

Interactions of Arsenic and the Dissolved Substances Derived from Turf Soils

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Monosodium methanearsonate (MSMA) is frequently used as an herbicide for the control of weeds in turf grasses at golf courses in Florida. There are concerns about arsenic (As) contamination of local shallow groundwater from the application of MSMA. The distinction between “free” As and colloid-bound/complexed As in soil solution is important for understanding the mobility and bioavailability of As in the environment. In this study, the equilibrium membrane (500 and 3500 Da) dialysis method was employed to determine the “free” and “bound” As in water extracts of five types of golf-course soils containing coated and uncoated sands in various proportions with peat. All samples were evaluated for arsenic species (arsenite, As^{III} and arsenate, As^V), dissolved organic matter, and additional constituents (iron, aluminum, and calcium). The impacts of microbial growth were evaluated by conducting experiments with and without the addition of sodium azide for one particular soil type. Results indicate that (1) the presence of peat in the soils plays a significant role in the distribution of As in the dissolved phase of soil solutions; (2) the majority of As present in the soil extracts from soils containing peat was associated with substances of molecular weight (MW) between 500 and 3500 Da; (3) the association of As and dissolved organic matter (DOM) in the soil solution strongly affected As bioavailability, thus determining As transformations via microorganism-mediated processes; and (4) the presence of peat greatly enhanced the release of iron, aluminum, and calcium from soil. Amendment of sand with peat is a common practice at Florida golf courses. However, the addition of peat will alter the properties of the soils, which in turn could affect As transport and transformation. The results of this study are useful for

understanding the factors controlling As trapping and transport within porous soil media and in developing comprehensive plans for managing and remediating As contaminated environments, such as golf courses.

I. Introduction

Health problems associated with exposure to toxic As species have drawn attention worldwide (1) and the use of arsenical pesticides may contribute to the arsenic burden of the environment thereby increasing the likelihood of human exposures. It was found that about 96% of Florida golf courses use herbicides containing the active ingredient monosodium methylarsenate (MSMA) 2–3 times every year at an application rate of ~0.224 g/m² (2). Due to the local shallow groundwater, significant migration of MSMA and arsenate out of the vadose zone and into the water table has been found after MSMA application (3). A laboratory study on As mobility in the soils collected from some golf courses (4) demonstrated that As present in these soils was relatively mobile, suggesting potential for As leaching. Recently, a field study was conducted to evaluate the influence of substrate composition on As retention and species conversion after application of MSMA (5). The results indicated that substrate composition significantly influenced As mobility and As species transformation in the percolate water. Arsenic species transformation occurred in soil, resulting in co-occurrence of four As species, arsenite (As^{III}), arsenate (As^V), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) in percolate water.

It is widely accepted that a large portion of toxic chemicals is associated with inorganic or organic colloids in aquatic systems (6, 7). Studies of these associations based on molecular size distribution in soil and sediment pore waters have attracted much attention in recent years since these associations were found to be an important factor controlling the fate and bioavailability of these toxic chemicals (8). However, very little work has been done on the association of As with colloids and DOM and the facilitated transport of As in soil. Arsenic distributes between the two phases in the soil–water system, liquid soil solution, and solid soil substrate. In the liquid solution, As species may exist in “free” form and/or in association with the DOM or colloids derived from the soil. With regard to the As in golf courses, it is expected that the interactions between As and the colloidal materials would play an important role in As fate and transport in the soils based on the fact that the soils used in the golf courses are usually composed of sand and are often amended with organic matter (peat) to improve nutrient and water retention. The large amount of colloidal materials derived from frequent watering could move rapidly through the soil components. The potential As movement accompanying the colloids could have potential negative impacts on the surrounding environment.

