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Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments

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Abstract

The arsenic contamination of aquifers has been linked to the input of dissolved organic matter (DOM). In light of this suggestion, the aim of this study was to quantify chemical effects of DOM on desorption and redox transformations of arsenic bound to synthetic iron oxide and natural samples from different geochemical environments (soils, shallow aquifer, lake sediment). In batch experiments, solutions containing 25–50 mg/L of two different types of DOM (purified peat humic acid and DOM from a peat drainage) were used as extractants in comparison to inorganic solutions. DOM solution was able to mobilize arsenic from all solid phases. Mobilization from iron oxides (maximum: 53.3%) was larger than from natural samples (maximum: 2.9%). The mobilization effect of extractants decreased in the order HCl > NaH_2PO_4 > DOM > $NaNO_3$. DOM solutions, therefore, mainly targeted weakly sorbed arsenic. Mobilization was complete within 24–36 h and DOM was sorbed during incubation indicating competition for sorption sites. The same patterns were observed for different DOM types and concentrations. Addition of DOM lead to (a) enhanced reduction (maximum 7.8%) and oxidation (6.4%) of arsenic in aqueous solution and (b) the appearance of arsenite in aqueous phase of soil samples (5.5%). As the primary mechanism for the arsenic release from solid phases we identified the competition between arsenic and organic anions for sorption sites, whereas redox reactions were probably of minor importance. The results of this study demonstrate that sorption of DOM has a strong potential to mobilize arsenic from soils and sediments.

Keywords: Arsenic; Dissolved organic matter; Iron oxide; Groundwater

1. Introduction

Arsenic is widely recognized as a dangerous contaminant and as a threat to some of the world's water resources (Smedley and Kinniburgh, 2002). Problems with arsenic arise on a local scale related to mining or abandoned hazardous sites (Stueben et al., 2001) and on a regional scale, as in the aquifers of Bangladesh (Anawar et al., 2003). In natural waters, the oxyacids arsenite (H_3AsO_3; pK_1=9.2; uncharged at neutral pH) and arsenate (H_3AsO_4; pK_1=2.2; anionic at neutral pH) are the most important arsenic

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species (Cullen and Reimer, 1989). Changes in speciation may be caused by abiotic reactions, for instance with MnO_2 (Chui and Hering, 2000) or H_2S (Rochette et al., 2000). Microorganisms can oxidize arsenite for detoxification (Cullen and Reimer, 1989) or reduce arsenate to arsenite during respiration (Newman et al., 1998). More reduced and organic species represent only a minor fraction of the total arsenic.

The mobility of arsenic is primarily determined by processes at mineral surfaces, particularly precipitation, dissolution, ad- and desorption. These processes are controlled by geochemical parameters such as pH, Eh, ionic composition, and mineral type (Bissen and Frimmel, 2003; Masscheleyn et al., 1991). At neutral pH and oxic conditions, arsenic is effectively immobilized by sorption or co-precipitated with metal oxides (Bissen and Frimmel, 2003; Smedley and Kinniburgh, 2002) involving surface complexation reactions and formation of specific inner sphere complexes (Sun and Doner, 1996). Low pH and reduced redox potential increase the mobility by dissolution of metal oxides. Under strongly reducing conditions the formation of sulfide minerals controls arsenic concentrations (Harvey and Swartz, 2002; Masscheleyn et al., 1991). Dissolved calcium enhances the sorption of arsenic, while in the presence of anions like phosphate and bicarbonate, arsenic sorption is reduced by competition for sorption sites (Appelo et al., 2002; Smith et al., 2002).

Dissolved organic matter, whose concentrations range from 1–20 mg/L in most fresh waters and reach higher values in wetlands (Abbt-Braun, 2002), may also influence arsenic mobility by several mechanisms. Fulvic or humic acids form stable complexes with mineral surfaces (Kaiser et al., 1997), effectively blocking arsenic from adsorption on iron oxides, alumina, quartz or kaolinite (Grafe et al., 2001; Grafe et al., 2002; Xu et al., 1991). Organic anions have consequently been found to enhance arsenic leaching from soil material (Lin et al., 2002), in which arsenic is mainly associated with the metal oxide fraction (Lombi et al., 2000), and also from fly ashes (Janos et al., 2002). A small but substantial increase of arsenic mobility was also found in wetland soils in the presence of high DOC concentrations (Kalbitz and Wennrich, 1998). The formation of aqueous arsenic/DOM complexes either by positively charged amino groups in DOM (Saada et al., 2003) or by metal cation bridges (Redman et al., 2002) can additionally contribute to a higher mobility of arsenic. In some sediment layers of Bangladesh 10–30% of the arsenic present is associated with the solid organic phase (Anawar et al., 2003). Microbial degradation of organic matter in these sediments therefore contributes to reductive dissolution of metal oxides and release of arsenic bound in the oxides and in the organic phases as well (Harvey and Swartz, 2002). Moreover, DOM contains redox active functional groups and can thus act as an electron shuttle between microorganisms or H_2S and iron or organic pollutants (Lovley et al., 1996; Schwarzenbach et al., 1990). Accordingly, it has recently been demonstrated that the addition of arsenic to DOM solutions results in arsenate reduction as well as arsenite oxidation (Redman et al., 2002). Complexed metals are proposed to take part in these reactions. This observation is important because changes in speciation would influence the arsenic mobility.

