

Article

The Impact of Dissolved Organic Matter on Arsenic Mobilization from Goethite in the Presence of Silicic Acid and Phosphate under Reducing Conditions

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Abstract: The release of arsenic (As) adsorbed onto iron oxide (Fe-oxide) surfaces is affected by dissolved organic matter (DOM), phosphate (hereafter referred to as PO_4), and silicic acid (H_4SiO_4). Further, the reductive dissolution of As from Fe-oxide phases is also affected in reduced soils and sediments. Thus, the aim of this study was to understand the adsorption competition and redox-related mechanisms by which DOM affects As mobilization from Fe-oxide in a complex system containing both H_4SiO_4 and PO_4 . The results demonstrated that the DOM-driven, microbially mediated As biotransformation, and, thus, mobilization of As significantly increased when both dissolved inorganic H_4SiO_4 and PO_4 were present, as the co-presence of H_4SiO_4 and PO_4 decreased As adsorption sites on Fe-oxides. The availability of DOM in the co-presence of H_4SiO_4 and PO_4 increased the microbial activity in the system by providing more substrates for microbial metabolism, which also decreased the redox potential (reducing conditions) and consumed acidity, causing the pH to increase from 4 to 6.8. In addition, DOM, H_4SiO_4 , and PO_4 competed with As for sorption sites on Fe-oxides. The effects of DOM on As mobility by DOM-mediated or -triggered redox reactions were apparently stronger in the co-presence of H_4SiO_4 and PO_4 than DOM competition with arsenate for sorption sites on Fe-oxide alone. These findings advance our understanding of As mobilization processes in natural systems and can provide information for soil As management.

Keywords: arsenic; DOM; Fe-oxide; goethite; phosphate; redox reaction; silicic acid



Citation: Aftabtalab, A.; Moreno-Jiménez, E.; Henschel, J.; Nowak, S.; Schaller, J.; Knorr, K.-H. The Impact of Dissolved Organic Matter on Arsenic Mobilization from Goethite in the Presence of Silicic Acid and Phosphate under Reducing Conditions. *Water* **2022**, *14*, 2975. <https://doi.org/10.3390/w14192975>

Academic Editor: Helvi Heinonen-Tanski

Received: 2 September 2022

Accepted: 19 September 2022

Published: 22 September 2022

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1. Introduction

The International Agency for Research on Cancer classifies arsenic (As) as a Group 1 human carcinogen [1]. Natural and anthropogenic occurrences of As in various aqueous sources and agricultural soils pose a significant risk to human health in many parts of the world [2]. Among various sources of As contamination, considerable attention has been paid to groundwater contamination with geogenically released As [2,3].

Arsenic exists in the environment in both inorganic and organic forms, where inorganic As is more toxic than organic forms [2,4]. The inorganic forms of As most prominently include arsenate (As(V)) and arsenite (As(III)), which predominate under oxidizing and reducing conditions, respectively. The main organic forms of As are monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) [2,5]. Due to the vastly different properties of these species, the formation and interconversion of As species under different conditions determine its mobility in the environment [2].

Published literature in the past 30 years (from 1990 to 2020) [6–9] has demonstrated that Fe-(oxy)(hydr)oxides are the most prominent metal oxides controlling As mobilization.

However, dissolved organic matter (DOM) has been highlighted as an important factor that further influences As mobilization and transformation in groundwater, surface water, and soil solutions [9–14].

DOM interacts with As through different mechanisms and indirectly via interactions with mineral oxides. For example, DOM can affect As mobilization by complexation or by competition for sorption sites on mineral oxides [10,15,16]. Additionally, in waterlogged systems, DOM can trigger redox conditions and reductive dissolution of As from As-bearing mineral oxides [14,17–19]. For example, DOM has been shown to serve as electron shuttle to facilitate reductive dissolution of, for example, iron oxides [9,11,20–22] and may also serve as a direct electron acceptor affecting prevailing redox conditions [9,11,20–22]. Nevertheless, the onset of CH₄ production would indicate strictly reducing conditions and the depletion of other electron acceptors, including the availability of Fe-(oxy)(hydr)oxides for reduction, and, thus, a mobilization of As [10,13,23–26].

In addition to DOM, the presence of oxoanions, such as phosphate (hereafter referred to as PO₄) and silicic acid (hereafter total silicic acid, referred to as H₄SiO₄), also decreases As sorption by competition for sorption sites on Fe-oxides [27,28]. As PO₄ and H₄SiO₄ are structural analogs of arsenate and arsenite species, respectively [26–28], the presence of PO₄ and H₄SiO₄ may increase As mobilization in the soil solution. It is therefore crucial to understand the effect of PO₄ and H₄SiO₄ on the interaction of As and DOM and its biogeochemical cycling.

Many studies have pointed out the importance of DOM on the dynamics and turnover of As from Fe-rich systems, but the underlying mechanisms, particularly in complex systems, remain poorly understood [29,30]. Moreover, in organic matter-rich systems such as groundwater and wetland systems, we lack studies that address the fate of As in multi-component systems that include PO₄ and H₄SiO₄. Recently, Ahmad et al. [30] and Wu et al. [31] published studies on the effects of PO₄ and H₄SiO₄ on As mobilization. However, these studies were conducted in an aerated effluent collected from a water treatment plant with a pH of 7–7.5, but systems with a strong interaction among As, Fe, DOM, H₄SiO₄, and PO₄ are often linked to reducing groundwaters and wetland pore waters. As such, our understanding of the fate of As in multi-component systems remains incomplete, as previous studies have not considered interactions of PO₄ and H₄SiO₄ with As and DOM for sorption onto Fe-oxide under reducing conditions that mimic the ambient environments.

Therefore, the current study addressed the mechanisms by which PO₄ and H₄SiO₄ affect As mobilization in systems with different Fe-oxide availability. In particular, we aimed to include the impact of microbially mediated changes in redox conditions to more closely mimic natural conditions. We hypothesized that (i) the availability of DOM will initiate changes in the redox potential and subsequent reductive dissolution of As from Fe-oxide and that (ii) As mobilization is thereby positively related to the increasing competition of H₄SiO₄ and PO₄ with As for adsorption sites on remaining Fe-oxide (i.e., goethite) at elevated concentrations of these solutes.

