Influence of Natural Organic Matter on As Transport and Retention

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Natural organic matter (NOM) can affect the behavior of arsenic within surface and subsurface environments. We used batch and column experiments to determine the effect of peat humic acids (PHA), groundwater fulvic acids (GFA), and a soil organic matter (SOM) extract on As sorption/transport in ferrihydrite-coated sand columns. A reactive transport model was used to quantitatively interpret the transport of As in flow-through column (breakthrough) experiments. We found that As(III) breakthrough was faster than As(V) by up to 18% (with OM) and 14% (without OM). The most rapid breakthrough occurred in systems containing SOM and GFA. Dialysis and ultrafiltration of samples from breakthrough experiments showed that in OM-containing systems, As was transported mostly as free (noncomplexed) dissolved As but also as ternary As–Fe–OM colloids and dissolved complexes. In OM-free systems, As was transported in colloidal form or as a free ion. During desorption, more As(III) desorbed (23–37%) than As(V) (10–16%), and SOM resulted in the highest and OM-free systems the lowest amount of desorption. Overall, our experiments reveal that (i) NOM can enhance transport/mobilization of As, (ii) different fractions of NOM are capable of As mobilization, and (iii) freshly extracted SOM (from a forest soil) had greater impact on As transport than purified GFA/PHA.

Introduction

Arsenic is a toxic element that poses an environmental threat due to its contamination of surface and ground waters that are used for domestic consumption (*1*). In many areas of the world, concentrations of As are higher than the WHO drinking water limit of 10 μg/L (*1*). Understanding and quantification of physical and biogeochemical processes governing the transport and mobility of As in complex natural (*2*) and engineered systems (*3*) still remain a challenging task.

Arsenic is present in the environment mainly as inorganic As(III) and As(V) and to a lesser extent as organic species. At neutral pH, As(III) exists as H_3AsO_3 with pK_a values of 9.2, 12.7, and 13.4, whereas As(V) is present as $H_2AsO_4^-$ and $HAsO_4^{2-}$ with pK_a values (for H_3AsO_4) of 2.2, 6.9, and 11.5 (*4*).

Both oxidation states of As can coexist in solution, with As(III) considered to be generally more mobile than As(V) (*1, 5, 6*). The mobility of both species of As is controlled by adsorption onto, and redox reactions with, metal oxides and clay minerals (*7, 8*), by competitive adsorption of anions such as phosphate (*8–11*), and by redox and complexation reactions with natural organic matter (NOM) (*11–14*).

NOM is ubiquitous in both aquatic and terrestrial environments and can be part of the dissolved or solid phase. The concentration of NOM in groundwater (aquifers) and surface water (rivers and lakes) ranges from 0.1 mg C/L to several hundred mg C/L (*15*). Soil organic matter (SOM) refers to the organic compounds present in soil from decomposed plant/animal products and soil biomass with fulvic acids (FA) and humic acids (HA) as two of its operationally defined fractions. FA are soluble at all pH values, whereas HA are only soluble in base and insoluble in acid. Both FA and HA bind strongly to metal oxides and clay minerals (*15, 16*).

The interaction of As with metal oxides and minerals in the presence of HA and FA has been widely studied in batch experiments (*12, 17–20*). However, it has been less extensively studied in flow-through systems. In batch systems, in the presence of HA and FA, sorption of both As(V) and As(III) to minerals was found to decrease due to competition of As and NOM for sorption sites at different Fe-oxides (*12, 17, 19, 20*). However, unlike other findings, Grafe (2002) (*18*) found no significant impact of HA or FA in As(III) or As(V) adsorption to ferrihydrite in batch systems. Also, HA did not have any discernible effect on the transport of As(V) in HA-containing compared to HA-free column systems despite the competitive nature of HA on As sorption to Fe-(hydr)oxides (*18*). NOM can also mobilize Fe from Fe-(hydr)oxides forming Fe-NOM/ FH-NOM colloids as well as dissolved Fe-NOM complexes (*21, 22*). This can in turn form ternary As–Fe–NOM colloids/ complexes by interacting with As (*12, 22–24*). Additionally, NOM has been proposed to bind As directly (*25*), although recent experiments demonstrated that this complex formation is of minor importance in Fe-free humic substances (*22*).

Despite the recognized importance of As interactions with Fe-(hydr)oxides such as ferrihydrite (FH) in the presence of NOM, a comprehensive study of the influence of varying concentrations of different fractions of NOM on As transport/ desorption in Fe-(hydr)oxide dominated systems is lacking. Additionally, almost all studies with NOM have been carried out with purified HA and FA and not with environmentally relevant SOM extracts that were not treated/purified under harsh conditions as is usually done with HA and FA. Additionally, it is unclear in which forms the As is mobilized in the environment (i.e., as free As ion, as dissolved or colloidal As-OM/As–Fe–OM complexes, or as As-FH/As-FH-OM colloids).

Therefore, the objectives of this study are (1) to quantify adsorption–desorption and transport of As in ferrihydrite-coated sand (FH-sand) in the presence and absence of OM in both batch and flow-through systems, (2) to determine whether SOM can be as competitive as fulvic and humic acids in affecting As transport and desorption from FH-sand, (3) to describe As transport and its competitive interaction with different OM fractions with a reactive transport model, and (4) to determine in which form (speciation) As is mobilized in a flow-through system, as free (dissolved) As or as dissolved/colloidal As-OM, As–Fe–OM, As-FH, or As-OM-FH.

