Methylantimony and -arsenic Species in Sediment Pore Water Tested with the Sediment or Fauna Incubation Experiment

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In this study, the speciation of arsenic (As) and antimony (Sb) across a water−sediment interface and the formation of mono-, di-, and trimethylated species over time in a microfiltered pore water solution were examined. We used an experimental technique, known as the sediment or fauna incubation experiment (SOFIE), which enables the determination of chemical speciation across redox zones in undisturbed systems. Five different incubation experiments were run: Over a 76 day incubation period, pore water was sampled and speciated 5 times. These experiments revealed the complete methylated species pattern for arsenic and antimony in the microfiltered sediment pore water. This constitutes the first report of methylated As and Sb species in a true pore water solution of sediments. Predominant organic species were dimethylantimony (DMSb up to 2.7 μg/L) and dimethylarsenic (DMAs up to 4.3 μg/L) followed by monomethylated species (MMAs and MMSb). These data (i) indicate that methylation significantly influences the translocation of As and Sb in sediments, (ii) demonstrate good agreement between the occurrence of methylantimony and the occurrence of methylarsenic in the pore water, (iii) reveal that As transformation in sediments is faster than Sb transformation but is more susceptible to disturbances from acidification, and (iv) regarding the translocation of these elements and antimony in particular, methylation is clearly a relevant, and perhaps as yet underestimated, factor.

Introduction

Sediments, especially those with a significant degree of anthropogenic disturbances, act as a chemical sink for all kinds of pollutants and thus may represent sources of toxicity toward organisms. Pollutant uptake, storage, and subsequent release into pore water as well as associated biomagnification have been described for a number of different sediments. Most of the studies dealt with traditional inorganic pollutants (e.g., Cd, Cr, or Pb (*1*)). Pollutants such as antimony that occur with new industrial technologies in the environment are less studied. At the moment, aside from natural antimony contamination from rock weathering, mining, energy generation, and industrial applications (e.g., brake linings, flame retardants, or PET incineration and munitions hardening) play a major role in antimony release into the environment, resulting in local hot spots (*2–17*). Although arsenic and antimony are congeners and share many similarities in their biogeochemical properties, extensive pollution of drinking water, as is known for arsenic in many parts of the world, is not known to occur with antimony. A common characteristic of the two elements is the formation of methylated species in the biogeochemical cycles. These methylated species occur either via inorganic or via biological methylation. This latter process is usually dominant where biological activity occurs. Methylated arsenic and antimony species have been detected in many different environmental and industrial compartments (e.g., soils, fresh water, seawater, estuarine sediments, sewage sludge, or compost *18, 19*). While only few data concerning the environmental toxicity of methylated antimony species are available to date (*20*), much more relevant information has been published for the chemically akin element arsenic (*21*): As(III) species are much more toxic than As(V), regardless if they are organic or inorganic (*22*). Generally, methylation of metals increases their volatility and therefore their mobility within the biogeochemical cycle; furthermore, because of their lipophilicity, they may also be of ecological concern (e.g., potential enrichment in the food chain). Therefore, environmental niches that demonstrate a high biomethylation potential (e.g., methylation rate exceeding 1%) should be of prime research interest (*21, 23*).

The question concerning the speciation and translocation of methylated species in pore waters of soils and sediments, as well as the site-specific factors that promote the dislocation of especially methylated As and Sb species, has not yet been fully addressed in the literature. These questions are of significant concern with regard to the exposure of aquatic biota and potential transfer to the food chain (*24–28*).

This study focused on the speciation of As and Sb over redox gradients in undisturbed water−sediment interfaces. The emphasis was on the question as to if and in what quantity methylated Sb and As species occurred over the interface under different environmental conditions (e.g., eutrophication or acidification). In addition, the total concentrations (As_{tot} and Sb_{tot}) in the microfiltered sediment pore water were examined, and the concentration of As(III) and Sb(III) was quantified in one cell.