Previous studies about chemical factors influencing arsenic mobility primarily focussed on competition of DOM and arsenic for sorption sites on synthetic minerals and often did not account for redox transformations. The objective of our study was thus to determine the abiotic effects of DOM on arsenic mobility by investigating both desorption and redox transformation in synthetic and natural soil samples. Specifically we were interested in (I) what fraction of arsenic desorbs from natural samples compared to synthetic iron oxides, such as goethite, and how DOM solutions compare to other extractants, (II) whether kinetics obtained with synthetic samples can be extrapolated to natural samples, and (III) whether DOM chemically oxidizes or reduces arsenic.

2. Materials and methods

2.1. Materials

Goethite was synthesized according to the method of Schwertmann and Cornell (1991) and examined with X-ray diffraction. The BET surface area of goethite (Goe) was 51 m^2/g.

Natural samples were collected from four arsenic contaminated sites in Germany. They covered a wide range of geochemical characteristics and arsenic concentrations (Tables 2 and 3). The sandy Podsol horizons (labelled H 1; Neumarkt/Bavaria) received arsenic from infiltrating wood preservation solutions (e.g. copper–chromium–arsenic salts). In H 1/2 most arsenic was associated with metal oxides (Peiffer et al., 2003). The loamy soil columns (labelled W 1 and W 2; Wiesloch/Baden-Wuertemberg) were contaminated by an adjacent mining dump. Therefore primary sulfidic and secondary oxidic arsenic phases can be expected there (Ruede, 1996). Material from below the groundwater table (95 cm below surface at time of sampling) was obtained from an aquifer in the riparian zone of the Leimbach stream (labelled A 1 and A 2; Wiesloch/Baden-Wuertemberg). The arsenic stemmed from accumulation of eroded mining material or percolating solutes. A sediment core was collected from a depth of about 3 m in Lake Trebgast (labelled S 1; Bavaria). The lake is influenced by inflow of groundwater containing arsenic.

All samples were homogenized and freeze dried. Arsenic pools were quantified with the extractants proposed by Keon et al. (2001). Individual extractions with 0.1 M NaH_2PO_4 (pH 5; 24 h; strongly sorbed fraction), 1 M HCl (1 h; carbonate and amorph metal oxide fraction) and Aqua Regia (10 bar; 0.5 h; Microwave; total arsenic) were made (Tables 2 and 3). Before the DOM mobilization experiments all natural samples were autoclaved at 121 °C in wet heat for 30 min. Autoclavation can reduce the sorption of anions on soil material (Xie and Mackenzie, 1991) but was necessary to reduce microbial influences.

Two DOM solutions were used in mobilization experiments. The first solution was prepared by dissolving dry Pahookee Peat reference humic acid (labelled PA-HA; Florida; purchased from the International Humic Substances Society) at pH 8–9. PA-HA represents a well purified material (ash content ~1,7%) and has been thoroughly characterized by the IHSS. The peat humic acid has a carboxylic group content of 8.8 mmol/g C (pK_A=4.26) and a phenolic group content of 2.05 mmol/g C (pK_A=9.85). The high specific UV absorbance at 280 nm ($SUVA_{280}$) of 1180 L (mol organic carbon)$^{-1}$cm^{-1} and the low Absorption$_{465nm}$/Absorption$_{665nm}$ ratio (Abs_{465}/Abs_{665}) of 5.5 point out a high degree of condensation and aromaticity of this DOM (Chen et al., 2002). The second DOM was collected as a solute from a drainage tube of the mesotrophic Lehstenbach wetland (labelled FI-DOM; Bavaria). It was degassed and filtered (0.45 μm). The DOM solution also contained nitrate (51 μmol/L), sulphate (140 μmol/L) and ammonium (280 μmol/L). By acid-base titration of FI-DOM no specific pK_A value could be determined, but a proton uptake capacity between 8.5 and 22 mmol/g C was calculated. The $SUVA_{280}$ value (864 L (mol organic carbon)$^{-1}$cm^{-1}) indicates a lower condensation and aromaticity in FI-DOM than in PP-HA and the Abs_{465}/Abs_{665} ratio of 8.7 is within the fulvic acid range. Before use both solutions were brought to pH 6–6.5 and 10 mM ionic strength (NaCl or $NaNO_3$) and stored for up to 3 months in darkness at 5 °C.

2.2. Batch experiments

All batch experiments were carried out in acid conditioned PE-vessels and as triplicate assays except for the arsenic sorption in protocol B (duplicate assays). After the addition of any solid phase (iron oxide or natural sample) the PE-vessels were individually kept in nitrogen filled 300 mL glass containers during the whole experiment. Addition of solute and sampling was done through a mounted septum and a syringe. The pH was adjusted with 100 mM solutions of NaOH or HNO_3. The samples were deaerated by purging them with N_2 through a cannula for 15 min. During incubation the assays were shaken (horizontal shaker, 100 rotations/min) at 20±1 °C in the dark. Suspended particles in the sample aliquots were removed by centrifugation (20 min, 18,000 u/min) for iron oxide experiments and by filtration (0.45 μm, Nylon) for natural samples. The clear samples were stabilized with 1% HNO_3 in 1.5 mL Eppendorf caps and stored in darkness at 5 °C. Arsenic speciation was always determined within 48 h after sampling. Microbial activity was inhibited as far as possible by using only purified substances, conditioned reaction vessels and short reaction times.