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Material and Methods

Reagents. Stock solutions of 1 mM As(III) ($NaAsO_2$) and As(V) ($Na_2HAsO_4 \cdot 7H_2O$) were prepared. Pahokee peat humic acid (PHA) was purchased from the International Humic Substances Society (IHSS) (Minnesota, USA), and Gorleben groundwater fulvic acid (GFA) was kindly provided by Manfred Wolf (Munich, Germany). The isolation procedure for the GFA can be found in ref *26*. The PHA and GFA contain approximately 5.1 μg Fe and 100 ng Fe per mg C, respectively (*22, 26*). All stock solutions of As, PHA, and GFA were prepared in solutions containing both 5 mM NaCl and 1 mM PIPES in deionized water. PHA and GFA solutions were readjusted to pH 7.0 using 1 M NaOH and filtered with a 0.45 μm mixed cellulose ester (MCE) filter. Dissolved organic carbon (DOC) concentrations of 5 and 50 mg C/L were chosen since they represent environmentally relevant concentrations in aquifer systems (*14, 15*).

Soil Organic Matter (SOM) Extraction. The SOM protocol and chemical data of the SOM extract is given in the Supporting Information (SI) S1 and SI Table S1.

Synthesis of Ferrihydrite-Coated Sand. Two-line ferrihydrite (FH) was synthesized by hydrolyzing 0.2 M $Fe(NO_3)_3 \cdot 9H_2O$ with 1 M KOH (*27*). Quartz sand (Unimin Corp., Spruce Pine, NC) was washed with DI water twice and mixed with wet ferrihydrite to prepare ferrihydrite-coated sand (FH-sand) (*5*) with a final Fe content of ∼0.1% (∼1030 μg/g) (determined by 0.1 M HCl extraction followed by the ferrozine assay, see below).

Adsorption Isotherms. As(III) and As(V) adsorption isotherms were determined by equilibrating 1 g FH-sand in 5 mM NaCl with 30 mL of As(III) and As(V) solutions with concentrations ranging from 10−3000 μM; the isotherms were prepared in either OM-free solutions or in the presence of 30 mL of either 50 mg C/L PHA, 50 mg C/L GFA, or the SOM extract (SI Table S2). After equilibrating the mixtures for 48 h (23 °C, 100 rpm) on a horizontal shaker, samples were taken, filtered (0.45 μm MCE), and prepared for As total measurements (see below). Sampling from As(III) adsorption experiments was conducted in an anoxic glovebox (100% N_2). Adsorption experiments done in the absence of PIPES buffer (data not shown) showed no significant differences to the experiments done in the presence of PIPES suggesting that the PIPEs buffer did not influence As sorption.

Column Experiments. Breakthrough of As through FH-sand and desorption of As from As-loaded FH-sand in the presence of OM (PHA, GFA, and SOM) and absence of OM (OM-free) was studied under flow conditions at 24 μL/min following (*5*) using Kontes FlexColumn Economy-Columns (1.3 cm diameter, 10 cm length) containing ∼15 g FH-sand (porosity of 0.44). All As(III) experiments were carried out in an anoxic glovebox (100% N_2). All column experiments were carried out in duplicates (SI Table S3). The pH of the effluent remained circumneutral throughout the experiments in all treatments.

To study transport (breakthrough) of As through FH-sand, 15 g of wet FH-sand was filled in columns and equilibrated with 5 mM NaCl and 1 mM PIPES solution for 48 h after which the solutions from the respective experimental setup were injected (SI Table S3). Concentrations of As used in all breakthrough experiments were 10 μM (750 μg/L), which is representative of As concentrations observed in As-contaminated aquifers (*1*). Breakthrough was considered complete when concentration of As in the eluate for each column was equivalent to that of the influent within experimental error (95% of influent concentration).

To study desorption of As from FH-sand, As(III) and As(V) were individually presorbed to FH-sand, targeting a surface loading of 60−65% (compared to the maximum value based on sorption isotherms - Figure 1, SI Table S2) for both As species (yielding 10.1 and 7.6 mmol As/kg FH-sand for As(III)

and As(V), respectively). Columns were filled with 15 g of wet FH-sand that was presorbed with As(III) or As(V), and the As was then desorbed by OM and OM-free solutions (SI Table S3). Desorption experiments were carried out for 200−250 h until cumulative As plots leveled off, and the As in the eluate yielded stable values. This cutoff was selected for practical purposes; however, it should be noted that the desorption might proceed for a longer duration at very low effluent As concentrations. A cumulative plot was obtained by summing the total moles of As desorbed from samples collected.

Dialysis and Ultrafiltration of Samples from Breakthrough Experiments. To quantify the mobilizable fraction (colloidal/dissolved) of As within column experiments, samples from pore volume 25 (∼250 h) were subjected to dialysis and ultrafiltration following the method of Sharma et al. (*22*) (SI S2, SI Table S6). Samples at pore-volume 25 were chosen based on results (As concentrations of 200−700 μg/L) found within previous As−Fe−OM batch experiments, where As−Fe−OM complexes/colloids were successfully analyzed after dialysis (*22*).