2. Materials and Methods

2.1. Sampling Site and Characteristics of the Peat

The peat material, as natural organic matrix, was sampled in May 2014 in the peatland Vechtaer Moor [53°17'18.1" N; 8°31'06.5" E] as described in detail by Agethen et al. [32]. The site is located in the Northwest German Plain (Lower Saxony, Germany), within a mild Atlantic to sub-Atlantic climate with a mean annual temperature of 9.6 °C and mean annual precipitation of 750–800 mm. The peat material of the ombrotrophic site, poor in mineral matter, was collected from cut and air-dried peat sods. The Vechtaer Moor includes both active peat extraction sites and rewetted polders with low to intermediately decomposed peat, and it is poor in inorganic solutes and Fe (Table 1). This peat material was air-dried under long-term aerated conditions, thoroughly homogenized, and stored dry at room temperature (20 °C) before the experiment; it was rewetted in the lab prior to incubation.

Table 1. Chemical composition of the Vechtaer Moor peat material used in [32].

C [g kg ^{−1}]	Si [mg kg ^{−1}]	Fe [mg kg ^{−1}]	P [mg kg ^{−1}]	As [mg kg ^{−1}]
491.0	848.0	200.0	200.0	0.53

2.2. Synthesis of Goethite

In this study, we used goethite (α -FeOOH) as a model metal oxide. Goethite was chosen because it is one of the most abundant Fe-oxides in the environment worldwide and has a high affinity for trace elements [5,33–35]. The goethite was synthesized following Schwertmann and Cornell [30]. Briefly, we prepared (A) a fresh 1 M iron (III) nitrate solution by dissolving unhydrolyzed $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98\%$ purity, Sigma Aldrich, St. Louis, MO, USA) in twice-distilled water and (B) a 5 M potassium hydroxide (85.0–100% purity, AnalaR NORMAPUR) solution at $\text{pH} > 12$ and then aged it at 70°C for 60 h. The preparation was carried out in a polyethylene vessel to prevent silicic acid mobilization from glassware due to alkaline conditions. During the heating stage, the voluminous, red-brown suspension of ferrihydrite converted to a compact, yellow-brown precipitate of goethite. After 60 h, the yellow-brown precipitation of goethite was repeatedly washed, shaken, and centrifuged. For the sequential washes, deionized water was used to remove OH^- and NO_3^- until a conductivity value of $0.1 \mu\text{S cm}^{-1}$ was obtained. Afterward, goethite precipitates were dried at room temperature.

2.3. Incubation Batch Preparation

The aerated peat material was homogenized by passing it through a 2 mm sieve. In the first step, 1000 mg of aerated and homogenized peat was filled into 120 mL crimp bottles (Pyrex, Stoke-on-Trent, UK) as triplicate assays for all treatments. In order to re-dissolve the organic matter that was present in dry soil, the soil was rehydrated by adding 25 mL Millipore water a week before other aqueous and solid reactants were added to the incubated soil. Then, 500 mg of fresh peat (equivalent to 54 mg dry weight) was also filled into bottles, as microbially active inoculate. The second step was preparing systems with different goethite concentrations. This was done by adding either no goethite (nFe), 4.4 mg g^{-1} (per gram of dry peat) goethite (medium goethite: mFe), or 44.6 mg g^{-1} goethite (high goethite: hFe). In a third step, 30 mL of $80 \mu\text{g L}^{-1}$ arsenate ($\text{NaH}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$, 98% purity, Sigma Aldrich, St. Louis, MO, USA) was added to obtain a final concentration of $44 \mu\text{g L}^{-1}$ As in 55 mL of solution. This concentration was determined as an environmentally relevant concentration of As in soil solution [36]. As a fourth step, to assess the individual and combined effects of PO_4 and H_4SiO_4 (treatments) on As and DOM interaction at different Fe availabilities (nFe, mFe, and hFe), we added 13 mg g^{-1} PO_4 (equivalent to 250.2 mg PO_4 per L of slurry) ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, $\geq 98\%$ purity, Sigma Aldrich, St. Louis, MO, USA) and 21.7 mg g^{-1} H_4SiO_4 (equivalent to $418.2 \text{ mg H}_4\text{SiO}_4$ per L of slurry) ($\text{Na}_2\text{O}_3\text{Si} \cdot 9\text{H}_2\text{O}$, $\geq 98\%$ purity, Sigma Aldrich), either individually or in combination, to the incubation bottles. A schematic of the experimental design is given in Figures S1i–ii and S2 in the Supplementary Materials S1. Also, an overview of the preparation of the incubation, PO_4 , H_4SiO_4 , and Fe additions to the respective treatments is provided in Table 2.

In the next step, the incubation bottles were loosely covered with caps and put aside for 3 days, which allowed the added solutes and solids to reach equilibrium. Then, after 3 days, the pH of the incubated material was adjusted to pH 4, mimicking typical conditions in wetland soils, by adding 6 M hydrochloric acid. The pH of the incubated material after the equilibrium time (before sealing the incubation bottles) was monitored by a pH meter (Sentix 41 and Multi 340i, WTW, Weilheim, Germany) with a combined pH electrode, calibrated using buffer solutions at pH 7.00 and 4.00 at room temperature. We sealed the incubation bottles right after pH adjustment with a butyl rubber stopper and aluminum crimp caps. In the last step, samples were purged with N_2 through a cannula and gently shaken for 1 h to remove present oxygen in order to obtain anoxic conditions. During incubation times, the bottles were stored at $20 \pm 1^\circ\text{C}$. The bottles were incubated for 336 h

to approach fully reducing conditions in the bottles and analyses were performed after sampling at 24, 72, 168, and 336 h of incubation under anoxic conditions.

2.4. Sample Collection

After 24, 72, 168, and 336 h of incubation, aqueous samples and gaseous samples were collected for chemical analyses and dissolved in CO₂ and CH₄ concentrations. In total, 6 mL of pore water and 1 mL of gas phase from the headspace were retrieved at each sampling time. The equal amount of sampled gas from the headspace was replaced by injecting pure N₂, and the final concentration of the sampled water was corrected based on the extracted volume. The aqueous and gaseous sampling was performed by syringes and cannulas. To avoid intrusion of O₂ during headspace sampling, the syringes and cannulas were purged with N₂ prior to use.

Table 2. The preparation of incubations and descriptions of labeling, solutes, and solid iron oxide added to the respective treatments.