2.2.1. Aqueous batch experiments

For the aqueous experiments 20 mL of a DOM solution was added to 20 mL of either arsenate or arsenite solution. The final conditions were 80 μg/L arsenite or 60 μg/L arsenate and 50 mg C/L in 10 mM

$NaNO_3$ at pH 6.2±0.2. These assays were sampled after 24 h.

2.2.2. Batch experiments with synthetic iron oxide

Two experimental protocols were used for the iron oxide assays. In protocol A, experiments were carried out in a NaCl matrix and the mobilization step was done with dried oxides. 10 mg goethite were suspended in 40 mL of NaCl solution (10 mM) and equilibrated for 24 h. Either arsenate or arsenite was added (2.5 mg/L), pH was adjusted to 6.2±0.2 and the assays were incubated. After the sorption the supernatant was decanted and the remainder was dried at 50 °C and used for the mobilization experiments. To these ends 10 mg goethite with sorbed arsenic was resuspended in 40 mL of DOM solution (concentration 0 or 25 mg C/L; pH 6.2±0.2) using sonication. The suspension was degassed and incubated under nitrogen atmosphere. Sorption and desorption assays were sampled after 2, 15 and 100 or 144 h for arsenate/goethite and after 2, 24, 72 and 240 h for arsenite/goethite.

In protocol B, the mobilization was carried out without a drying step and in a $NaNO_3$ solution. Goethite was suspended in $NaNO_3$ solution (10 mM) and equilibrated for 24 h before either arsenate or arsenite was added and pH was adjusted to 6.2±0.2. The final concentrations were 500 mg/L goethite with 1.9 mg/L arsenate or 1.8 mg/L arsenite at pH 6.2±0.2. Samples were taken after 24 and 160 h. Suspension aliquots of 10 mL were then removed from these goethite/arsenic stock solutions under strong mixing and transferred to 50 mL PE-vessels. 20 mL of DOM solution at pH 6.2±0.2 were added (final concentration 0 or 25 mg C/L). The mixture was degassed and incubated under nitrogen atmosphere. Samples were taken after 36 h and 160 h.

2.2.3. Batch experiments with natural solid phases

A series of different extraction experiments was carried out. One gram of soil or sediment material was suspended in 25 mL of DOM solution (concentration 0 or 50 mg C/L) solution. The suspensions were degassed, incubated under nitrogen atmosphere and sampled after 24 h. To investigate the mobilization kinetics, aliquots were removed from the H 1/2 soil assays additionally after 0.5, 2, and 100 h. The effect of DOM concentration was tested with 1 g H 1/2 material in 25 mL DOM solution of 0, 10, 50 or 100 mg C/L and sampling after 24 h. Arsenic speciation was analyzed for one set of H 1/2 samples as described above with 1 g soil suspended in 25 mL DOM (concentration 0 or 50 mg C/L) after 24 h of incubation.

2.3. Analytical techniques

Total arsenic (As_{tot}) was determined by graphite furnace atomic absorption spectroscopy (GF-AAS) (Analytik Jena AAS Zeenit 60; Limit of detection (LOD)=4.7 μg/L). Arsenic speciation was measured in a continuous HPLC-ICP-MS system, consisting of a Kontron pump 525, two guard columns (Dionex; AG7; 50×4 mm), an analytical column (Dionex; AS7/NG1; 250×4 mm) and an ICP-MS (Agilent 7500 c). The separation method of (Kohlmeyer et al., 2002) was used. Iron and manganese was measured by flame atomic absorption spectroscopy (Fl-AAS; Varian Spectr AA 20; LOD=0.8 mg/L) and dissolved organic carbon by TOC Analyzer (Shimadzu 5050; LOD=1.3 mg C/L). Solid phase organic carbon was determined by CHN analysis. Total reduced inorganic sulphur (TRIS) was measured photometrically as methylene blue at 665 nm (Varian Cary 1E) after digestion (Fossing and Jorgensen, 1989).

2.4. Thermodynamic calculations

Quinone moieties present in humic substances take part in redox reactions (Scott et al., 1998). We calculated Gibb's free energies for the redox reactions between arsenic and model quinones using data of Cherry et al. (1979) for arsenic and Schwarzenbach et al. (1990) for the two organic model quinones Juglone and Lawsone, assuming equimolar concentrations of oxidized and reduced species, and a pH of 6:

$$\begin{aligned} H_2AsO_4^- + H_2 - \mathrm{Juglone_{red}} + H^+ &= H_3AsO_3 \\ &+ \mathrm{Juglone_{ox}} + H_2O \ \mathrm{d}G = -8.1\mathrm{kJ/mol} \end{aligned}$$

$$\begin{aligned} H_2AsO_4^- + H_2 - \mathrm{Lawsone_{red}} + H^+ &= H_3AsO_3 \\ &+ \mathrm{Lawsone_{ox}} + H_2O \ \mathrm{d}G = -43.8\mathrm{kJ/mol} \end{aligned}$$

Arsenate reduction combined with DOM oxidation is thus the thermodynamically favoured process under the chosen experimental conditions.