Modeling of Batch and Column Experiments. A two-site Langmuir model, including strong and weak sorption sites, was used to describe sorption of As(III) and As(V) to ferrihydrite-coated sands within batch experiments in the absence and presence of different OM fractions (eq 1 and eq 2 in SI S4.1). The same two-site Langmuir model was adopted as a source/sink term in the one-dimensional transport equation to simulate the breakthrough of As in column experiments (*28, 29*). However, in our experimental setup the characteristic time of advection (∼2 × 10^4 s) (i.e., the ratio between the length of the flow-through system and the seepage velocity) is shorter than the one of adsorption (∼2 × 10^5 s) (i.e., time needed to reach equilibrium between the liquid and solid phase in the batch experiments) indicating that adsorption of As to FH-sand in the columns cannot be considered at local equilibrium. Therefore, a kinetic description based on a linear driving force approach was adopted to describe the mass-transfer between the aqueous and the solid phases (further details on the model formulation and fitting procedure are provided in SI 4.1, 4.2, and 4.3).

Analytical Methods. Samples from batch, breakthrough, desorption, and dialysis experiments were filtered (0.45 μm, MCE), acidified with 0.25 M HNO_3 and analyzed for total As by ICP-OES. Samples from ultrafiltration were acidified without filtration. Selected samples were analyzed for As speciation by LC-ICP-MS by following standard protocols (*30*). DOC was quantified using a TOC analyzer. To quantify total Fe from the eluates of the breakthrough experiments (pore volume 25), Fe was extracted with 1 M HCl at 90 °C at 150 rpm. After 30 min the suspension was centrifuged (14,000 g, 5 min), and the supernatant was analyzed for total Fe (and/or Fe(II)) by the ferrozine assay (*31*). Fe(total) was also quantified in the dialyzed and ultrafiltered samples to obtain colloidal and dissolved Fe(total). The ratio of the absorbance at 465 and 665 nm (E4/E6), which gives the degree of condensation of organic matter (*15*), was determined by a plate reader (FlashScan 550, Jena Analytik, Germany). Particle size measurements were carried out using a Mastersizer 2000 (Malvern, Germany).

Results and Discussion

Effect of GFA and PHA on As Sorption to Ferrihydrite-Coated Sand. To quantify adsorption of As on FH-sand, As(III) and As(V) were incubated with FH-sand in the presence and absence of OM (Figure 1). For both As(III) and As(V), the adsorption maximum in the presence of PHA and GFA was appreciably lower than that for OM-free systems (Figure 1, SI Table S2). Arsenic(III) showed greater adsorption than As(V) on FH-sand in As-only (16.2 compared to 11.4 mmol
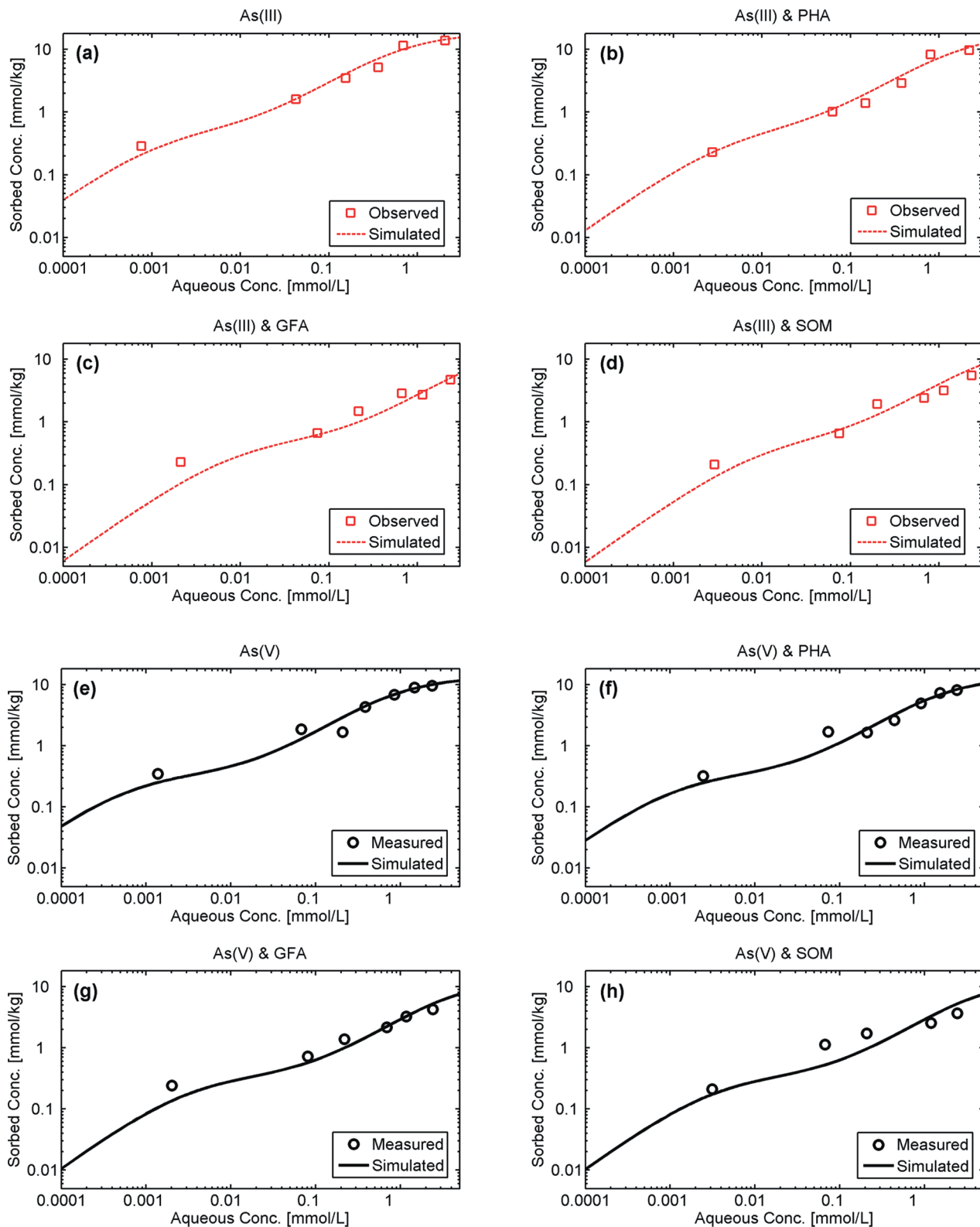
FIGURE 1. Sorption isotherms of As(III) and As(V) onto FH-sand in organic-matter-free systems compared to systems containing Pahokee Peat Humic Acids (PHA), Gorleben Groundwater fulvic acids (GFA), and extracted soil organic matter (SOM).