The technique based on the separation of the smaller “free” molecules from the larger complexes by means of a dialysis membrane has been used successfully in several studies of the binding of metals to DOM in natural systems (9, 10). Very few studies, however, have dealt with the metalloid As (11). The purpose of this study was to investigate As distribution in soil solutions and association with dissolved substances derived from several well-characterized soils used in Florida golf courses. Since large amounts of inorganic arsenate have been observed in percolate water a few weeks after MSMA application in a prior field study (5), we decided

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to emphasize inorganic arsenate (As^{V}) in this study. Efforts were made to assess the size distribution of associated As and to evaluate the effects of naturally occurring heterogeneous inorganic Fe-, Al-, and Ca-containing colloids and DOM on As transport and transformation in the soil–water systems. Arsenic speciation in soil solutions was determined by two different operative procedures: an ion-exchange based procedure carried out using high-performance liquid chromatography–hydride generation–atomic fluorescence spectrometry (HPLC–HG–AFS) and a molecular weight based procedure carried out using equilibrium dialysis with membranes characterized by different molecular weight cutoffs (MWCO).

II. Materials and Methods

Chemicals and Materials. Individual As^{III} and As^{V} stock solutions (1000 mg/L) were prepared by dissolving appropriate amounts of sodium metaarsenite (98%, Aldrich) and sodium hydrogen arsenate heptahydrate (98%, Aldrich) in distilled deionized (DDI) water. Standard solutions used for other metal analyses were ICP-MS grade standards (1000 mg/L in 5% HNO_3) (GFS Chemicals, Inc.). To prevent metal contamination, all glassware was acid-cleaned prior to experimentation. All other chemicals used in the experiments were analytical or trace metal grade.

Instrumentation. Soil extractions were conducted using an Orbital Shaker (model DS-500, VWR International, West Chester, PA). Total elemental analysis was performed using an inductively coupled plasma mass spectrometer (ICP-MS) (Hewlett Packed, model HP4500 PLUS, Wilmington, DE). Arsenic speciation was conducted using HPLC–HG–AFS. Separation of the individual As species was performed using a SpectraSYSTEM P4000 (Thermo Separation Products, San Jose, CA). This HPLC system was coupled to a PS Analytical Millenium System with fluorescence detector (PS Analytical, UK). The mobile phase (1.5 mM phosphate, pH 5.8) was pumped isocratically at 1 mL/min through a Hamilton PRP-X100 polymeric guard and analytical anion exchange columns (Hamilton Company, NV). Al and Fe analysis was conducted using an atomic absorption spectrometer (Model AAnalyst 600, PerkinElmer Instruments, Shelton, CT). Total organic carbon (TOC) was measured by acidifying to pH < 2 with 3 N HCl, purging the sample with CO_2 -free air, and analyzing for total carbon using a hot platinum catalyst direct injection analyzer (Shimadzu TOC 5000).

Soil Selection and Preparation of Soil Extracts. Five different soil components were used for the experiments, including uncoated sand (plain sand; UC); naturally coated sand (naturally coated with hydroxy-interlayered vermiculite and kaolinite; NC); Canadian Sphagnum peat moss (P); uncoated sand plus Canadian Sphagnum peat moss at 10% (V/V; UCP); and naturally coated sand plus Canadian Sphagnum peat moss at 10% (V/V; NCP). The uncoated sands and naturally coated sands are the normal substrates for golf course putting greens. The uncoated sand used was common quartz sand, light gray or colorless, and did not have clay-sized coatings. Naturally coated sand, collected from Lake County, Florida, had a reddish-brown hue due to oxidized Fe and Al in the clay-sized fraction of the coating. It consisted of quartz and clay fractions including hydroxy-interlayered vermiculite ($(\text{Mg}, \text{Fe}^{2+}, \text{Al})_3(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), goethite ($\text{FeO}(\text{OH})$), and gibbsite ($\text{Al}(\text{OH})_3$). The cation exchange capacities of uncoated sands, naturally coated sands, and Canadian Sphagnum peat moss were 0.1, 4–5, and 110–130 cmol/kg, respectively (12).

Soil extracts were prepared by adding 100 mL of DDI water to 20 g of soil. The resulting suspension was shaken on the orbital shaker at 300 rpm for 24 h. The samples were then centrifuged at 2800g for 10 min. The supernatant was filtered through a 0.45 μm Millipore membrane. Prior to the

dialysis experiments, As was analyzed in the five soil extracts and was found to be below the detection limits of both methods: ICP-MS (0.02 $\mu\text{g/L}$ for total As) and HPLC–HG–AFS (2 and 1 $\mu\text{g/L}$ for As^{V} and As^{III} , respectively). The soil extracts were immediately used for dialysis experiments.