3. Results

3.1. Arsenic speciation in the aqueous DOM solution

Both arsenite and arsenate could be detected after incubation with DOM (Fig. 1). Other As species could not be detected. Arsenite oxidation was strongest with FI-DOM (7 µg/L or 8% of total arsenic present), whereas strongest arsenate reduction occurred with PA-DOM (4 µg/L or 8%). The results were reproducible with small deviations in a similar experiment with 72 h instead of 24 h reaction time. A small change in speciation was also observed in the reference samples without DOM.

3.2. Arsenic sorption on goethite

Sorption of arsenic was rapid in the beginning and slowed down with experimental duration (Fig. 2). Only for the arsenite in protocol B an equilibrium concentration in solution was reached within 24 h. The sorption capacity of goethite was larger for arsenate than for arsenite in both protocols used. Roughly twice the amount of arsenate was sorbed compared to arsenite. Arsenic immobilization was smaller using protocol B than protocol A (Fig. 2).

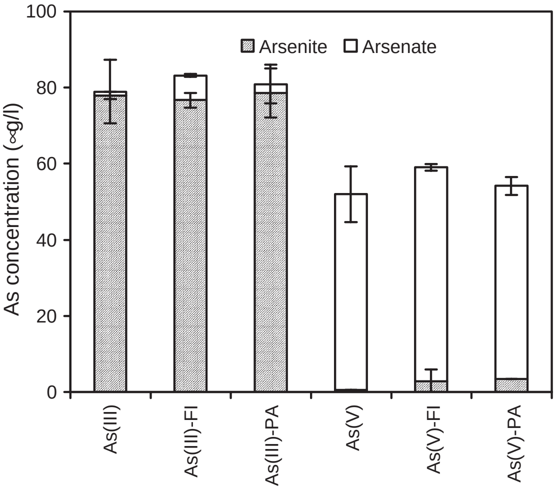

Fig. 1. Arsenic speciation measured by HPLC-ICP-MS after incubation of 80 µg/L arsenite and 60 µg/L arsenate, respectively, in solutions containing no DOM, 50 mg C/L FI-DOM or 50 mg C/L PA-HA (I=10 mM $NaNO_3$). Averages of triplicate assays are shown.

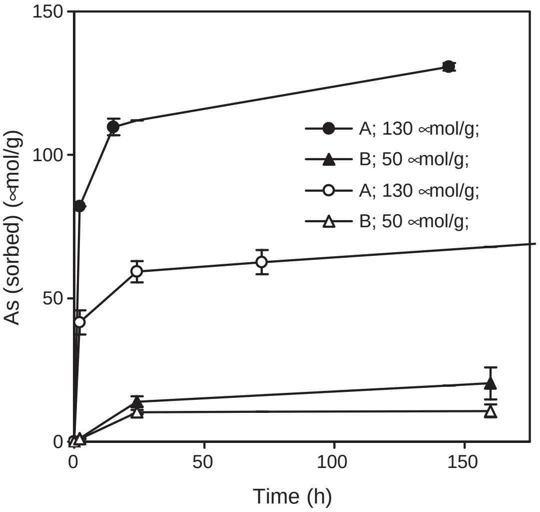

Fig. 2. Sorption of arsenic species in goethite suspensions. Closed symbols represent arsenate experiments and open symbols arsenite experiments. The experimental protocol applied and the initial As/Fe relation are shown in the legend. As described in the text in protocol A NaCl was used to adjust ionic strength while protocol B used $NaNO_3$.

3.3. Arsenic mobilization from goethite in DOM solution

The addition of arsenic-free solution to dried (protocol A) or suspended (protocol B) arsenated iron oxides resulted in an initial increase of the total amount of dissolved arsenic in all assays (Fig. 3). In the protocol A experiment with arsenate, arsenic desorption continues until the end of the incubation after 100 h. In the other assays, arsenic was mobilised only at the beginning (2 h in protocol A experiments with arsenite, 36 h in protocol B experiments). Subsequently arsenic concentration in the solution decreased again. A maximum net mobilization of arsenic by DOM was calculated as the maximum release with DOM minus the maximum release without DOM at the same time step (Table 1). Net mobilization was higher adding PA-HA than for FI-DOM. Pre-sorbed arsenite was released more easily than pre-sorbed arsenate (Table 1).