As/kg sand) and in As-PHA systems (11.8 compared to 8.5 mmol As/kg FH-sand). In the presence of GFA, As(III) and As(V) adsorption was even lower, yielding 4.5 and 3.8 mmol As/kg FH-sand, respectively. The total Fe content of the FH-sand did not decrease extensively after addition of PHA/GFA, and in all cases less than 5% of the total Fe in the FH-sand was reduced to Fe(II) (data not shown).

Comparison between observed and simulated results (SI S4.1 - eqs 1 and 2) shows that a two-site isotherm model (including one weak and one strong binding site, distributed according to the ferrihydrite data provided by Dzombak and Morel (*32*)) reasonably describes the measured As concentrations in both absence and presence of OM (Figure 1). In the presence of OM, adsorption of both As(III) and As(V) to
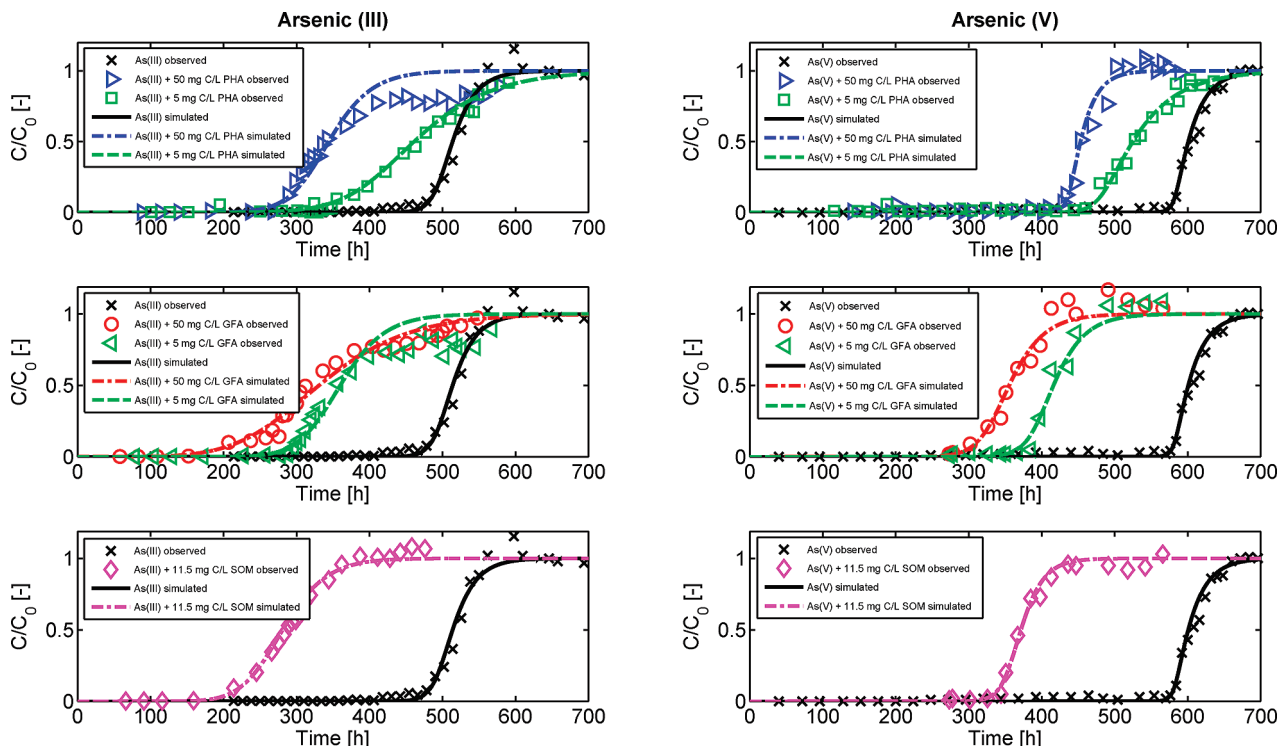
FIGURE 2. Breakthrough curves of 10 μM As(III) (left) and As(V) (right) in FH-sand filled columns in the presence and absence of various concentrations and types of OM: Pahokee Peat Humic Acids (PHA), Gorleben Groundwater fulvic acids (GFA), and extracted soil organic matter (SOM).

FH-sand decreased significantly, thus indicating the competitive effects of PHA, GFA, and SOM on arsenic sorption. A competitive effect of OM on As adsorption to Fe-(hydr)oxides has been previously reported (*12, 17, 19, 20*). However, in a study by Grafe et al. (*18*), FA did not affect As(V) adsorption onto ferrihydrite but only affected As(III) adsorption. In that study, no influence of PHA on As(III) or As(V) adsorption was found. The authors attributed this to the fact that saturation of FH surface sites by As leads to adsorption onto microporous structures of FH which are not accessible to FA or HA for competitive adsorption.