Equilibrium Dialysis Experiments. Before experimentation, the dialysis membrane bags (Spectra/Por CE, Fisher Scientific) with molecular weight cutoff (MWCO) of 500 or 3500 Da were soaked in DDI water for 30 min, and then rinsed thoroughly with DDI water. This procedure removed the sodium azide that was used as membrane preservative. Pyrex glass beakers (600 mL) were used as dialysis containers. The containers were filled with 400 mL of 50 $\mu\text{g/L}$ As^{V} solution referred to hereafter as outside solution. In this outside solution a dialysis bag filled with 15 mL of soil extract (or with conductivity-adjusted water alone for control experiments) referred to hereafter as the inside solution, was immersed. Solid KCl was added to the outside solutions until the ionic strength as measured by a conductivity meter (model 441, Corning Inc., NY) matched that of the inside solution. The volume ratios of the outside/inside solutions was set to 26:1 (9). Then the beakers were sealed with Parafilm to avoid water evaporation during the course of the experiments and the outside solutions were continuously stirred at room temperature (20 °C) using magnetic stirring bars. All experiments were conducted in duplicate. Free As ions could penetrate the dialysis membranes and become associated with the dissolved substances present in the soil extract, and some of the associated As species would stay inside the dialysis bag depending on the membrane pore sizes. Free As and those bound As forms less than the MWCO would reach equilibrium after a certain period of time. Arsenic recovery for all dialysis experiments was between 85 and 105%.

There were several reasons why As^{V} was spiked in the outside instead of the inside soil extract solution. Arsenic concentration inside the dialysis bag is expected to increase after equilibrium dialysis and the increase in As concentration is caused solely by the association of As with the dissolved materials (e.g., DOM and/or colloids). This arrangement eliminates potential problems for data interpretation, that is, higher As concentrations inside the dialysis bag may be caused by insufficient dialysis time if As^{V} is originally spiked in inside the dialysis bag. In addition, dramatic changes in As concentration in the outside solution would not occur after dialysis equilibrium due to the large volume ratio (outside to inside solutions) (26:1) selected. This would reduce the possibility of disturbing the As association equilibrium inside the dialysis bag. If As is spiked inside the dialysis bag, however, the sharp decrease in free As concentration, because of the distribution to outside solution could substantially influence the As association equilibrium inside the dialysis bag, making data interpretation difficult.

Experiments were first conducted to determine the time needed for the dialysis to reach equilibrium. To do this, dialysis bags were filled with 15 mL of DDI water and then submerged in 400 mL of a solution containing 50 $\mu\text{g/L}$ As solution. A small amount (0.2 mL) of solution was sampled at different time intervals from both inside and outside solutions and transferred into a 2 mL glass HPLC injection vial with an insert. The dialysis bags and the beakers were then resealed. The results indicated that the dialysis equilibria were reached at 7 and 14 days for the 3500 and 500 Da membranes, respectively, and therefore these times were selected as equilibration periods for all dialysis experiments.

To investigate the role played by microbe-involved processes in As species transformation and distribution, further dialysis experiments using one soil type (type NCP) was conducted with the addition of sodium azide (NaN_3). NaN_3 (0.02%) was used to inhibit microbe growth (13).