Larger initial DOM concentrations mobilized more arsenic and immobilized more DOM. A linear relationship between arsenic release and DOM concentrations was not observed, though. DOM concentrations in solution decreased by about 5–10 mg C/L

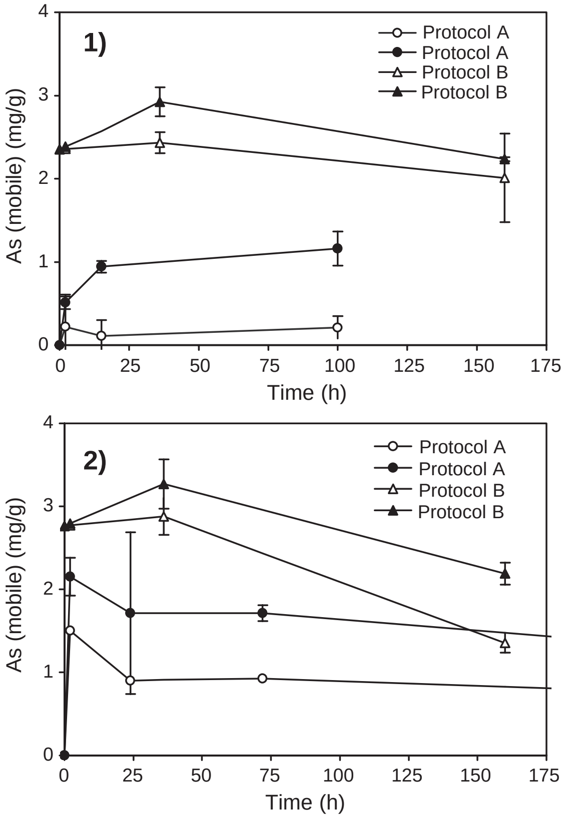

Fig. 3. Mobile As_{tot} during incubation of goethite with pre-sorbed (1) arsenate or (2) arsenite (I=10 mM); open symbols: solutions without DOM; closed symbols: solutions with 25 mg/L PA-HA. The legend shows the experimental protocol applied. As described in the text protocol A represents the use of NaCl as ionic strength while protocol B uses $NaNO_3$. Protocol A also includes drying the goethite after the arsenic sorption.

during incubation. Assuming a sorption of 5 mg C/L for PP-HA (8.8 mmol carboxylic groups/g C), 176 μmol/g Goe of carboxylic group were immobilized, which exceeds the maximum molar arsenic release by a factor of 10 (maximum of 13.3 μmol/g Goe for arsenate with protocol A; Table 1). In the protocol B mobilization experiments only arsenate was found in solution after incubation, no matter the arsenic species previously sorbed and the DOM used.

3.4. Arsenic mobilization from natural samples in DOM solution

For all samples except the lake sediments arsenic extractability increased in the order "no DOM" < PA-HA < NaH_2PO_4 < HCl (Table 3). Extraction with PA-HA revealed a higher relative mobility of arsenic in the H 1 and A 1+2 samples (0.43–4.3% of As_{tot}) than in the W 1+2 and S (<0.4%). The total amount of arsenic released ranged from 0 (S 1) to 3.8 mg/kg (H 1/1). The biggest differences between "no DOM" and PA-HA extractable arsenic was found in the H 1 horizons. Release of arsenic with FI-DOM (applied to some samples only, results not shown) was between "no DOM" and PA-HA extracts. Initial DOM concentrations were positively correlated to dissolved arsenic concentrations for H 1/2 material (Fig. 4). An almost linear relationship was found for PA-HA (R^2=0.999) and also for FI-DOM (R^2=0.968). On a molar basis the amount of sorbed carboxylic groups in PA-HA (2.2–6.2 mmol/kg) exceeded the amount of arsenic molecules released (maximum: 0.05 mmol/kg) by more than one order of magnitude.

In the kinetic experiments with H 1/2 material two phases were observed (Fig. 5). The first phase ended within 24 h and was characterized by arsenic release to the solution. In the second phase arsenic was immobilised. DOM sorption continued throughout the experiment. Mostly arsenate and only small amounts of arsenite were found in the speciation analysis (Fig. 5). The addition of DOM, however, resulted in an increase of arsenite concentrations compared to the control.

3.5. Characterization of the natural solid phases

The analytical results of this section are summarized in Tables 2 and 3. The pH in the H 1 Podsol soil samples was significantly lower than in the other materials. The W 1+2 and A 1+2 samples from Wiesloch contained between 0.23% and 2.59% inorganic carbon. Calcite signature (1428 and 878 cm^{-1}) was visible in the FTIR spectra. Large amounts of organic carbon were particularly present in the sediment samples, whereas in the H 1 soils and A 2/2 aquifer amounts were low. Except for the H 1 horizons and the A 2 sediment all samples contained substantial amounts of iron (up to 6.3%) and manganese (up to 1.2%). The amorphous metal oxides, comprised about 1/10th of the total metal content in these samples, but was larger in the H 1 and A 2 material. Total reduced inorganic sulphur (TRIS) was increased in the aquifer material (A 2) and high in

Table 1
Sorption and desorption of arsenic from goethite or hematite (*) in this study and estimated from literature