Treatments ¹		As	PO ₄ ³⁻ -P	H ₄ SiO ₄ -Si	No Fe	Medium Fe	High Fe
Fe Conc.–Treatments	(n = 3)	[44 µg L ⁻¹] *	[13 mg g ⁻¹] **	[21.7 mg g ⁻¹]	[-]	[4.4 mg g ⁻¹]	[44.6 mg g ⁻¹]
nFe-C	✓	✓			✓		
nFe-PO ₄	✓	✓	✓		✓		
nFe-H ₄ SiO ₄	✓	✓		✓	✓		
nFe-H ₄ SiO ₄ +PO ₄	✓	✓	✓	✓	✓		
mFe-C	✓	✓				✓	
mFe-PO ₄	✓	✓	✓			✓	
mFe-H ₄ SiO ₄	✓	✓		✓		✓	
mFe-H ₄ SiO ₄ +PO ₄	✓	✓	✓	✓		✓	
hFe-C	✓	✓					✓
hFe-PO ₄	✓	✓	✓				✓
hFe-H ₄ SiO ₄	✓	✓		✓			✓
hFe-H ₄ SiO ₄ +PO ₄	✓	✓	✓	✓			✓

Notes: ¹ Fe concentrations (Fe Conc.); no Fe: nFe; medium Fe: mFe; high Fe: hFe; and control: C. * µg L⁻¹ refers to the total As concentration. ** mg g⁻¹ refers to PO₄-P, H₄SiO₄-Si, and total Fe concentrations.

2.5. Analytical Methods

Aqueous Samples

All measurements included three analytical replicates for each sample. Total As measurements were performed by graphite furnace-atomic absorption spectroscopy (GF-AAS) (AA 800, Perkin-Elmer, Waltham, MA, USA). For total As analysis, 1 mL water samples were routinely filtered by 0.45 µm (nylon filters) and stabilized with 25 µL of 7 M nitric acid. Inorganic As speciation (arsenate and arsenite) was measured according to the method of Alava et al. [37] with continuous liquid chromatography (1290 Infinity II, Agilent, Santa Clara, CA, USA) using a PRP-X100 anion chromatography column (250 × 4.1 mm, 10 µm; Hamilton, Reno, NV, USA) coupled to a single quadrupole inductively coupled plasma mass spectrometer (CP-MS; Agilent 7900, Agilent Technologies Inc., Santa Clara, CA, USA). Thereby, additional 1 mL water samples were routinely filtered to 0.2 µm and stabilized with 20 µL of 6 M hydrochloric acid. The method of Alava et al. [37] allowed for separation, identification, and quantification of arsenite, arsenate, dimethylarsinic acid (DMAV), and monomethylarsonic acid (MMAV). Dissolved organic carbon was determined with a total organic carbon analyzer (TOC-VCN, Shimadzu, Kyoto, Japan), where samples were filtered to 0.45 µm before measurement. Concentration of phosphate (soluble reactive phosphorus; SRP) was analyzed according to the ammonium molybdate method [38]. Both ferric and ferrous iron (Fe⁺³ and Fe⁺²) were determined spectrophotometrically at 512 nm with the phenanthroline method (ferric iron as the difference between total iron, after reduction with ascorbic acid, and ferrous iron) (UV-VIS spectrophotometer

Agilent Cary 100 E, Santa Clara, CA, USA) [39]. Silicic acid and other dissolved elements were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES; SpectroBlue, Spectro/Ametek, Kleve, Germany). Since carbon mineralization is not under discussion in this study, the gaseous sampling method and the result are described only in Supplementary Materials S2.

2.6. Statistical Analysis

An independent Kruskal–Wallis (pairwise comparison) test was performed using IBM SPSS Statistics 26 (Armonk, NY, USA) for the dependent variables at each sampling time in order to assess significant differences. Statistical significance was determined at $p < 0.05$ on a 95% confidence interval.

3. Results

3.1. Solute Total Arsenic Turnover in Presence of Varying Amounts of Goethite

The total As solute concentration did not change (100% of all As added was still in the solution) within the first 168 h and at the onset of reducing conditions. Thereafter, total As concentrations tended to decrease (to approximately 50% of the initial solute concentration) over the later course of the incubation (Figure 1a–c). In particular, the system with the high Fe concentration ($\sim 44 \text{ mg g}^{-1}$) potentially immobilized/adsorbed more As compared with the systems with nFe or mFe (nFe = 0 and mFe $\sim 4 \text{ mg g}^{-1}$). Overall, the observed solute concentration of As was notably higher, regardless of Fe addition, in the presence of PO_4 , $\text{H}_4\text{SiO}_4 + \text{PO}_4$, or H_4SiO_4 . The least amount of As adsorption onto Fe-oxides occurred in $\text{H}_4\text{SiO}_4 + \text{PO}_4$ and PO_4 compared with the controls (hFe-C: with no H_4SiO_4 and PO_4 but DOM only) and hFe- H_4SiO_4 . The concentration of total As in the soil solution significantly ($p < 0.05$) increased in $\text{H}_4\text{SiO}_4 + \text{PO}_4$ and PO_4 treatments, particularly in the presence of hFe (Figure 2a–c), whereas concentrations of As were lowest in the hFe samples without H_4SiO_4 and PO_4 . As shown in Figure 2c, As adsorption in hFe- $\text{H}_4\text{SiO}_4 + \text{PO}_4$ at 24 h was significantly lower than hFe-C at 24 and 72 h, followed by hFe- PO_4 at 24 h, which was lower than hFe-C at 336 h. Moreover, As adsorption in hFe- $\text{H}_4\text{SiO}_4 + \text{PO}_4$ at 24 h was again lower than in any other treatments.

In the presence of the mFe concentration, the As concentration in mFe- PO_4 at 168 h was found to be higher than in mFe-C and mFe- $\text{H}_4\text{SiO}_4 + \text{PO}_4$ at 336 h. Here, in the presence of mFe, As adsorption was significantly lower in the mFe- PO_4 treatment at 168 h compared with other treatments (Figure 2b). With no Fe addition and background concentrations only (nFe), the concentration of As in the nFe- H_4SiO_4 treatment at 24 h was significantly higher than nFe-C, nFe- H_4SiO_4 , and nFe- $\text{H}_4\text{SiO}_4 + \text{PO}_4$ treatments at 336 h (Figure 2a). Notably though, at the nFe and mFe concentrations, there was no significant difference in total As concentration between treatments (H_4SiO_4 , PO_4 , or $\text{H}_4\text{SiO}_4 + \text{PO}_4$) and controls.

The obtained results suggest that under microbially mediated reducing conditions, the presence of H_4SiO_4 and PO_4 in As-bearing, Fe-rich soils increases As mobility.

3.2. Arsenate Concentration and Arsenite Formation

Only the inorganic arsenate (Figure 1d–f) and arsenite (Figure 1g–i) species were detected in the analyzed samples, whereas MMA and DMA were not detected in the assays and, thus, remained below the detection limit of $0.02 \mu\text{g L}^{-1}$.