The two As species, As(III) and As(V), showed different adsorption behavior to Fe-(hydr)oxides. With our FH-sand, we saw greater adsorption of As(III) compared to As(V) in both OM-containing and OM-free systems confirming previous studies (*10, 33, 34*). The adsorption maxima in OM-free systems for As(III) (16.7 mmol/kg) and As(V) (12.1 mmol/kg) FH-sand correspond to 0.87 mol As(III) and 0.65 mol As(V) per mol Fe. These values for As per mol Fe are ~5 times larger than the ones reported by Dixit and Hering (2003) (*10*) who obtained 0.16 mol As(III) and 0.13 mol As(V) per mol Fe (calculated from their sorption values of ~1500 μmol/g for As(III) and ~1200 μmol/g for As(V)). The higher sorption values compared to Dixit and Hering (2003) could partly be due to the relatively high amount of divalent/trivalent cations present in the quartz (Al: ~8 ppm, Fe: ~200 ppb, Ca: ~1 ppm, Mg: ~100 ppb, information provided by Unimin Corp., Spruce Pine, NC). These cations could leach out during the batch experiments providing cation bridges for As to bind to the FH or even to the quartz mineral surface. The high As/Fe ratio may also be due to the fact that the FH in our systems is distributed on sand particles, preventing aggregation of FH particles and thus providing more exposed surface area for As binding. Alternatively, our higher adsorption values may arise from higher concentrations of As used for adsorption isotherms (up to 3 mM As), in comparison to 100 μM used by Dixit and Hering (2003). Additionally, our experiments with As(III) were carried out in an anoxic

glovebox flushed with N_2 and therefore there might be higher bicarbonate concentrations in As(V) experiments that had been done outside the glovebox. However, control experiments with As(III) done outside the glovebox showed no appreciable differences to experiments done inside (data not shown) suggesting that competition of As adsorption with bicarbonate was of minor importance.

Effect of GFA and PHA on As Transport and Desorption in Fe(III) Ferrihydrite Systems. After having quantified adsorption of As(III) and As(V) on FH-sand in batch experiments, we conducted breakthrough experiments where As-enriched solutions were injected into FH-sand filled columns in the presence and absence of OM to quantify transport behavior of As in flow-through systems. In the column experiments, the total time for arsenic breakthrough was up to 700 h which is considerably larger than the time scale of our conservative tracer (i.e., bromide), whose breakthrough occurred in less than 5.5 h. The asymmetrical shape of the measured breakthrough curves is consistent with rate-limited adsorption behavior (Figure 2), and it is well described by the reactive transport simulations (eqs 3 and 4) with the fitted values of the affinity constants for As(III) of 1.2×10^{-3} and 4.2×10^{-6} mol/L for the weak and strong sites, respectively, and 5.2×10^{-4} and 9×10^{-7} mol/L for As(V) (SI S4.3, SI Table S8).

In systems with OM present in the influent, we observed more rapid breakthrough of both As(V) and As(III) compared to OM-free systems (Figure 2). The rapid breakthrough in the presence and absence of OM is given as mean arrival time of the advective front (i.e., arrival time of 50% of the inflowing As concentration; SI Table S4). Breakthrough of both As(III) and As(V) was faster in the presence of PHA and GFA than in OM-free systems. In fact, the longest breakthrough times were observed in the OM-free systems: 522 h for As(III) and 609 h for As(V), respectively. In the presence of OM, breakthrough times were significantly shorter: ≤470 h for As(III) and ≤531 h for As(V), respectively. GFA were more effective than PHA in causing more rapid arsenic
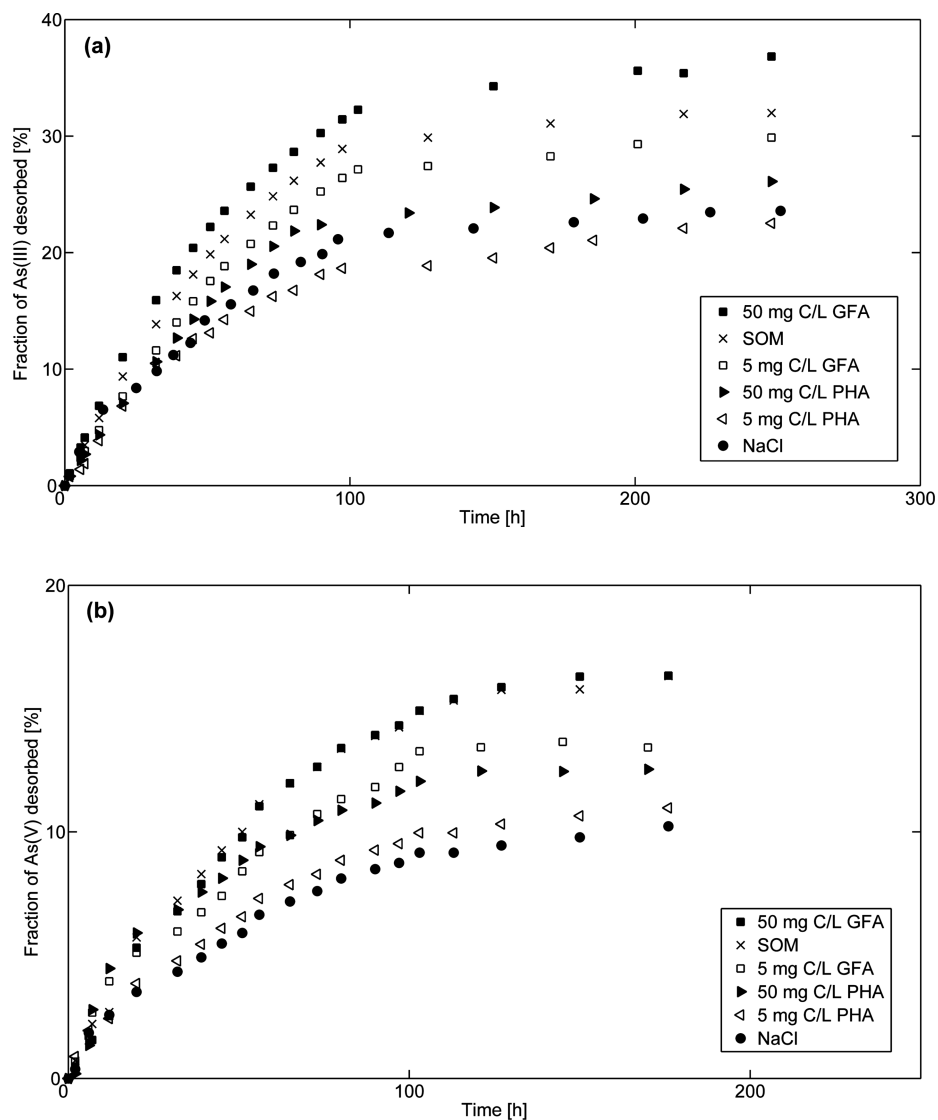
FIGURE 3. Desorption curves of As(III) (a) and As(V) (b) from FH-sand filled columns in the presence and absence of various concentrations of Pahokee Peat Humic Acids (PHA), Gorleben Groundwater fulvic acids (GFA), and extracted soil organic matter (SOM).