Materials and Methods

General Description of SOFIE. This study was performed with a novel experimental technique (EU Patent 1018200/02077121.8), known as the sediment or fauna incubation experiment (SOFIE). Full and detailed experimental capabilities were described previously (*1, 29*). The technique allows a nondestructive handling and a true-to-nature assessment of water−sediment systems. It was developed to measure chemical speciation of metals over redox zones in undisturbed systems. In short, the cell consists of a circular core, which is used as a sampling device to obtain undisturbed water−sediment systems. Field samples including the overlying surface water are taken in such a way that the physical

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and geochemical integrity of the sample (e.g., bulk density and redox status) is guaranteed. The cell wall contains 15 gastight connectors for probes. These probes (diameter 1 mm and length 50 mm) consist of semipermeable polyether sulfone, which acts as a membrane to discriminate colloidal fractions >100 nm. This mesh size is impermeable to bacteria, so pore water that crosses the polymer membrane is sterile. In this study, one cell with one compartment and two cells with two compartments were used, the latter allowing scenario treatments of two identical cores that are simultaneously sampled.

pH-Gradient Hydride Generation Gas Chromatography Coupled to Inductively Coupled Plasma Mass Spectrometry (HG-PT-GC/ICP-MS). Metal(loid)organic compounds display a broad range of pH derivatization optima, and dismutation is a problem during derivatization. To measure several species of different elements in a single run, HG is commenced at pH 7 (adjusted by a citrate buffer system) and gradually decreased to pH 1 while the derivatization agent was added continuously. First, samples are purged with helium, and volatile (permethylated) species are cryotrapped on a U-shaped glass tube filled with Supelcoport (10% SP-2100; 80/100 mesh). To volatize nonvolatile (ionic) methylmetal(loid) species, derivation was started by adding $NaBH_4$ (Sigma Aldrich). By purging and lowering the pH continuously, the metal(loid)organic species were derivatizated as described previously by Duester et al. and Diaz-Bone et al. (*30, 31*). Separation and quantification were performed by heating the trap and the GC column coupled to an ICP-MS (Agilent 7500a) as described by Feldmann (*32*). The detection limits were defined as 3× the standard deviation of the blank value: MMAs 0.015 μg/L, DMAs 0.036 μg/L, TMAs 0.064 μg/L, MMSb 0.005 μg/L, DMSb 0.013 μg/L, and TMSb 0.007 μg/L. Quantification of organometal(loid) species was validated by measuring a multiorganometal(loid) standard containing $(CH_3)As(ONa)_2$, $(CH_3)_2AsO(OH)$ (both Strem), $(CH_3)_3AsO$ (Tri-Chemical Laboratories), and $(CH_3)_3SbBr_2$ (Sigma Aldrich).

As(III) and Sb(III) Speciation Technique. To quantify As(III) and Sb(III) species in a single analytical step via hydride generation, the HG methods as described by Yamamoto et al. (*33*), Cutter et al. (*34*), and Ellwood and Maher (*35*) were further modified and adapted. The experimental setup and detection mode were similar to the pH-gradient setup described previously, albeit omitting the GC column. The helium flow rate was also lower than that used for the pH-gradient setup. Thirty milliliters of pH 5.6 citrate buffer (Merck) and 1 mL of sample were purged with He (Air Liquid) in the reaction vessel for 2 min. Derivatization was performed by adding 2.5% w/v $NaBH_4$ (Sigma Aldrich) with a ceramic piston head pump dropwise over a period of 100 s. To stabilize the pH, at $t = 50$ s, 0.31 M citrate acid (Merck) was added simultaneously with $NaBH_4$. Quantification was performed by external calibration using As_2O_3 and $SbCl_3$ standards from Kraft, using a 5 point calibration from 0.1 to 1000 μg/L, and all results consist of $n = 3$. Measurements were validated, as no As(III/V) and Sb(III/V) reference material was available, by spiking the CRM 610 (trace elements in groundwater: high level, Community Bureau of Reference, Brussels, Belgium) with As_2O_3 and $SbCl_3$ standards. Additionally, standard addition was performed using the pore waters. Recovery of As(III) and Sb(III) was always better than 95.4%. Reduction of As(V) and Sb(V) (Merck) was below 3.4 and 1.0%, respectively. Triplicate analysis of a single sample using this methodology required <20 min; hence, the method is a fast and reliable complement to total content measurements in laboratories that routinely utlize ICP-MS. The pore water samples of SOFIE cell 2b in its chronological sequence were analyzed exemplarily for As(III) and Sb(III) concentrations.

Total Element Content Determination. The pore water samples from the SOFIE cells were acidified and stored at −20 °C until analysis of the total element content (Fe, Mn, Al, P, S, As, and Sb total content) using ICP-MS (Agilent 7500ce). For each sample, the pH, redox, and conductivity (all Consort C835) were determined. To minimize chloride interference on the arsenic signal, the ICP-MS instrument was operated in helium mode (i.e., helium was delivered at 3.4 mL min^{-1}) using a 1% HCl solution for tuning the collision cell. To control chloride interference, ^{35}Cl was monitored. Quantification was performed by external calibration with standard solutions (Merck-CertiPur) and validated by analyzing CRM 610 (trace elements in groundwater: high level, Community Bureau of Reference). As an example, the efficiency of arsenic recovery was always >92%.