At 24 h from the start of the anoxic incubations, arsenate—the added form of arsenic—was still the dominating species in the system. While after the first 24 h arsenite concentrations were still very low, at approximately 6% (in nFe- PO_4 and nFe- H_4SiO_4) to 47% (in hFe-C) of the arsenate, the formation of arsenite in solution rapidly increased at 72 h, as the redox potential (E_H) apparently decreased in the system along with increasing concentrations of Fe (Figure 1). Thereafter, despite persistent reducing conditions (reaching methanogenic conditions, see Figure S3, Supplementary Materials S2), the detected concentrations of arsenite decreased again with experimental duration. The details of arsenite dynamics over the course of the experiment are available in Table S1 of Supplementary Materials S2.

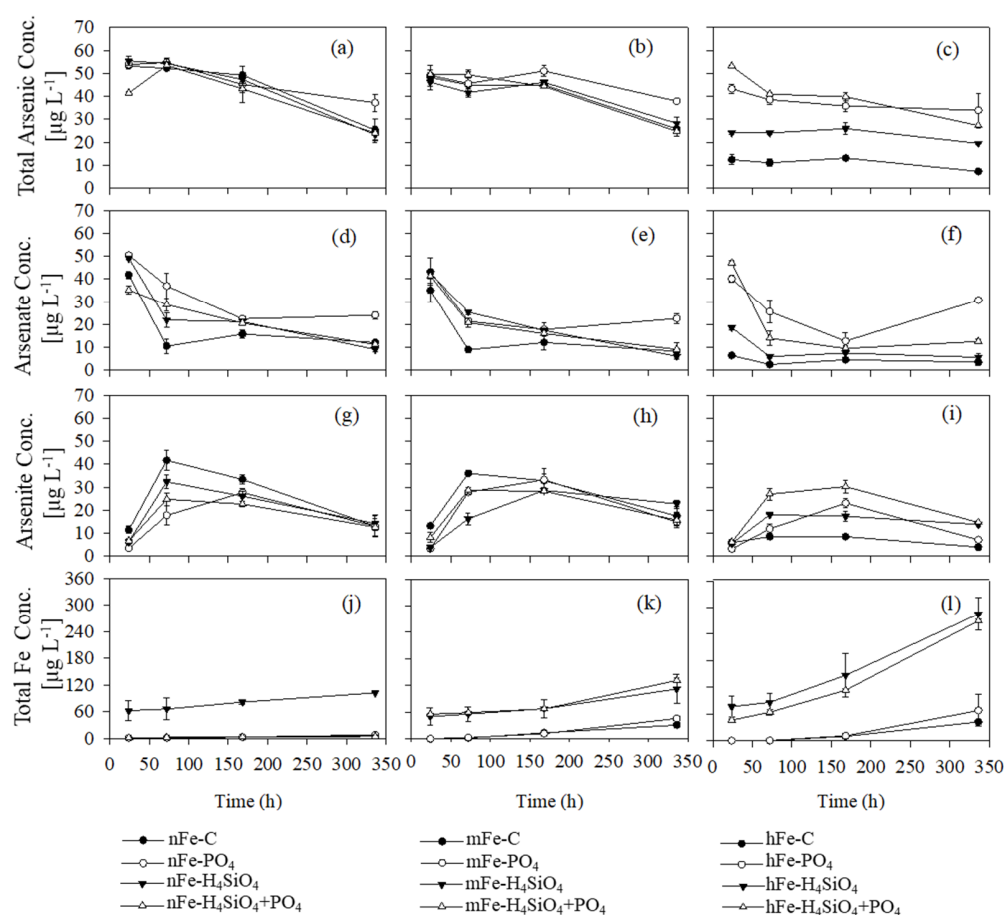


Figure 1. The concentration changes of total arsenic (a–c), arsenate (d–f), arsenite (g–i), and total iron (j–l) versus time upon anoxic incubation. Data represent the mean ($n = 3$); whiskers represent the standard deviation ($n = 3$). Phosphate: PO_4 ; silicic acid: H_4SiO_4 ; control: C; goethite: Fe; no goethite: nFe; medium goethite: mFe; and high goethite: hFe.

The solute concentration, i.e., the fraction of arsenate and arsenite in solution increased for all treatments in nFe and mFe systems (Figure 1d,e,g,h). However, in the hFe system, the concentrations of arsenate and arsenite were higher only in the presence of H_4SiO_4 and PO_4 compared with the control sample (hFe-C) (Figure 1f,i). The concentrations of arsenate and arsenite in the hFe-C sample always remained below the WHO guideline value ($10 \mu\text{g L}^{-1}$) also under strongly reducing conditions [40].

Although the reducing conditions extended over the later course of the incubation (Figure S3 Supplementary Materials S2), arsenate and arsenite concentrations remained low and constant in hFe treatments, as there was still Fe(III) available in the hFe system (99.8% of added goethite in hFe-C, 99.7% in hFe- PO_4 , 98% in hFe- H_4SiO_4 , and 93.5% in hFe- $\text{H}_4\text{SiO}_4 + \text{PO}_4$, respectively), which prevented arsenate mobilization and its transformation to arsenite. As shown in Figure S3 Supplementary Materials S2, the high availability of Fe(III) in the hFe system also slowed CH_4 formation by serving as an alternative electron acceptor for microbial respiration, keeping the system in an iron-reducing state (see below).

Overall, in the hFe system the concentrations of arsenate decreased with experimental duration from $50 \mu\text{g L}^{-1}$ at 24 h (particularly in H_4SiO_4 and $\text{H}_4\text{SiO}_4 + \text{PO}_4$ treatments) down to approximately $10 \mu\text{g L}^{-1}$ at 336 h (Figure 1f) (Table S2 Supplementary Materials S2 shows the significant effects of different treatments on solute arsenate concentrations).