breakthrough; this effect can be attributed to the smaller molecule size and higher polarity of GFA which results in a stronger competition with As(III) and As(V) for the available adsorption sites on the FH-sand. Furthermore, we also found that As(III) breakthrough was generally faster than As(V) by up to 23% and 14% in systems with and without OM, respectively, which shows that As(III) is more mobile than As(V).

For each OM fraction, concentrations of 5 and 50 mg C/L were injected in the columns (SI Table S3). The breakthrough of arsenic was always faster in the presence of higher OM concentrations. This was particularly true for As(III) with PHA (Figure 2a), resulting in a 13% and 26% shorter breakthrough time in 5 and 50 mg C/L PHA, respectively. For As(V) breakthrough time was shorter by 10, 34, 32, and 40% in the presence of 5 and 50 mg C/L PHA or 5 and 50 mg C/L GFA, respectively, compared to OM-free systems (Figure 2d and 2e, SI Table S4). This behavior is described by the competitive adsorption formulation given in eq 2 and eq 4 (SI S4.1) where the competitive effects depend on both adsorption affinity and concentration of OM. Although similar values of the affinity constants were obtained from fitting both batch and flow-through experiments (SI Tables S7 and S8), it was not possible to obtain a satisfactory match of the column breakthrough curves directly using the parameters

determined in the isotherm experiments. Such discrepancies between adsorption behavior in batch and flow-through systems have been frequently observed (e.g., Hanna et al., (2010) (35)) and may be attributed to factors including different soil/solution ratios, presence of immobile water regions in the porous medium, and changes in sorption site accessibility in packed beds of FH-sand.

To further understand arsenic mobilization in flow-through systems, As desorption from FH-sand was examined for OM and OM-free solutions. The time scale for desorption experiments was shorter than for the breakthrough experiments (about ~220 h for desorption as compared to ~700 h for breakthrough). With the exception of the experiments with 5 mg C/L PHA, the results of the desorption experiments were consistent with what we observed in the breakthrough experiments. We found that the amount of As desorbed in the presence of OM was significantly higher than in OM-free systems (Figure 3a and 3b, SI Table S5). A solution of 50 mg C/L GFA showed the largest amount of As desorption with 32% in As(III) and 16% desorbed in As(V) systems, respectively. A solution of 5 mg C/L GFA was more effective in desorbing both redox species of As than 50 mg C/L PHA despite the 10-fold concentration difference used between GFA and PHA. Five mg C/L GFA solution desorbed 30% As(III) and 13% As(V) compared to 50 mg C/L PHA which desorbed

26% As(III) and 11% As(V). This can again be explained by the differences in size and polarity of the GFA and PHA molecules as described above already for batch (sorption) and breakthrough experiments. Besides their higher polarity due to higher carboxylic group content, FA have a smaller molecular size than HA and thus are situated closer to the oxide surface, causing stronger repulsive electrostatic interactions compared to HA (*15, 20*).

In our experiments we found that As(III) was more mobile than As(V) at pH 7, confirming findings from previous studies (*5, 6, 10, 34, 36*). In our desorption experiments, the cumulative amount of As(III) desorbed from the FH-sand was almost twice as much as that for As(V) (~21−37% for desorbed As(III) and 10−16% for As(V)) (Figure 3a and 3b, SI Table S5). These results confirm previous studies where the total amount of As desorbed in abiotic columns was reported between 22−27% for As(III) and 10−12% for As(V) (*34*). Interestingly, our initial sorption (batch) experiments showed that more As(III) than As(V) binds to FH-sand. The two different experimental treatments (batch adsorption vs desorption experiments) therefore show that although As(III) is initially sorbed to a larger extent, the binding to the FH-sand is weaker than As(V) binding and As(III) is more mobile and transported faster than As(V) in the environment.