TABLE 1. Experimental Setup: Spiking of Five SOFIE Cells

SOFIE cell	target As(V) concentration (mg/L)	target Sb(V) concentration (mg/L)	eutrophication	acidification
1	none	none	none	none
2a	0.1	1		
2b	0.1	1	X	X
3a	0.1	1		X
3b	0.1	1	X	

Linear Correlation. Coefficient of determination (r^2, square of coefficient of correlation) and probability of error (p) with a maximum tolerable probability of 5% were ascertained using the open source program R (r was determined by linear regression and p by the Student's t test; when $p < 0.05$, the null hypothesis was rejected).

Experimental Setup and Spiking of the Cells. The maturation pond is part of the wastewater facility Bochum−Oelbachtal in the south of the city of Bochum, Ruhr Basin, Germany. The treatment plant is comprised of a mechanical, biological, and chemical purification system. Subsequently, the water is lead into three maturation ponds (two parallel and one downstream). Additionally, the Oelbach Brook leads into the ponds. The runoff from several former mines feeds into the Oelbach Brook, and hence, the maturation ponds are loaded with several metal(loid)s such as arsenic (sediment concentrations of 2−5 mg/kg per dry weight). As a sampling site, a sedimentation area close to one of the inlets of the final pond was chosen. The sediment was characterized in 0−15 and 15−25 cm depths as aerobic ochre Gyttja.

The experimental setup consisted of three SOFIE cells (cell 1 was a one compartment cell, and cells 2 and 3 were two compartment cells). For reasons of reproducibility, the samples were taken in close vicinity. To ensure an adequate oxygen supply to the surface water and associated biota, each cell was connected to an aquarium pump using high porosity air stones (Tetratc; venting time 15 min h^{-1}). The cells were placed in a fume cupboard with a temperature between 20 and 25 °C and were kept in the dark. The sampling frequency was as follows: day 0, field sampling; day 14, pore water sampling; day 16, spiking with antimony and arsenic; and days 26, 36, 56, and 76, pore water sampling. In Table 1, the parameters for spiking of the cells are detailed, and in Table S1, the experimental time table is presented. As the native sediment contained ∼10-fold higher concentrations of arsenic than of antimony, artificial contamination of the cells was performed with a reversed ratio. The spiked As ($Na_2HAsO_4 \cdot 7H_2O$; Aldrich, 100 μg/L end concentration per cell) and Sb (KH_6O_6Sb; Aldrich, 1 mg/L end concentration per cell) represent concentrations that appear commonly in an industrially or geochemically influenced environment (*3, 7, 14, 36–45*).

The pentavalent inorganic species were used as these oxides are the dominant inorganic species found in surface