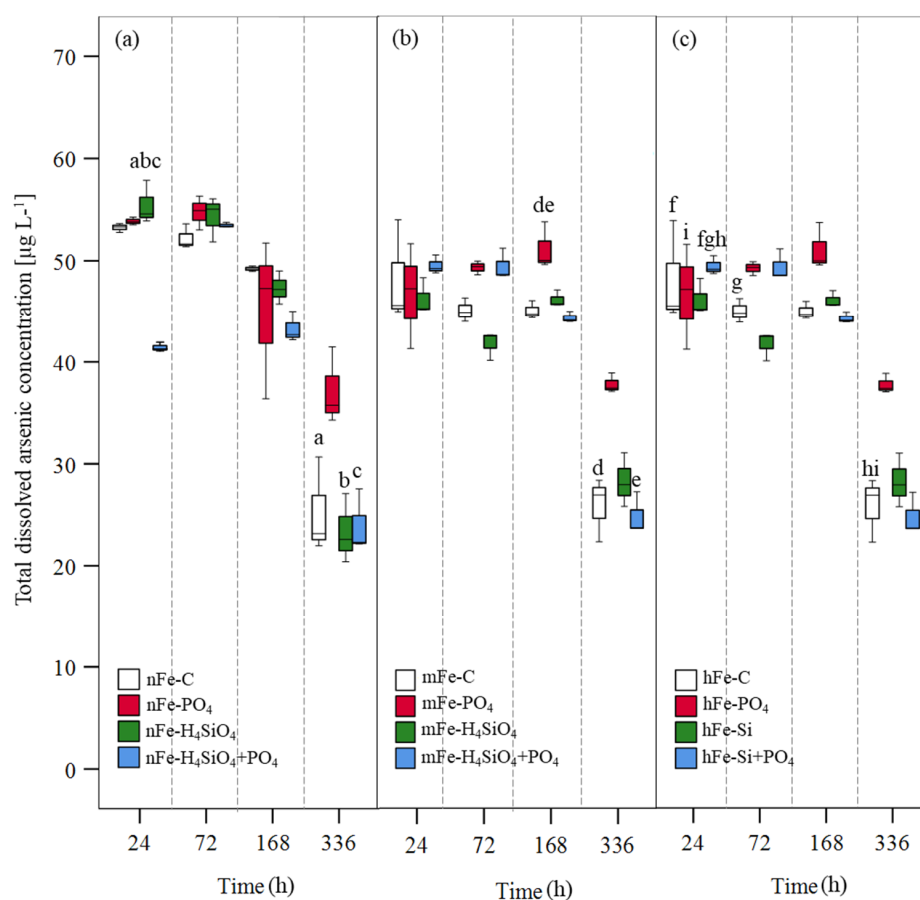


Figure 2. Box plots represent the total arsenic concentrations with different treatments and different goethite (Fe) concentrations (no Fe: nFe; medium Fe: mFe; and high Fe: hFe) versus time during the onset of anoxic conditions. Control: C; phosphate: PO₄; and silicic acid: H₄SiO₄. The boxes show quartiles and the medians; the whiskers denote data within 1.5 times the interquartile range; data from incubation over time ($n = 3$). Boxes with same letters are significantly different from each other ($p < 0.05$).

Over the course of the incubation, the solute concentration of arsenate decreased in the system, but the concentration of arsenite increased significantly. This opposing trend of arsenate decrease and arsenite increase particularly indicates the reductive transformation of the added arsenate in solution under strongly reducing conditions. Thereby, for total dissolved As, hFe-C had the lowest arsenite concentration, whereas the hFe-H₄SiO₄+PO₄ treatment had the highest arsenite formation under the most reducing conditions (Figure 1i). Arsenite concentration reached up to 30 µg L⁻¹ in the H₄SiO₄+PO₄ treatment, which was notably higher than the concentrations in hFe with H₄SiO₄ or PO₄ application alone (up to 20 µg L⁻¹). Table S3 Supplementary Materials S2 shows the significant effect of treatments on arsenite release. Overall, the effects of H₄SiO₄ and PO₄ on As reductive transformation in the hFe system was much larger than that observed in the nFe and mFe systems, indicating the effects of competitive sorption on reductive transformation and mobilization.

3.3. Dissolved Iron

The formation of Fe²⁺ from microbial reduction of the added goethite was observed in the aqueous phase of all treatments, indicating that the system was dominated by Fe-reducing conditions. Only in the later course of the experiment did several treatments, in particular those with low amounts of iron, reach methanogenic conditions (see Figure S3 Supplementary Materials S2). Noticeably, all dissolved Fe was present in the reduced form of Fe⁺² and represented as Fe total in graphs. From an overall perspective,

the concentration of dissolved Fe increased mainly in H_4SiO_4 and $\text{H}_4\text{SiO}_4+\text{PO}_4$ treatments in the hFe system (Figure 1l). The concentration of total Fe increased from 80 to 290 $\mu\text{g L}^{-1}$ for H_4SiO_4 and from 50 to 260 $\mu\text{g L}^{-1}$ for the $\text{H}_4\text{SiO}_4+\text{PO}_4$ treatment in the hFe system. The dissolved concentration of Fe in hFe- H_4SiO_4 and hFe- $\text{H}_4\text{SiO}_4+\text{PO}_4$ was approximately 2% (98% remaining as solid phase) and 6.5% (93.5% remaining as solid phase), respectively, of the Fe-oxide pool added to treatments. In addition, total Fe concentration slightly increased in hFe-C and hFe- PO_4 (from 0 to approximately 60 $\mu\text{g L}^{-1}$). In the nFe and mFe systems, the addition of H_4SiO_4 and $\text{H}_4\text{SiO}_4+\text{PO}_4$ led to a higher dissolved Fe concentration (with approximately 7% and 5.5% of the Fe-oxide added pool becoming reductively dissolved in mFe- H_4SiO_4 and mFe- $\text{H}_4\text{SiO}_4+\text{PO}_4$, respectively) compared with their respective controls (nFe-C and mFe-C). Overall, the addition of H_4SiO_4 or PO_4 on total Fe concentration was most significant in the hFe system under reducing conditions, and, here, due to the high amounts of iron present, methanogenic conditions were notably retarded.

3.4. Phosphate, Silicic Acid, and Dissolved Organic Matter

In the unamended peat soil samples (i.e., no additional H_4SiO_4 or PO_4 added), the concentrations of PO_4 and H_4SiO_4 were below the detection limit ($\text{DL} = 0.1 \text{ mg L}^{-1}$ for PO_4 and H_4SiO_4). For the PO_4 and $\text{H}_4\text{SiO}_4+\text{PO}_4$ treatments, the concentration of PO_4 in the solution was approximately 10 mg L^{-1} after 24 h, compared with its initially added concentration 80 mg L^{-1} at different Fe levels. Solute phosphate concentrations also remained almost constant over the incubation time. However, with the H_4SiO_4 addition, the concentrations of PO_4 decreased slightly by 2 mg L^{-1} at the later course of incubation, leveling out at approximately 8 mg L^{-1} at all Fe levels (Figure 3m–o).