Effectiveness of SOM in Desorbing As from FH-Coated Sand in Comparison to GFA/PHA. To investigate the effect of NOM for transport/mobilization of As under more environmentally relevant conditions, we carried out sorption, breakthrough, and desorption experiments with a SOM extract and compared the results to the results obtained with HA/FA. The SOM extract contained 11.5 mg C/L, falling within the high range of DOC concentrations typically observed in soils/aquifers (*15*). The maximum adsorption of As in the presence of SOM (4.3 and 3.6 mmol/kg FH-sand for As(III) and As(V), respectively) was only slightly lower than that for 50 mg C/L GFA (4.5 and 3.8 mmol/kg FH-sand for As(III) and As(V), respectively) and represented ~50% and ~25% of the maximum As adsorption values in the presence of 50 mg C/L PHA and OM-free systems, respectively, for both As(III) and As(V) (Figure 1, SI Table S2). In breakthrough experiments, the time needed for breakthrough of As in the presence of SOM was in the same range as observed for the other OM (Figure 2A/2B, SI Table S4). Specifically, in the case of As(III), the 50% breakthrough time with 11.5 mg C/L SOM was 287 h which was faster than with 50 mg C/L GFA (312 h). In the case of As(V), the breakthrough time obtained with 50 mg C/L GFA was slightly more rapid, with 50% breakthrough at 352 h compared to 372 h for SOM. In desorption experiments (Figure 3A/3B, SI Table S5), SOM and 50 mg C/L GFA desorbed similar amounts of As(V) from FH-sand (both 16%) whereas for As(III), 50 mg C/L GFA desorbed slightly more (37% for 50 mg C/L GFA) compared to 32% for SOM.

Our results suggest that the SOM extract was more effective as the HA/FA in transporting and desorbing As. This result is even more significant given the low DOC concentration of SOM that was 11.5 mg C/L which is almost five times lower than the highest concentration (50 mg C/L) of PHA and GFA used. The strong competitive effect of SOM on adsorption of both As(III) and As(V) is also substantiated by the fitted values of the affinity constants for SOM, which yielded smaller values than the ones for other OM fractions in both batch and flow-through experiments.

Results from ion chromatography showed that the SOM extract did not have high concentrations of silicate (below detection limit) or phosphate (~100 μg/L) (SI Table S1) that could potentially compete with As for sorption sites (*9*). Nevertheless, small quantities of phosphate or other trace constituents in the SOM extract, such as metal oxide nanoparticles, will affect As adsorption. However, the E4/E6 ratio of 6.4 and DOC concentration of 9.9 mg C/L after 6 M

HCl addition (82.1% of the original DOC value) showed that SOM had appreciable FA character and likely consists of small, reactive, polar organic molecules, thus explaining why the SOM is more effective than the HA tested. Additionally, the average molecular size of the SOM was ~95 nm as compared to ~80 nm for the GFA and ~160 nm for the PHA (SI Table S1). This suggests that with a smaller particle size, the SOM is more effective than the PHA in competing with As. Most importantly, while SOM was extracted in an environmentally relevant manner (extraction with DI water), the PHA and GFA used were isolated by repeated additions of concentrated acids and bases including treatment with hydrofluoric acid followed by adsorption on hydrophobic XAD resins (e.g., Kappler et al. (2001) (*37*)). This harsh and selective isolation protocol probably destroys and removes environmentally relevant polar organic fractions of PHA and GFA which could otherwise be present and probably more effective in influencing arsenic mobility (*38*). These fractions were present in our SOM extract, since no purification of the SOM was carried out and therefore explain the high efficiency of the SOM extract.

Although the SOM extract was filtered (0.45 μm), it could potentially still contain a small quantity of microorganisms. However, in all SOM-experiments, concentrations of Fe^{2+} were below detection limit, no As(V) reduction was observed, and As(III) oxidation was <7% (Table S6); thus, even if microorganisms were present, reduction of Fe(III)/As(V) and As(III) oxidation were not significant. Additionally, the E4/E6 ratio of the SOM extract did not change significantly within 30 days, confirming that microbial degradation of SOM was of minor importance.

The greater effectiveness of the SOM in affecting As transport and desorption from FH-sand in comparison to GFA/PHA shows that results obtained from extracted and purified humics could possibly underestimate the effects of SOM on As transport. In some of the As contaminated areas in the world, for example in Bangladesh, the effect of SOM on As mobilization/desorption could be even stronger where high phosphate and silicate concentrations are present in surface water infiltrating the aquifers; thus, further increasing the effect of SOM and causing a cumulative effect on the mobilization of As (*39*).