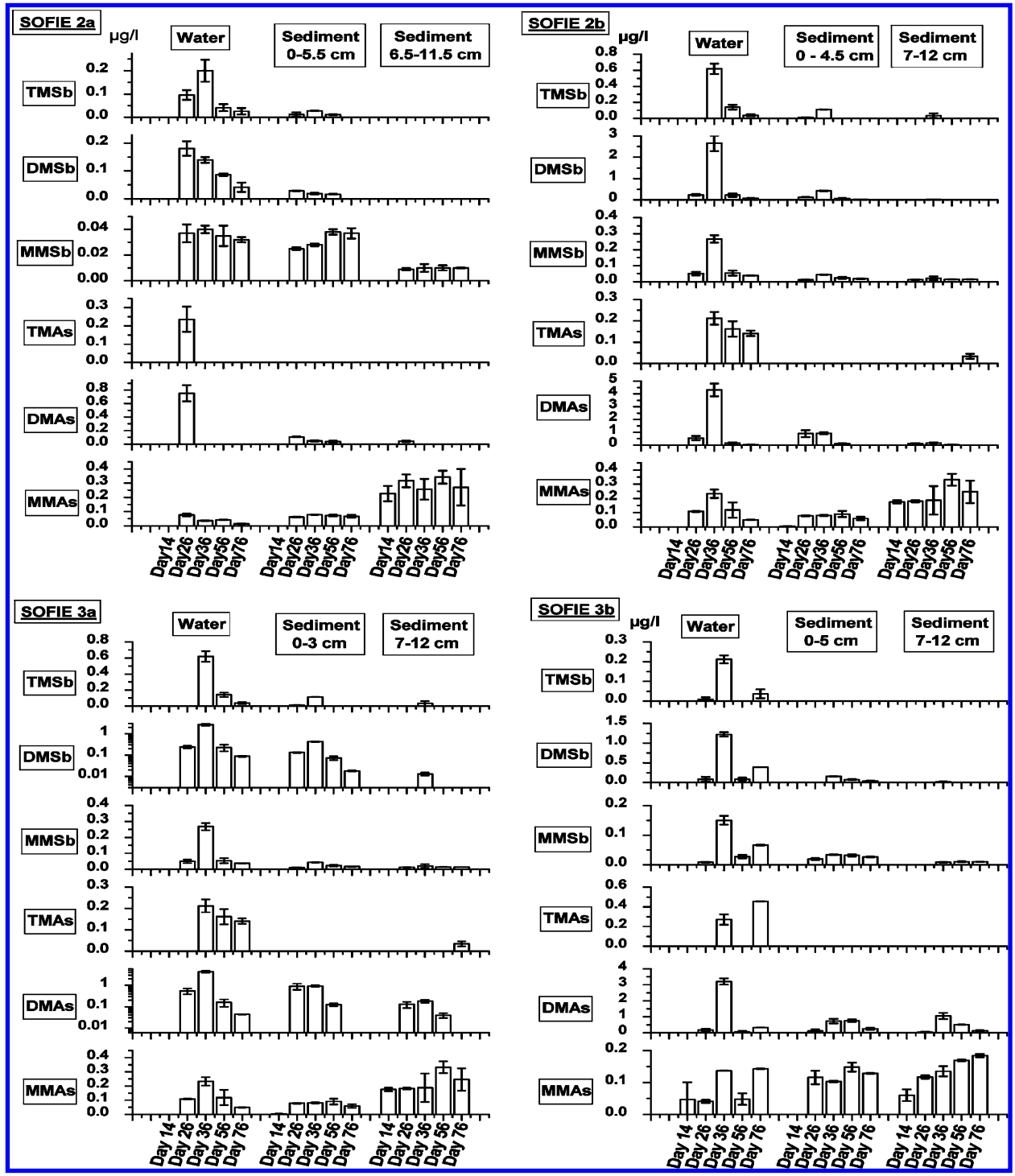

FIGURE 1. Time and depth dependence of methyl As and Sb species concentration (μg/L). SOFIE 2a: As and Sb added; SOFIE 2b: As and Sb added, eutrophicated, and acidified; SOFIE 3a: As and Sb added and acidified; and SOFIE 3b: As and Sb added and eutrophicated.

water. In line with methods described in DIN ISO 17155 (*46*), we simulated a eutrophication ($C_6H_{12}O_6/KH_2PO_4/(NH_4)_2SO_4$, (80:13:2); 10 g of substrate per kg of dry weight of the sediment) of cells 2b and 3b to study the influence of enhanced biological activity on the availability of inorganic As and Sb and the concentration of methylated species in the <100 nm discriminated pore water fractions. To simulate episodic acidification and selective nitrate eutrophication, we lowered the pH in the water phase of cells 2b and 3a using 65% HNO_3 dropwise over a 6 h period.

Results and Discussion

Biota Shift during the Experiment. By using a conventional aquarium pump, it was possible to preserve the mesofauna in the cell. The following classes were observed: Gastropoda, Annelida (subclass: Hirundinea, Tubificidae, and Lumbriculidae), Crustacea (order: Onychura, e.g., *Daphnia magna*; order: Copepoda), and Insecta (order: Ephemerotera and Plecoptera) (*47, 48*). Following eutrophication, increased turbidity, associated with the growth of a thick epipelon and mortality of parts of the mesofauna organism not able to