As shown in Figure 3p–r, the maximum concentration of H_4SiO_4 in the aqueous phase was up to 90 mg L^{-1} in the beginning. The silicic acid concentration decreased at 72 h down to approximately 35 mg L^{-1} , but it then increased to the same level as at the beginning and remained constant over the remaining time. Evidently, despite careful adjustment in the beginning to pH 4, the pH increased in H_4SiO_4 and $\text{H}_4\text{SiO}_4+\text{PO}_4$ treatments at all Fe levels (Figure 4i–iii), due to either the slow but continuous increase in alkalinity from H_4SiO_4 addition or an increase in the microbial anaerobic respiration, which consumed acidity (Figure S3 Supplementary Materials S2).

The concentrations of DOM tended to increase for the H_4SiO_4 and $\text{H}_4\text{SiO}_4+\text{PO}_4$ treatments, compared with their controls, over the later course of the incubation at all Fe levels. However, the concentration of DOM did not change with the addition of only PO_4 compared with the controls. DOM concentration showed a greater increase upon H_4SiO_4 addition in the hFe system, reaching approximately 350 mg L^{-1} , compared with concentrations in the nFe and mFe systems of $\sim 280 \text{ mg L}^{-1}$. Overall, the concentration of DOM increased in parallel to dissolved Fe^{+2} after reducing conditions had been fully established (Figure 3s–u).

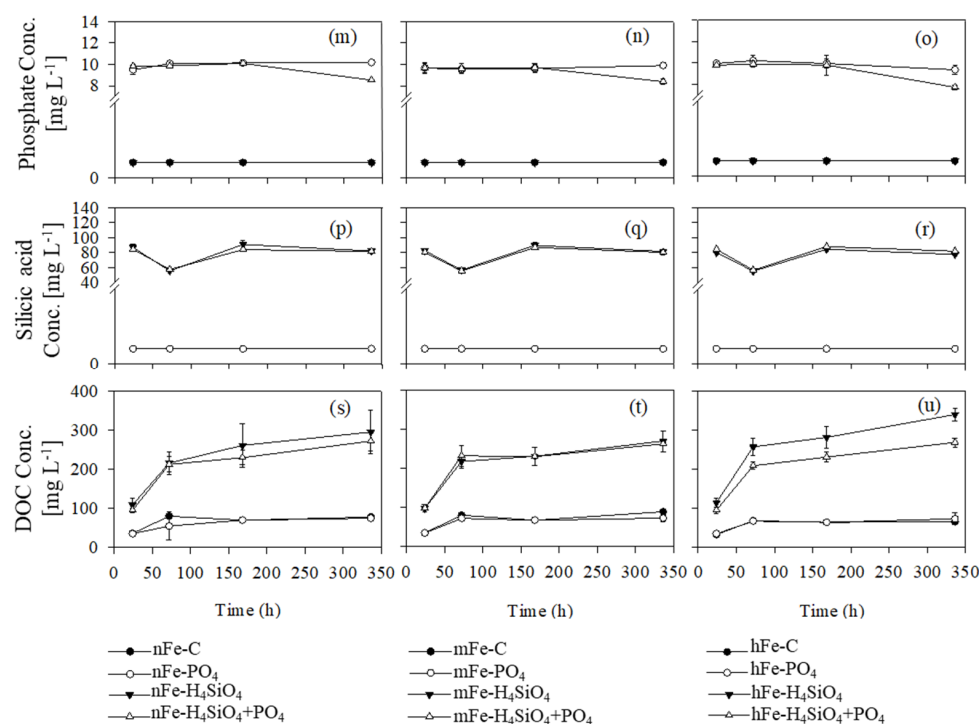


Figure 3. The concentration of phosphate: PO₄ (m–o); silicic acid: H₄SiO₄ (p–r); and dissolved organic carbon: DOC (s–u) versus time during anoxic conditions. Data represent the mean; whiskers represent the standard deviation ($n = 3$). Goethite: Fe; no Fe: nFe; medium Fe: mFe; and high Fe: hFe.

4. Discussion

4.1. The Effects of Phosphate, Silicic Acid, and DOM on Arsenic Mobilization

The competing effects between H₄SiO₄ and PO₄, either individually or in combination, with As for sorption on Fe-oxides have already been studied [30,31,41,42]. However, the role of DOM in the co-presence of H₄SiO₄ and PO₄ and the possible mechanisms that can increase As release from Fe-oxides have not yet received much attention.

The results of this study highlight the importance of the co-presence of DOM, H₄SiO₄, and PO₄ on As release from substrates with varying availability of Fe-oxides. Thus, our findings confirm and extend observations recently reported by Ahmad et al. [30] and Wu et al. [31] who also investigated the effects of both H₄SiO₄ and PO₄.

Extending these findings, our results suggest that under microbially mediated reducing conditions, the presence of H₄SiO₄ and PO₄, particularly the co-presence of H₄SiO₄ and PO₄, prevent As adsorption onto Fe-oxide in substrates with high concentrations of Fe. This can be explained by the slightly higher pH in the hFe condition, because the polymerization of silicic acid increases at higher pH, and, in turn, polysilicic acid has a higher binding affinity to mineral surfaces [43,44]. The greatest effect on As adsorption occurred in the treatment containing both PO₄ and H₄SiO₄, and this may also be explained by the fact that H₄SiO₄ increases PO₄ mobility [45–47], whereby this intensifies the effect of PO₄ on As mobility. In the single presence of either H₄SiO₄ or PO₄, both solutes showed lower effects on As adsorption, likely because each of the anions had low coverage of surface sites, whereas (the initially present) arsenate is known to have a high affinity for Fe-oxide surface sites [26,28,48,49]. Therefore, when H₄SiO₄ and PO₄ coexisted in the system, this reduced As adsorption on Fe-oxide, which, in turn, increased the mobility of total As and monitored As species (Figures 1 and 2). Thus, we attribute the high mobility of As primarily to competitive surface complexation of PO₄ and H₄SiO₄ for sorption sites onto Fe-oxide. This finding is also in agreement with previous studies [26,27,35,50,51]. In addition, we found a slightly stronger effect of PO₄ on arsenate and H₄SiO₄ on arsenite

adsorption, because of the structural analogs of arsenate and arsenite with PO_4 and H_4SiO_4 , respectively [26–28].