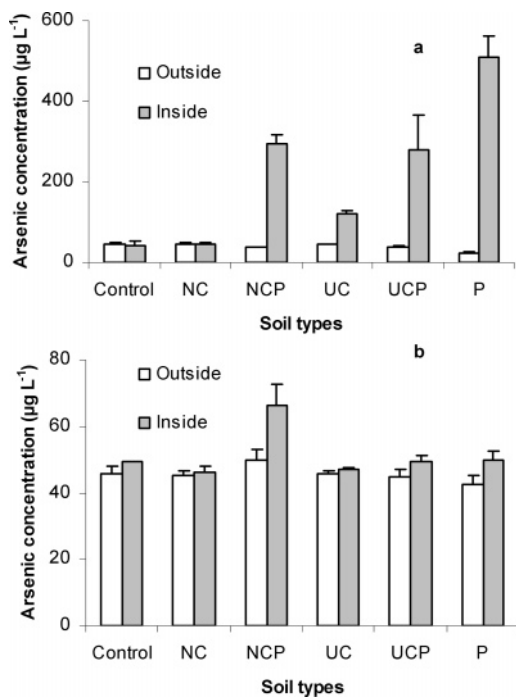


FIGURE 1. Arsenic concentrations inside and outside 500 Da (a) and 3500 Da (b) dialysis membranes analyzed by ICP-MS after reaching dialysis equilibrium for different soil extracts. The dialysis experiments for each soil type were conducted in duplicate. Soil types: UC, uncoated sand (plain sand); NC, naturally coated sand; P, Canadian Sphagnum peat moss; UCP, uncoated sand plus peat (9:1 v/v); NCP, naturally coated sand plus peat (9:1 v/v).

III. Results and Discussion

Arsenic Distribution. Results from the control experiment (without soil extract inside the bags) indicated that As could freely pass both 500 and 3500 Da membranes and reach equilibrium after the selected dialysis time (Figure 1a and b). When soil extracts were added inside the dialysis bags, significant differences in As concentrations inside and outside the 500 Da membrane were observed for most of the soil extracts (Figure 1a). Arsenic tended to concentrate inside the 500 Da bag whenever peat was present in the soils (NCP, UCP, and P), with the highest corresponding to the extract of pure peat. For soils without the presence of peat, different As partitioning patterns were observed, with a small amount of As concentrated inside the bag for the uncoated sand (UC) and no difference in As concentrations for the naturally coated sand (NC). When the 3500 Da membrane was used, slight differences in As concentrations inside and outside the bag were observed for soils with the presence of peat (NCP, UCP, and P), whereas no differences were found for uncoated and naturally coated sands (UC and NC) (Figure 1b).

These results indicate that (1) the presence of peat in the soils plays a significant role in the distribution of As in the dissolved phase of soil solutions; (2) the majority of As present in the extract of soils with peat was associated with substances between 500 and 3500 Da in size and with only a small fraction of As being associated with higher MW substances (MW > 3,500 Da); and (3) the dissolved substances derived from the naturally coated sand and uncoated sand did not show strong binding capability with As although As was associated to some extent with substances from 500 to 3500 Da in size in the extract from uncoated sand. Based on the differences in As concentrations between inside and outside the 500 Da membrane, about 95, 88, and 87% of As inside the dialysis bag were found to be associated with substances with MW > 500 Da in the extracts of P, NCP, and UCP, respectively. For soils without peat (UC and NC), about 63 and 4% were

associated with substances with MW > 500 Da. Only 15, 25, 10, 2, and 1% of the As inside the 3500 Da membrane was associated with substances with MW > 3500 Da for P, NCP, UCP, UC, and NC soils, respectively.

Fe, Al, and Ca Distribution. The majority of these elements were retained inside the dialysis bags for most soil extracts regardless of the dialysis membranes used (Figure 2). The dialysis results indicated that most of Al, Fe, and Ca in the soil extracts existed in the fraction larger than 3500 Da. By comparing the results of As (Figure 1) and those of Fe, Al, and Ca (Figure 2), it is clear that the distribution of As inside and outside of the dialysis bags did not correlate with that of Fe, Al, and Ca. It appears that Fe, Al, and Ca were mainly present in the soil extracts with MW > 3500 Da and As was not primarily associated with these metals in this fraction. Furthermore, comparing the results of Fe, Al, and Ca in soil extracts for the same soil type with or without the presence of peat (NC vs NCP or UC vs UCP), the presence of peat greatly enhanced the release of Fe, Al, and Ca from soils. Inorganic colloids could be stabilized by charge reversal through sorption of humic substances (14). Similarly, sediment grain dissolution and mobilization of clay colloids by sorption of humic substances is observed (15). Dissolved substances from peat could act as reactants or ligands to promote the dissolution of Fe, Al, and Ca minerals from soils either by competing for soil surface adsorption sites of Fe, Al, and Ca or by forming complexes with Fe, Al, and Ca originally existing on soil surface (16).

These results again indicate that the dissolved substances derived from peat play an important role in As partitioning in the water/soil systems. On one hand, the reactive functional groups of the dissolved materials could readily scavenge the adsorption/binding sites generated on the Fe-, Al-, and Ca-containing colloids (17), making the adsorption/binding sites not available for As. On the other hand, the dissolved materials released from peat could interact with As directly, providing less “free” As available for the adsorption by Fe, Al, and Ca-containing colloids/surfaces.