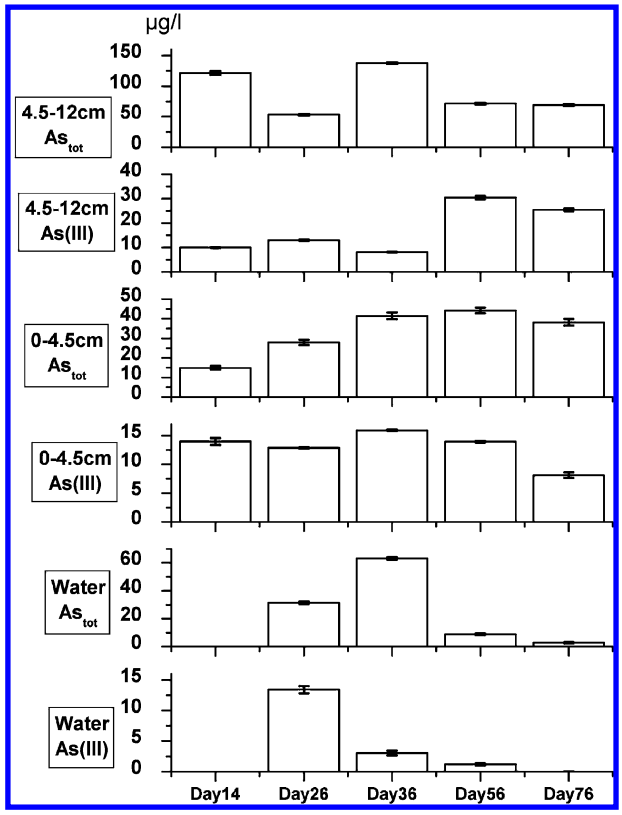

FIGURE 2. Time and depth dependence of As(III) and As_{tot} concentration (μg/L) in cell 2b (As(V) added, eutrophicated, and acidified).

take refuge into deeper sediment layers or to implement survival strategies, occurred. Of particular interest was the explosive reproduction of the Onychura order in the eutrophicated cells ~20 days after contamination as the water started to clarify. Despite mechanical oxygenation, after ~2 weeks, the eutrophicated cells suffered a massive oxygen deficiency as a result of biological oxygen consumption.

Depth and Time Dependence of pH, Redox, and Conductivity. The pH in cells 2b and 3a was successfully lowered by one pH unit, along with a decrease of pH for eutrophicated cells 2b and 3b with one unit as well. All cells showed a relative constant pH trend over the depth profile. The reproducibility of redox gradients is generally very high using the SOFIE method (*1, 29, 49*). All samples showed a strong decrease in redox potential over the first 3 cm depth. The redox data of the five cells were very similar, and the most significant redox changes occurred in the water body of cell 2b. The largest effect with regard to an increased ionic burden in the pore water was detected in eutrophicated cells 2b and 3b.

Total Elemental Concentration. In Figure S1, the total dissolved concentrations of SOFIE cells are presented. In all cases, antimony was detected in the microfiltered water column. Arsenic is bound to a large extent to colloids or is present in organisms in the water column. Here, the arsenic concentration was observed to increase with depth. The time dependent distribution showed a decline after the artificial spike. Statistical correlation of the total dissolved concentrations of the different metal(loid)s of all samples showed good agreement between Mn and Fe ($r^2 = 0.67$, $p \ll 0.05$) but a poor agreement for all other elements examined (e.g., As vs Sb; $r^2 = 0.08$).

Methylated Species. In Figure 1, the results of analyses of methylated species in pore water are presented. For SOFIE cell 1, (reference cell) no significant changes in methylated species content during 76 days of incubation were detected (Table S4). The concentrations of methylarsenic and methylantimony species in the microfiltered pore water and water column were close to and below the detection limits. Cell 2a was spiked with inorganic metal(loid)s. The organometalloid compound concentrations were initially as low as those in the reference cell; however, 10 days after addition of the elements (on day 26), the complete methylated species pattern of As and Sb was detectable in the water column. The maximum of all methylated arsenic species was detected at this time point; in contrast, the methyl Sb maximum occurred a further 10 days later (day 36). Significant changes in the species pattern of the sediment pore water appeared in cell 2a between day 26 and 36, but the concentrations of the species were well below 1 μg/L. The highest methylated species concentrations occurred in the inorganic spiked, eutrophicated, and acidified cell 2b. A maximum of 4.3 μg/L DMAs and 2.6 μg/L DMSb was detected after 36 days of incubation in the water column. At the same time, a maximum of 0.9 μg/L DMAs and 0.4 μg/L DMSb was detected in the upper sediment layer. Cell 3a was spiked and acidified. With this cell, a clear negative influence of acidification toward methylation of As and Sb was observed, with a stronger depression of arsenic methylation. In spite of the inorganic spiking, the methylated species content of the water samples was of a similar order to that observed in the untreated reference cell.