4.2. Silicic Acid and Phosphate Interactions with Fe

In addition to increases in As concentration, under H_4SiO_4 and PO_4 addition the concentration of Fe also increased in the solution, along with a progressive reduction of the added goethite. This finding is also in line with a study by Reithmaier et al. [52] who showed that H_4SiO_4 mobilizes Fe, DOM, and As from natural peat material without significantly changing the pH (Figures 1 and 3s–u). However, in our study, it is possible that H_4SiO_4 addition had an indirect effect on As adsorption onto Fe-oxide, and this cannot be clearly separated from other effects, since under high Si addition the pH had increased (Figure 4).

This higher pH could be explained by either a higher anaerobic respiration (Figure S3 Supplementary Material S2), consuming acidity, or a retarded increase of pH (up to values of approximately 6.8) after pH adjustment due to the alkaline nature of sodium silicate fertilizer (Figure 4).

Overall, the pH is an important parameter in determining the sorption and surface properties of Fe-oxides. Fe-oxides are able to adsorb more As under neutral or slightly acidic pH, decreasing the As mobility in the environment [2,53]. Since the maximum As immobilization on Fe occurred at pH 6, the presence of H_4SiO_4 likely reduced the adsorption of As on Fe (goethite) due to the increased pH and formation of polysilicic acid (Figure 1). Yet, several studies have shown that arsenate adsorption on amorphous Fe is not significantly affected at pH values lower than 7, but at pH values above 7 this decreases rapidly [54,55]. Therefore, H_4SiO_4 's ability to reduce the adsorption of As on Fe likely occurred because most of Fe's binding sites were already occupied by H_4SiO_4 , and this effect was strengthened by the formation of polysilicic acid at higher pH.

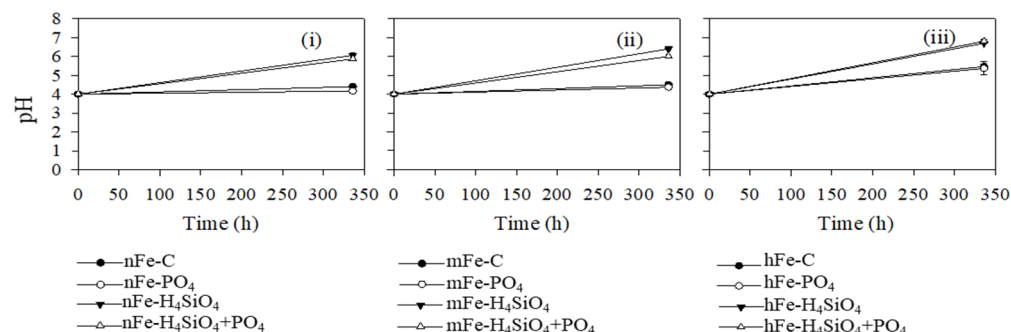


Figure 4. The initial pH changes with treatments (i–iii) versus time during anoxic conditions. Data represent the mean; whiskers represent the standard deviation ($n = 3$). Goethite: Fe; no Fe: nFe; medium Fe: mFe; high Fe: hFe; phosphate: PO_4 ; silicic acid: H_4SiO_4 ; and control: C.

4.3. Silicic Acid Effects on DOM Concentration

In addition to the concentrations of As and Fe, the concentration of DOM also increased in the solution in the presence of H_4SiO_4 and PO_4 (Figure 3s–u). This increase in DOM concentration presumably resulted from H_4SiO_4 competing for sorption sites on Fe-oxides (direct) [52,56]. Thus, DOM concentrations were found to be higher with H_4SiO_4 and H_4SiO_4 + PO_4 treatments compared with controls (nFe-C, mFe-C, and hFe-C) or PO_4 only treatments (nFe- PO_4 , mFe- PO_4 , and hFe- PO_4) (Figure 3s–u).

However, the existence of DOM increased the microbial activity in the solution by providing more substrates (DOM served as an electron donor) for microbial metabolism. An increase in the decomposition of the peat material likely increased dissolved organic carbon (DOC) concentration in pore water. Decomposition of organic matter also reduced the soil redox potential (E_H) [13,57,58]; subsequently, soil redox potential affected CO_2 and CH_4 formation (Figure S3 Supplementary Materials S2) [59,60]. In hFe- H_4SiO_4 and hFe-

H₄SiO₄+PO₄ treatments, incubations apparently remained in the E_H range of Fe reduction. By contrast, in the nFe and mFe systems, as well as in H₄SiO₄ and H₄SiO₄+PO₄ treatments, methane formation was observed. This indicates a much lower E_H to make methanogenesis thermodynamically competitive and, presumably, this elevated arsenate reduction [61,62].

4.4. The Role of DOM on Arsenic Mobilization

High DOM availability considerably increased concentrations of Fe in the solution (Figures 1 and 3), yet the effect on As was not straightforward. The presence of DOM not only influences As sorption onto Fe-(oxy)(hydr)oxides, but, as mentioned above, it also causes a reduction in the soil E_H. The decrease of E_H leads to a sequential consumption of electron acceptors, including iron (Fe⁺³) and arsenic (As^V), and potentially to the onset of methanogenic conditions if thermodynamically more powerful electron acceptors are depleted [18,63,64].

DOM reduces soil E_H most prominently by serving as a substrate for microbial metabolism (Figure S3 Supplementary Materials S2) [9,57,58,65], but it may also directly serve as an electron acceptor and donor or function as an electron shuttle [66,67]. While microorganisms use electron acceptors for anaerobic respiration, converting them to reduced forms, the reduction processes consume protons and increase the soil pH [63,68,69]. This may at least partly explain the increased pH values in the presence of H₄SiO₄ (see higher CO₂ production in these treatments, Figure S3 Supplementary Materials S2), in addition to the alkalinity release from the added form of H₄SiO₄. Thus, different mechanisms might have contributed to pH dynamics in the current experiment.

Upon oxidation of DOM via dissimilatory reduction of electron acceptors, ferric iron phases can be reduced to ferrous iron (Fe⁺²) either directly or indirectly with DOM acting as a shuttle facilitating electron transfer [9,11,20–22]. Consequently, the concentration of As in the hFe-H₄SiO₄+ PO₄, and hFe-PO₄ treatments would be expected to increase significantly, as is obvious from Figure 1 [5,63,64,70,71]. Although the reductive dissolution of Fe-oxide was higher in the hFe-H₄SiO₄ treatment, the concentration of As decreased. Presumably H₄SiO₄'s lower competitive strength for sorption, compared with PO₄ and DOM, contributed to a higher share of As adsorption [56], since in hFe treatments, ferric iron phases still remained throughout the experiment. However, in the co-presence of H₄SiO₄ and PO₄, the reductive dissolution of ferric iron phases (to ferrous) under reducing conditions in parallel also led to a microbial reduction of arsenate to arsenite species, as As sorption was lowered and availability higher in competition with PO₄, further facilitating the mobility of As. Consequently, the concentration of arsenite reached high levels in the soil solution (Figure 1g–i). However, only inorganic species of As were detected, as microorganisms reduced arsenate to arsenite under reducing conditions. Organic species of As, namely MMA and DMA, were not detected, since they were presumably present at concentrations [72,73] below the detection limit (DL = 0.02 µg L^{−1}).