Speciation of As Mobilized by OM under Flow-through Conditions. The interaction of OM with FH can produce FH-OM colloids and dissolved Fe-OM complexes (*21, 22*). Free As ions can bind to FH/FH-OM-colloids or dissolved Fe-OM complexes to form ternary As−Fe−OM complexes/colloids (*22, 40*). In flow-through systems, however, it is unclear which of these fractions dominates As transport. Therefore, we selected samples from breakthrough experiments (pore volume 25) and used dialysis and ultracentrifugation to separate the different fractions (SI Table S6). The highest total Fe concentrations (before dialysis) were found in the eluates from columns running with OM. This suggests that OM is able to mobilize Fe from FH-sand and form Fe-OM/FH-OM colloids as well as binary Fe-OM complexes also in flow-through systems. These processes have also been observed recently in batch systems (*22*). Dialysis of column eluates showed that As was present (and thus transported) predominantly as a free ion (>90%) with less than 10% of total As remaining in the dialysis bags (i.e., As probably bound to OM molecules larger than 0.45 μm) (SI Table S6). It is noted, however, that the amount of free As could have been slightly overestimated due to desorption of As from colloids present in the eluate during dialysis, although we consider this of minor importance based on the results of previous batch studies (*22*). After dialysis, >70% of total Fe stayed in the dialysis bags in samples stemming from columns running with OM (SI Table S6) suggesting that most of the Fe was present in OM molecules/aggregates larger

than 0.45 μm. Quantification of As and Fe in the fractions separated by dialysis showed that after completion of dialysis, ~1.6–20 μg/L of total As and ~140–330 μg/L of total Fe remained inside, with the highest concentration of As and Fe in treatments with SOM followed by GFA, PHA, and last OM-free system for both As(III) and As(V) related treatments (SI Table S6). When comparing the treatments containing different OM sources we found that the highest concentrations of total Fe after dialysis were present in systems containing SOM (284 for As(III) and 334 μg/L for As(V)), followed by treatments running with GFA (192 for As(III) and 251 μg/L for As(V)) and PHA (141 for As(III) and 165 μg/L for As(V)). This demonstrates that OM with smaller molecular weight fractions (i.e., GFA) was generally able to mobilize more Fe from FH-sand than PHA. Interestingly, the amount of Fe in the original SOM extract even decreased from ~600 μg/L at the inlet of the column to ~300 μg/L at the outlet of the column, suggesting that during column passage, Fe present in the original extract precipitated or sorbed; it also demonstrates that no additional Fe was mobilized by the SOM extract. A small fraction of As even remained inside the dialysis bag in the OM-free system together with very low concentrations of Fe suggesting that As can also be transported by colloidal FH particles in the absence of OM.

To quantify the amount of As in the 'truly' dissolved fraction compared to the colloidal fraction, all samples that were dialyzed were subjected to 3 kDa filtration. We found that approximately ~15–50% (1.5–7.3 μg/L) of total As and ~35–67% (~90–140 μg/L) of total Fe from the dialyzed fraction remained in the 3 kDa filtrate (i.e., the dissolved fraction) in treatments containing OM. Analysis of DOC contents in the colloidal and dissolved fractions showed that between 0.9–1.4 mg C/L remained in the 3 kDa filtrate (i.e., the dissolved fraction). This corresponds to ~2% of the PHA, ~2% of the GFA, and ~10% of the SOM of the DOC present in the PHA, GFA, and SOM samples before 3 kDa filtration. These values in the 3 kDa filtrate are comparable to values that have been reported for similar studies (22, 40). The results obtained in the present study with samples from breakthrough experiments confirm the formation of both ternary colloids/complexes of As–Fe–OM, which have been proposed previously (12, 22, 24, 40). Dissolved As–Fe–OM complexes can form when Fe ions act as a cation-bridge to bind As to Fe-OM complexes, and colloids containing FH and Fe-OM complexes can form when OM interacts with FH-sand. Interaction of free As with the Fe-OM complexes or FH-OM colloids can then form As-FH-OM colloids or As–Fe–OM complexes. Release of FH colloids from FH by OM was described previously (22).

In samples with SOM, even more total As was found in dissolved fraction (6.7 μg/L in As(V) and 7.3 μg/L in As(III)) compared to GFA (5.5 μg/L in As(V) and 3.6 μg/L in As(III)) and PHA (1.5 μg/L in As(V) and 1.9 μg/L As(III)). This again confirms the efficiency of SOM in comparison to other purified OM fractions in affecting arsenic transport. There were no significant differences in the total amount of As in the dissolved fraction between As(III) and As(V) treatments. In samples from OM-free systems, no detectable total As and total Fe was obtained which shows that As was only transported as free dissolved species in treatments containing no OM.

Environmental Relevance of Effects of NOM on As Transport. In this study we demonstrated the effect of different fractions of NOM on As transport and mobilization. Experiments with SOM showed that fresh OM from natural soils is even more effective than FA and HA in affecting As transport/mobilization from Fe-oxide minerals. This suggests that fresh NOM infiltrating from surface waters (e.g., from surface ponds or during monsoon) into aquifers, subject to excessive groundwater use (41), may promote efficient and rapid As mobilization. Our data also suggest that results solely based on experiments obtained with purified OM may underestimate the role of NOM in As-contaminated aquifers.

Supporting Information Available
Soil organic matter (SOM) extraction (section S1) and chemical data of the SOM extract (SI Table S1). Sorption and column experimental treatments (section S2) with sorption maxima of As(III) and As(V) to FH-sand (SI Table S2). Treatments and experimental conditions for breakthrough and desorption experiments (SI Table S3). Average As breakthrough times for different experimental treatments (SI Table S4). Total amount of As desorbed from FH-sand in desorption experiments (SI Table S5). Dialysis and ultrafiltration of samples from breakthrough experiments (SI section S2) with As(total) and Fe(total) in samples from breakthrough experiments before and after dialysis and after 3 kDa centrifugal filtration (SI Table S6). Modeling approach and fitting procedure (SI section S4) with modeling of batch and column experiments (S4.1). Fitting parameters for isotherm experiments (SI S4.2, Table S7) and column experiments (SI S4.3, Table S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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