In contrast, the spiked and eutrophicated cell 3b displayed comparable behavior to that observed in cell 2b. For both 2b and 3b cells, the maxima of metalloid species detection correlated well with the occurrence of the highest biological activity and highest aerosis once oxygen saturation was recovered. The transformation of arsenic and antimony in the sediments was slower as compared to the water column (e.g., the buildup of MMAs in the lower layer was not completed even after 76 days). (Note: Data point cell 3b, sample day 56, is treated as an outlier as the results of all species are against all concentration trends.) Comparison of cells 2a and 3b show that eutrophication increases MMSb, DMSb, and DMAs by a factor of ~5. Analysis of all total methylated As and total methylated Sb species concentration data in the microfiltered water revealed a significant positive correlation ($r^2 = 0.85$ and $p \ll 0.05$). Statistical correlation with all other parameters (e.g., total content or redox) was poor, with the exception of the methyl Sb species concentration correlation to the Sb_{tot} content of the previous sampling ($r^2 = 0.48$, $p \ll 0.05$). In 61% (DMAs) and 76% (DMSb) of 55 and 63 samples, respectively, the dimethyl species are the dominant methylated species in the microfiltered water. In 15 of 63 samples, the percentage of the sum of methylantimony species to Sb_{tot} was >10%. In contrast, only 6 of 55 samples contained methylarsenic species at >10% of As_{tot}. These data indicate that methylated species can play an important role in exchange processes between sediment and sediment pore water; however, the higher percentage of methylated antimony species as compared to methylated arsenic species was unexpected. As mentioned in the Introduction, arsenic is known to be methylated by microorganisms and in the environment to a higher degree than antimony.

As(III) and Sb(III) Concentrations in Cell 2b. With respect to the high toxicity of trivalent inorganic noncomplexed species, for cell 2b, the As(III) and Sb(III) pore water content was detected. Figure S3 shows the time and depth profiles of As(III) as a percentage of As_{tot}. Initially, no As(III) was detectable in the water column, but 94% of the arsenic in the sediment−water interface before spiking was As(III). This can be ascribed to the high microorganism density in this region and by microbial As reduction by bacteria and fungi, followed by subsequent As(III) export by the organisms. Spiking with As(V) initially disrupted the As(III)/As_{tot} ratio,

but the As(III) concentrations subsequently increased until day 36 of incubation in this layer (Figure 2).

In contrast to the water column and deeper layer, the As_{tot} and As(III) concentrations in the 0−4.5 cm layer increased in a roughly parallel manner over time. In the 4.5−12 cm layer in the microfiltered fraction, the As_{tot} maximum was initially observed followed by the As(III) maximum. In contrast, in the water column, the process was inverted: first, we detected the As(III) maximum and then the As_{tot} maximum. This can be taken as an indication of a fast transformation in the water column (high elevated organic load) and a slower transformation in the less active deep layer. Hence, it is likely that the As(III) distribution is strongly influenced by microbial activity and is not solely dependent upon redox potential. For antimony, Sb(III) was detected in only one water column sample 36 days after incubation (0.32 μg/L representing 2.4% of Sb_{tot}). This may be explained by an inefficient transformation of Sb(V) to Sb(III), as a result of stronger binding of Sb(III) by biota or soil constituents, and consequent reduced bioavailability and hence agrees with the literature (*24, 26*).

In summary, the transformation of As and Sb to methylated species was generally promoted by eutrophication. The highest concentrations of methylated species were found in a eutrophicated and acidified environment, in which acidification most probably lead to an increased availability of elements necessary to microbial metabolism (e.g., manganese release (Figure S4) and conductivity (Figure S5)) (*50*). These results are the first report of methylarsenic and methylantimony species in a true pore water solution and therefore pose the question as to whether the methylation of As and Sb has been underestimated to date with regard to its relevance to the translocation and remobilization of these elements from polluted sediments. As arsenic levels are a problem in the groundwater of many countries in the world and as antimony has become one of the most commonly used new metal(oid)s in the industry during the last few decades, better knowledge of the biogeochemical cycling of these elements in an anthropogenic modified environment is needed to limit or avoid adverse humanitarian and environmental situations. In particular, for antimony, the question of biomagnification through the food chains of aquatic and terrestrial ecosystems has not as yet been examined satisfactorily in the literature.

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Supporting Information Available

Background information on time and depth dependence of As_{tot}, Sb_{tot}, and Mn_{tot} concentrations (Figures S1 and S4), redox data and conductivity data (Figures S2 and S5), and ratio of As(III) to As_{tot} of microfiltered water column and pore water (Figure S3). Time table of incubation experiments (Table S1) and all species concentrations (Tables S2−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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