Protocol/author	Solute	Sorption			Desorption		
		Init. As/Fe-ratio	As sorbed		c(DOM)	Net mobilization (As)	
		(µmol/g)	(µmol/g)	(%)	(mg C/L)	(µmol/g)	(%)
Arsenate experiments							
A	NaCl	130	130	100	25	13.3	10.3
B	$NaNO_3$	50	20	40	25	6.5	32.7
Dixit and Hering (2003)	$NaClO_4$	100	90	90			
Dixit and Hering (2003)	$NaClO_4$	50	50	100			
Grafe et al. (2002)	$NaNO_3$	200	160	80	12	46.7	23.3
Redman et al. (2002) (*)	$NaNO_3$	100	90	90	10	0.7	22.2
Arsenite experiments							
A	NaCl	130	70	55	25	9.3	13.3
B	$NaNO_3$	50	10	22	25	5.3	53.3
Dixit and Hering (2003)	$NaClO_4$	100	75	75			
Dixit and Hering (2003)	$NaClO_4$	50	40	80			
Grafe et al. (2002)	$NaNO_3$	200	240	>100	12	26.7	13.3
Redman et al. (2002) (*)	$NaNO_3$	100	90	90	10	0.4	13.3

The first columns display the applied salt solution, As/Fe ratio at the beginning of the sorption experiment and the amount of As sorbed. The last columns show the reaction condition and results of the arsenic desorption with DOM.

the lake sediment (S 1/2) compared to the soils. Total arsenic content was highest in the W 1+2 materials (Table 3). Arsenic in these samples was present to a large extent in forms not extracted by phosphate or HCl. Using these extractants the largest relative quantities were extracted from the H 1/2 soil and from the S 1/2 and A 2 sediments.

4. Discussion

Due to pressing concerns about arsenic contamination of water resources (Smedley and Kinniburgh, 2002), efforts have been undertaken to identify mechanisms that can increase arsenic mobility in soils, aquifers and sediments. The mobilization in Bangladesh/West Bengal type aquifers has primarily been linked to an indirect mobilization by DOM, particularly to increased substrate availability for iron reduction, causing enhanced release of iron oxide bound arsenic (Harvey and Swartz, 2002). Recent studies have also focussed on the redox activity and on electron shuttling capacity of organic matter with some organic pollutants and inorganic substances (Chen et al., 2003; Gu and Chen, 2003; Lovley et al., 1996). Chemical redox reactions and electron shuttling between DOM and arsenic have, however, not received much attention yet.

The results of this study suggest a strong potential for DOM to mobilize arsenic from goethite and natural soil and aquifer materials within short periods of time by purely chemical interactions. Net release from goethite was up to 46 mg/kg and 53% of the total sorbed arsenic. These results are in agreement with previous studies reporting arsenic desorption from different iron oxides (goethite, ferrihydrite, hematite) in the presence of bulk DOM (Redman et al., 2002) and fulvic or humic acids (Grafe et al., 2001; Grafe et al., 2002; Simeoni et al., 2003). Adsorption capacities for arsenate and arsenite on goethite were in agreement with previously reported findings (Dixit and Hering, 2003, Table 1) increasing our confidence that the results are valid.

Also in natural samples, DOM released up to 2.48 mg/kg or 2.88% of total arsenic. This was up to three times the amount released by our weakest extractant 0.01 M $NaNO_3$. Lombi et al. (2000), Kalbitz and Wennrich (1998) and Keon et al. (2001) were able to desorb 0.07–5 mg/kg of arsenic from soil and sediment samples with 1 M NH_4NO_3 or 1 M $MgCl_2$. Despite the much lower extractant concentrations used in our study, the arsenic release was in a similar range.

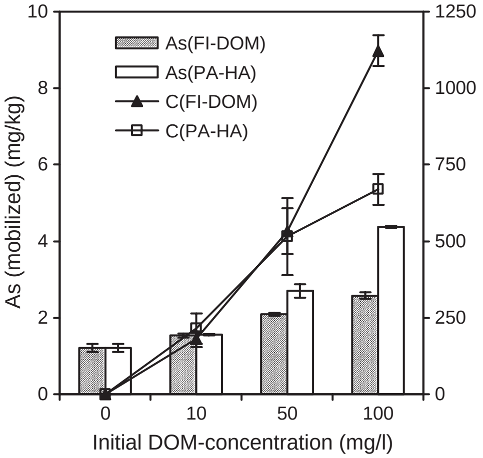

Fig. 4. Release of As_{tot} and sorption of DOM in experiments with soil material and the effect of different initial DOM concentrations. Bars represent the amount of arsenic released from H 1/2 samples during incubation with different concentrations of PA-HA and FI-DOM. Lines reflect the amount of DOM removed from solution in the same experiments.

In general the mobility of arsenic (as % of the total content) in natural samples treated with DOM was smaller than the mobility in the goethite assays. This can be explained by the reduced chemical availability of the arsenic. Arsenic bound to goethite is mainly sorbed in surface complexes. Instead in natural materials often only a small fraction of arsenic is in an exchangeable state (Lombi et al., 2000) and more is incorporated in minerals. So differences occur between synthetic minerals and natural samples as well as among natural samples. A high percentage of arsenic release with DOM (H 1 soil, A 2 sediment) concurred with high arsenic mobilities using phosphate and HCl as extractants. The iron content in these samples is rather low but mostly in an amorphous state and soluble with HCl. We therefore believe that arsenic in these samples was primarily sorbed to metal oxides, iron in the sediment and possibly aluminium in the H 1 horizon. In contrast only little arsenic was mobilized from the W 1 + 2 soils is mobile by DOM and phosphate solutions. Roughly 70–90% of arsenic were not accessible with HCl and therefore incorporated (not sorbed) in the structure of more stable minerals, most likely crystalline oxides as TRIS content was low.