In sum, in the soil, H₄SiO₄ increased the availability and solubility of DOM, which, in turn, led to higher microbial activity under anoxic conditions, also yielding elevated pH values. Therefore, with the depletion of available Fe(III)-oxides (as sites for As adsorption) in the solid phase, due to its microbial reduction, arsenate increased in the aqueous phase. Additionally, the availability of soluble DOM stimulated As transformation by microbial reduction of arsenate to arsenite. Moreover, adding PO₄ and H₄SiO₄ anions in the presence of DOM affected arsenate mobilization due to a combination of the following effects: (i) Competition of H₄SiO₄/PO₄ and DOM with As decreased the available As adsorption sites on Fe-oxide. (ii) In the co-presence of H₄SiO₄ and PO₄, more of the sorption sites on Fe(III) were covered by H₄SiO₄ and PO₄, which subsequently decreased As (re)adsorption. (iii) Finally, as a result of H₄SiO₄ and PO₄ addition, DOM became more available, leading to increased microbial reduction of arsenate to arsenite by DOM.

5. Conclusions

This study elucidates the complex and diverse impact of the co-presence of H_4SiO_4 and PO_4 in soils on the mobility of As. Our results indicate that H_4SiO_4 had additional, indirect effects on As adsorption, either by increasing the pH via releasing alkalinity from the H_4SiO_4 phase or by increasing the DOM concentration, thus favoring anaerobic respiration and organic matter degradation that further led to acidity consumption and pH increase. Because the high availability of DOM caused reducing conditions through increased microbial respiration under anaerobic conditions using either arsenic, iron, or organic matter as abundant electron acceptors, the redox conditions were adjusted to be favorable for As reduction. Arsenite was the predominant species of As under reducing conditions, and Fe-oxide availability was controlled by the redox conditions and corresponding dissolution under reducing conditions.

Overall, this study highlights the importance of the co-presence of H_4SiO_4 and PO_4 for As mobilization. On the one hand, the presence of H_4SiO_4 and PO_4 appears to have a negligible effect on arsenate mobilization in low-Fe systems. On the other hand, since all Fe (as active surface sites for competitive sorption) may be immediately microbially reduced, possibly facilitated by redox-active DOM, the competition between H_4SiO_4 , PO_4 , and DOM with As for sorption sites on Fe is, thus, more likely to occur in Fe-rich soils. Further, the potential of DOM to affect arsenate mobilization is mainly related to the presence of reducible Fe under reducing conditions. For example, the mobilization of arsenate increased when all the available Fe had been reduced in the nFe and mFe systems. In the hFe system, despite Fe(III) reduction to Fe(II) by microbial oxidation of DOM, there was still a large pool of available Fe(III) to provide sorption sites for arsenate (re)adsorption and, thus, As mobilization was minimized. As such, in the hFe system, addition of H_4SiO_4 and PO_4 had the most prominent effects, competing for sorption sites on the remaining Fe. At the narrow solid/dissolved boundary line in natural environments, this process has the potential to enhance arsenic concentrations to levels exceeding the drinking water standard.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1. **Figure S1.** (i) photograph of incubation bottles; (ii) sketch of treatments and Fe addition in the form of goethite: Fe; no Fe: nFe; medium Fe (4.4 mg g^{-1} , the weight of Fe): mFe; high Fe (44.6 mg g^{-1} , the weight of Fe): hFe; addition of phosphate is indicated by PO_4 ; addition of silicic acid by H_4SiO_4 . **Figure S2.** Schematic of the incubation batch preparation and the respective treatments with phosphate: PO_4 ; silicic acid: H_4SiO_4 ; goethite: Fe; no goethite: nFe; medium goethite: mFe; high goethite: hFe. **Figure S3.** The rate of CO_2 (a–c) and CH_4 production (d–f) versus time during incubation under anoxic conditions. Data represent the mean; whiskers represent the standard deviation ($n=3$). Addition of goethite is indicated by Fe, where no Fe: nFe; medium Fe (4.4 mg g^{-1}): mFe; high Fe (44.6 mg g^{-1}): hFe; addition of phosphate is indicated by PO_4 ; addition of silicic acid indicated by H_4SiO_4 . **Table S1** Arsenite (As(III)) release rate (in % of total As in the system) during the course of the experiment. See methods section for analytical methods. **Table S2** The significant effects of different treatments on arsenate (As(V)) mobilization in each sampling time, showing the significant effects of different treatments on arsenate release in the soil solution. **Table S3** The significant effects of different treatments on arsenite (As(III)) mobilization in each sampling time, showing the significant effects of different treatments on arsenite release in the soil solution.

Author Contributions: Conceptualization, A.A. and K.-H.K.; methodology, A.A. and K.-H.K.; software, A.A.; validation, A.A. and K.-H.K.; formal analysis, A.A.; investigation, A.A.; resources, A.A., E.M.-J., J.S., and K.-H.K.; data curation, A.A.; writing—original draft preparation, A.A.; writing—review and editing, A.A., E.M.-J., J.H., S.N., J.S., and K.-H.K.; supervision, K.-H.K. All authors have read and agreed to the published version of the manuscript.

Funding: A.A. was supported by the German Academic Exchange Service (Deutscher Akademischer Austauschdienst—DAAD) (NAWAM program: grant number 57260501). The work was further supported by the German Research Foundation (DFG), projects SCHA 1822/7-1 and KN 929/11-1.

Data Availability Statement: All data in the article are publicly available and have no limitations.

Acknowledgments: We thank Mikaela Frame, Celeste Brennecke, Emma Jane Menzies, Michael Fleischer, and Marcel Schmiedeskamp. We thank the laboratory technicians of the laboratory of the Institute of Landscape Ecology Ulrike Berning-Mader, Madeleine Supper, Melanie Tappe, and Viktoria Ratachin. Tanja Broder evaluated data of ICP-OES analyses. This paper is dedicated to the memory of Christian Blodau, who initiated the project. We acknowledge support from the Open Access Publication Fund of the University of Münster.

Conflicts of Interest: The authors declare no conflict of interest.

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