natural waters at low pH to further resolve the boundaries of acceptable deployment conditions for this technique.

Capacity. The capacity of mercapto-silica DGT and Metsorb DGT for Sb^{III} was tested to ensure that the binding layers have sufficient reactive sites for extended deployments, or deployment at high antimony concentrations (e.g. at contaminated sites). The results of these experiments (Figure S2) show that these DGT techniques exhibit linear accumulation capacity for Sb^{III} in excess of 100 μg of Sb^{III} per binding layer disc. This capacity is sufficient, for example, to allow deployment for over 30 days at an Sb^{III} concentration of 100 μg L^{-1} (25°C), although other factors such as biofilm formation may restrict deployments to shorter durations in natural waters. This capacity is similar to that reported for As^{III}

with mercapto-silica DGT (77.5 μg), but much higher than that reported for As^{III} with Metsorb DGT (8.5 μg).[19] The high capacity for antimony indicates that these techniques are suitable for measurements at both contaminated and uncontaminated sites, however, we recommend that DGT techniques are evaluated at field-relevant concentrations and deployment times before their application to new deployment conditions. Users of this technique should also account for the possibility of exceeding the analyte capacity due to the adsorption of non-target solutes that are accumulated by the binding layer (e.g. arsenite), particularly at contaminated sites.

High-resolution, porewater measurements of Sb^{III} and As^{III} with mercapto-silica DGT. To demonstrate the capability of the newly developed mercapto-silica DGT technique, it was applied to measuring co-distributions of Sb^{III} and As^{III} in a contaminated freshwater sediment (Figure 2). The calculated DGT detection limits of Sb^{III} and As^{III} were 0.06 μg L^{-1} and 0.04 μg L^{-1}, respectively, and all measured concentrations were above these values. It should be noted that the pH of the overlying water in this mesocosm was ~5.2 during the DGT deployment, which could result in the measurement of some Sb^{V} if it were present in the system, as explained earlier (see Figure 1).



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316 **Figure 2. Porewater profile of Sb^{III} (●) and As^{III} (○) measured by mercapto-silica DGT in a**

317 **contaminated freshwater wetland sediment at 2.5 mm resolution. The dotted line indicates the**

318 **position of the sediment-water interface.**

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320 Sb^{III} exhibits a sharp concentration maximum at the sediment-water interface, followed by a steep

321 concentration decrease over a depth of 20 mm. Conversely, As^{III} is present at very low concentrations

to 10 mm depth, after which point the concentration gradually increases and plateaus at ~30 mm depth. This is the first time that such contrasting porewater concentration profiles of Sb^{III} and As^{III} have been observed at the millimetre scale in aquatic sediments. The steep Sb^{III} concentration gradient across the sediment-water interface is clearly represented by numerous data points, due to the high spatial resolution possible with the DGT technique – such a concentration profile would not be obtainable with conventional sediment core slicing and porewater extraction techniques. Furthermore, the process of porewater extraction, transport and storage could result in antimony and arsenic speciation changes before analysis (e.g. oxidation), thus resulting in an erroneous interpretation of the sediment chemistry of these contaminants. In contrast, the mercapto-silica DGT technique selectively accumulates the reduced oxidation states of antimony and arsenic *in situ*, and thus preserves the speciation information at the time of sampling. The accurate measurement of different oxidation states is integral to investigating the complex biogeochemical processes associated with antimony and arsenic mobilisation and sequestration. Future work should systematically apply the mercapto-silica DGT technique for the selective measurement of Sb^{III} and As^{III}, in association with the Metsorb DGT technique for measuring total Sb and As, in order to further investigate the geochemical behaviour of antimony and arsenic in aquatic sediments.

Conclusion. The mercapto-silica DGT method presented here provides a significant advance in the speciation analysis of antimony in circumneutral natural waters. Combined with the existing Metsorb DGT method, it is possible to individually determine both Sb^{III} and Sb^{V} under a wide range of environmental conditions, including fresh and marine surface waters and sediment porewaters. Furthermore, this *in situ* approach avoids many of the common issues associated with conventional *ex situ* speciation analysis, such as speciation changes during sample collection, transport and storage.

The application of these DGT techniques to investigating the sediment biogeochemistry of antimony will allow researchers to selectively measure antimony species in sediment porewaters at higher spatial resolution than previously possible. This is particularly important in productive freshwater and coastal sediments, where changes in biogeochemical zonation, and possibly antimony speciation, can occur over small spatial scales. The insight gained from this approach will allow a greater understanding of the complex biogeochemical processes that govern the mobility of antimony in aquatic systems.

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