The arsenic mobilization patterns for synthetic and the H 1/2 natural samples were similar. This finding suggests that, within limits, results obtained with synthetic samples can be extrapolated also to natural conditions. Arsenic release was always fast and completed within the first 24–36 h of the experiments. The kinetic was in agreement with competition of DOM and arsenate for goethite sorption sites, which has been shown to be fairly rapid (Hongshao and Stanforth, 2001).

The experimental conditions had a substantial influence on the sorption efficiency (Table 1) and on

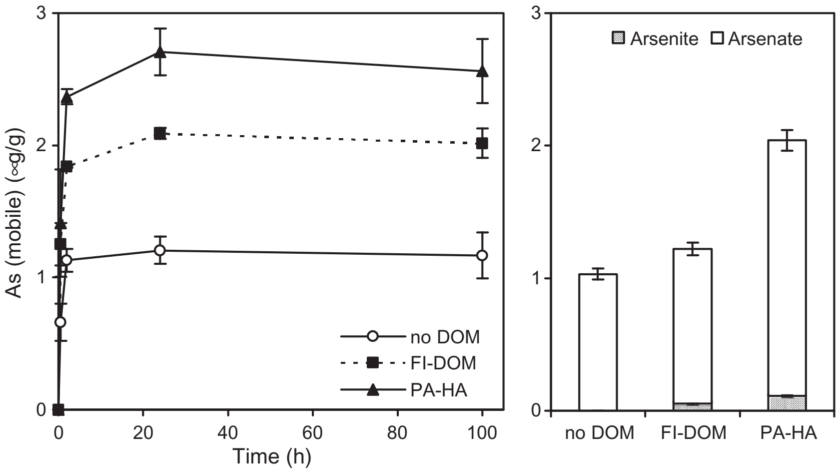

Fig. 5. Mobilization of As_{tot} from soil material and results of redox species measurement with HPLC-ICP-MS. Lines represent the As mobilization kinetic from H 1/2 samples in the first 100 h of incubation with different DOM types and concentrations. Bars represent the amount of arsenite and arsenate found in the assays.

Table 2
Characteristics of the natural samples

Sample	Type	Depth (cm)	pH	C_{inorg} (%)	C_{org} (%)	Fe_{tot} (g/kg)	Fe_{HCl} (g/kg)	Mn_{tot} (g/kg)	TRIS (mg/kg)
H 1/1	Soil	6–30	5.5	n/a	0.24	2±0.1	0.8±0.1	0.3±0.1	8.3
H 1/2	Soil	31–65	5.2	n/a	0.39	2±0.1	0.3±0.1	0.4±0.1	3.5
W 1/1	Soil	20–55	6.9	2.59	1.50	57±2.3	1.6±0.1	1.2±0.2	10.5
W 1/2	Soil	55–70	6.8	0.78	1.01	15±1.4	1.3±0.1	1.1±0.1	2.2
W 2/1	Soil	10–70	6.7	0.87	2.23	43±1.1	1.7±0.1	12.1±0.1	n/a
W 2/2	Soil	71–90	7.1	0.34	0.75	32±0.9	1.5±0.1	4.1±0.1	n/a
A 1/1	Aquifer	255–295	6.8	0.98	2.19	22±0.4	2.3±0.1	2.5±0.1	3.5
A 1/2	Aquifer	320+	6.4	0.38	2.02	63±0.7	4.3±0.1	11.1±0.1	n/a
A 2/1	Aquifer	130–220	6.9	0.23	2.23	4±0.7	3.3±0.1	0.4±0.1	66.9
A 2/2	Aquifer	250+	6.9	2.34	0.28	4±0.6	2.1±0.1	0.6±0.1	62.4
S 1/1	Sediment	0–2	n/a	n/a	9.79	34±1.5	11.3±0.1	7.2±0.3	n/a
S 1/2	Sediment	2–16	n/a	n/a	11.21	73±0.5	3.4±0.2	2.5±0.2	1008

the desorption process. Protocol A experiments showed a higher arsenic sorption than protocol B. These may be effects of the different anions Cl^- and NO_3^-, even though they are reported to have an equally small effect on arsenic sorption in soils (Livesey and Huang, 1981). Also in protocol A assays, including a drying step at 50 °C before DOM addition, a smaller fraction of arsenic was accessible to DOM in the mobilization step (Fig. 3). Intense hydrothermal treatment (150 °C; autoclave) reduces sorption capacity of goethite for oxyanions like phosphate as goethite crystallinity increases (Strauss et al., 1997). But a mild treatment, like air drying, is known to increase the sorption of oxyanions on soil material (Haynes and Swift, 1985). That effect is attributed to the formation of an increased number and stronger bonds between arsenic and minerals surfaces as water is removed. This could explain the observed reduced mobilization of arsenic after drying in our experiments. Another effect was a re-immobilization of arsenic when the goethite was treated according to protocol B without the drying step. This effect was particularly strong in samples amended with arsenite (Fig. 3). Diffusive transport to inner surfaces leading to higher sorption capacities and stronger binding of oxyanions (Matthess, 1994) may explain the re-immobilization during desorption experiments. Also it has been reported previously that DOM can raise the solid/solute partitioning coefficient of arsenic in solutions containing kaolinite (Saada et al., 2003), but such an effect was not yet observed for iron oxides or soils. The stronger re-