DOM Distribution. DOM concentrations (represented by TOC) inside the dialysis membranes were much higher than those outside for both the 500 and 3500 Da membranes for soils containing peat (Figure 3). As expected, the DOM concentration inside the 500 Da membranes was higher than that in the 3500 Da membranes. From the results of As (Figure 1) and DOM (Figure 3), it appeared that As tended to associate with small molecular weight (MW 500–3500 Da) DOM. During the dialysis process, most of the small As-containing complexes could be retained inside the 500 Da membrane, while only a small fraction of complexes could pass through.

In general, DOM readily forms aqueous complexes with cationic metals and metal oxides (18, 19). Aqueous DOM–metal complexes may, in turn, associate strongly with other dissolved anions, presumably by metal-bridging mechanisms. A ternary complexation mechanism, in which cationic metals mediated the strong association between DOM functional groups and As oxyacids was proposed as a plausible mechanism to explain aqueous complexing of DOM with As oxyanions (11, 20), although no solid proof has confirmed this hypothesis. From the present study, it seems that most anionic arsenate associated with DOM with molecular weight less than 3500 Da. The complexing ability of different fractions of DOM also varied considerably for different metal elements (21, 22). Kalbitz and Wennrich (23) found DOM correlated very well with As in the aqueous extracts of the soils they studied.

Since As was mainly present in the fraction from MW 500 to 3500 Da, the capability of As association with the dissolved substances derived from different soils was estimated by apparent distribution coefficients (K_d) between the truly dissolved and the associated phases, operationally defined