Table 3
Arsenic extraction from the natural samples

Sample	Type	As_{tot}	As(HCl)	As($H_2PO_4^-$)	As($NaNO_3$)	As(PA-HA)	Net mobilization	
		(mg/kg)	(%)	(%)	(%)	(%)	(mg/kg)	(%)
H 1/1	Soil	197±17	26.1	3	0.67	1.93	2.48±0.09	1.26
H 1/2	Soil	85±10	109.5	29	1.48	4.36	2.46±0.04	2.88
W 1/1	Soil	2122±716	31.4	5	0.07	0.13	1.18±0.07	0.06
W 1/2	Soil	842±90	25.4	8	0.04	0.19	1.32±0.04	0.16
W 2/1	Soil	1394±210	8.9	n/a	0.01	0.04	0.51±0.01	0.04
W 2/2	Soil	326±58	15.2	n/a	0.02	0.14	0.41±0.02	0.12
A 1/1	Aquifer	229±19	10.3	n/a	0.31	0.43	0.29±0.04	0.13
A 1/2	Aquifer	40±2	34.5	n/a	1.54	2.17	0.25±0.1	0.63
A 2/1	Aquifer	67±14	43.3	20	2.18	2.47	0.19±0.12	0.29
A 2/2	Aquifer	22±1	52.7	18	2.07	3.52	0.32±0.02	1.45
S 1/1	Sediment	44±4	1.3	n/a	0.64	0.38	n/a	n/a
S 1/2	Sediment	6±4	100.1	n/a	0.00	0.00	0.00±0.0	0.00

immobilization of added arsenite (Fig. 3) is potentially explained by oxidation to arsenate (observed in goethite suspensions) leading to the subsequent sorption of formed arsenate. The effects of the experimental protocols on the exchange behaviour suggest that the exact laboratory setup is crucial for sorption experiments of arsenic, especially when extrapolations on processes in the environment are attempted.

The results of this study suggest a potential for DOM to chemically oxidize and reduce arsenic within short periods of time. In aqueous solution, DOM both oxidized arsenite and reduced arsenate, albeit only a small fraction of the total. In contrast to abiotic chromium reduction with DOM (Gu and Chen, 2003) the reaction was essentially completed within the first day. Redman et al. (2002) reported comparable quantities of arsenite oxidation with a variety of DOM solutions but observed reduction of arsenate only for one type of DOM. The observation of both reduction and oxidation is in contradiction to the results of our thermodynamic estimates using model compounds. The thermodynamic calculations suggested arsenate reduction with DOM to be the energetically favoured process. The redox properties of the natural DOM are therefore not accurately described by the model compounds suggesting that DOM covers a wider spectrum of redox potentials. The relative amounts of reduction of arsenate to arsenite were larger using PA-HA than using FI-DOM, which could be an effect of its higher aromaticity as indicated by $SUVA_{280}$ and Abs_{465}/Abs_{665}. A further observation was that in goethite suspensions, arsenite was completely oxidized, while arsenate speciation did not change. This reaction was independent of DOM presence and may have been caused by nitrate or dissolved Fe(III) as oxidants (McCleskey et al., 2004).

The hypothesis that reduction of solid phase arsenate by DOM may significantly contribute to the mobilization of arsenic could not be substantiated by our experiments. In the H 1/2 samples which contained only arsenate (Marx, 1993), only small amounts of dissolved arsenite were found after incubation. Reduction of solid phase arsenate was not a relevant process in the goethite experiments and was only of minor importance in the experiments with natural samples.

In conclusion, the results demonstrate that DOM has the potential to chemically mobilize arsenic from iron oxides, soils, aquifers and sediments. In goethite suspensions with pre-sorbed arsenic, dissolved concentrations increased up to 6 times in the presence of 25 mg/L DOM compared to samples without DOM. In a variety of natural samples, concentrations increased by a factor of 1.5–3. It also has to be considered that we used wide solute/solid ratios of 1 g/25 mL solution. Using narrow solute/solid ratios, as they are found in soils, the mobile arsenic fraction decreases, but absolute concentrations in solution increase (Peiffer et al., 2003).

Arsenic release to ground water is a major concern worldwide. Direct interactions of arsenic and DOM have not yet received attention to a large extent. Taking into account only sorption competition reactions, pore waters rich in DOM may release more than 3 times the amount of arsenic from some soils than waters poor in DOM. At the narrow solute/solid ratios of natural environments, this process has the potential to raise arsenic concentrations to levels exceeding drinking water standards.

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