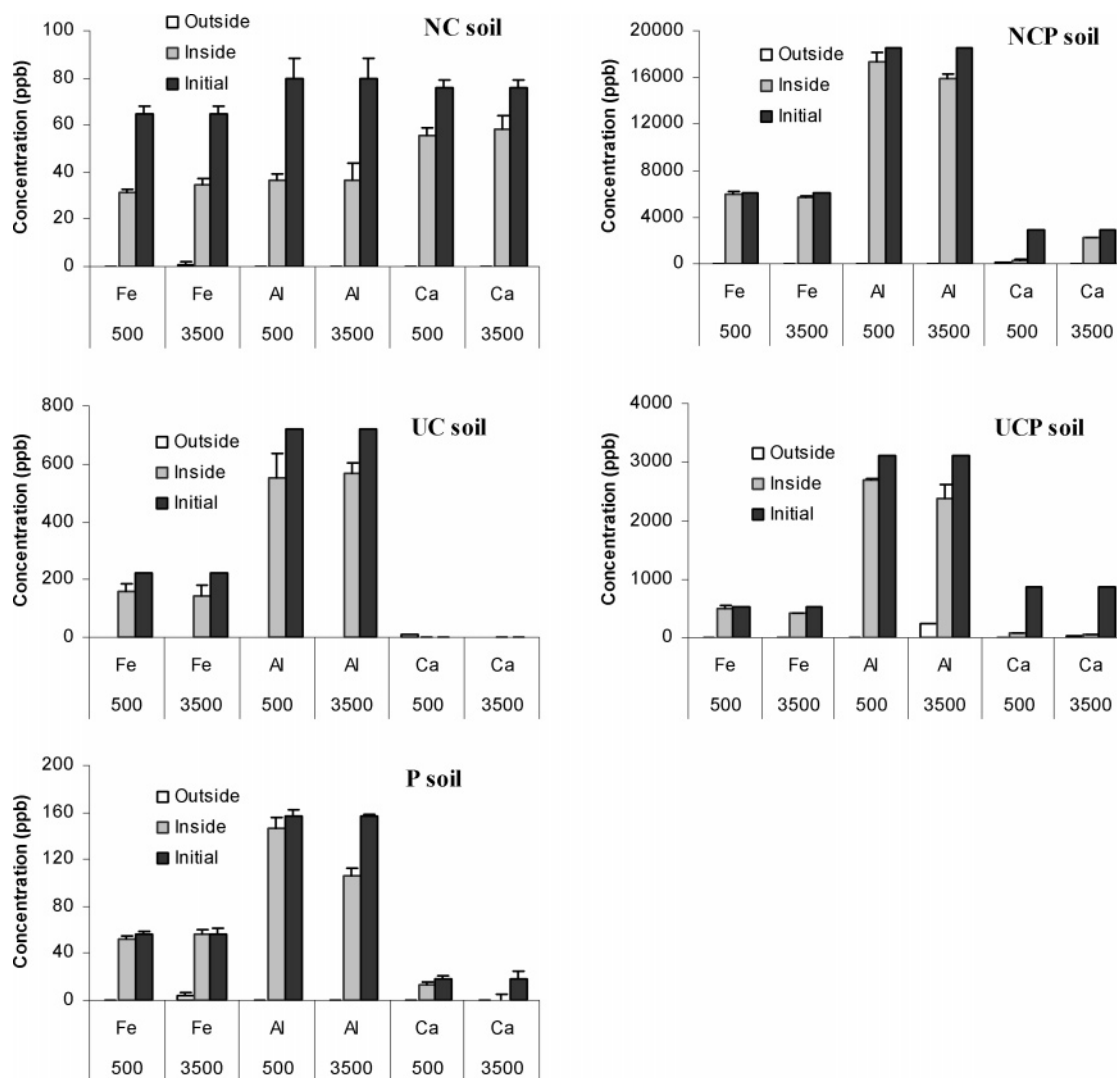


FIGURE 2. Concentrations of Fe, Al, and Ca inside and outside 500 and 3500 Da membranes after reaching dialysis equilibrium for different soil extracts. Soil types: UC, uncoated sand (plain sand); NC, naturally coated sand; P, Canadian Sphagnum peat moss; UCP, uncoated sand plus peat (9:1 v/v); NCP, naturally coated sand plus peat (9:1 v/v).

here as $MW < 500$ Da and between 500 and 3500 Da, respectively. These apparent K_d values were calculated on the basis of DOM concentrations in the solutions of inside 500 and 3500 Da bags after reaching dialysis equilibrium (Table 1). Distribution coefficients (K_d) that describe the distribution of chemicals between dissolved and associated phases are defined as (24)

$$K_d = C_s / C_i \text{ [L/kg]} \quad (1)$$

where C_s is As concentration in the associated phase ($\mu\text{g/kg}$) and C_i is As concentration in the dissolved phase ($\mu\text{g/L}$). K_d values for the two soils without the addition of peat (NC and UC) could not be calculated because no significant differences in As concentration for NC (Figure 1) and in DOM concentration for UC (Figure 3) were observed between inside and outside solutions for both 500 and 3500 Da membranes. Log K_d values for NCP, UCP, and P were found to be 7.66, 7.12, and 6.18, respectively. It should be noted that although DOM (500–3500 Da) likely dominated in the As partitioning in the soil solutions, other factors including pH and the contents of Fe and Al may also play a role. Nevertheless, the apparent K_d values calculated using this method could roughly estimate the strength of interactions between As and DOM. Due to the lack of data on DOM effects on the As partitioning in soil

solutions, direct comparisons of our results to others are impossible. Some K_d values can be obtained from literature where As adsorption studies were conducted using varied soils and synthetic mineral materials (Table 2) (25–30). In a study on As extraction using dispersed ultrafine magnetite (Fe_3O_4) from aqueous solution, the log K_d value of As was observed to be around 4 (29). Most of the log K_d values for soil samples listed in Table 2 are less than 4. The K_d values calculated based on low MW DOM derived from peat were 2–3 orders higher than those obtained using soils or other solid materials, indicating strong association between these DOM and As.

DOM/As Interaction and As Speciation. Arsenic species transformation was found during the course of the equilibrium dialysis. Figure 4 is regenerated from Figure 1 by including As speciation data. Only As^{V} and As^{III} were detected and both were present in all dialysis solutions after equilibrium. For the 500 Da membrane dialysis (Figure 4a), the major As species outside the membranes was As^{III} for all soils and the control. As^{III} also predominated in the inside solutions of soil NC and the control. It should be noticed that As remained in As^{V} form inside the membrane for soils with the presence of peat. As^{V} was also dominant in the inside solution of soil UC. For the 3500 Da membrane experiments (Figure 4b), similar As speciation patterns were observed

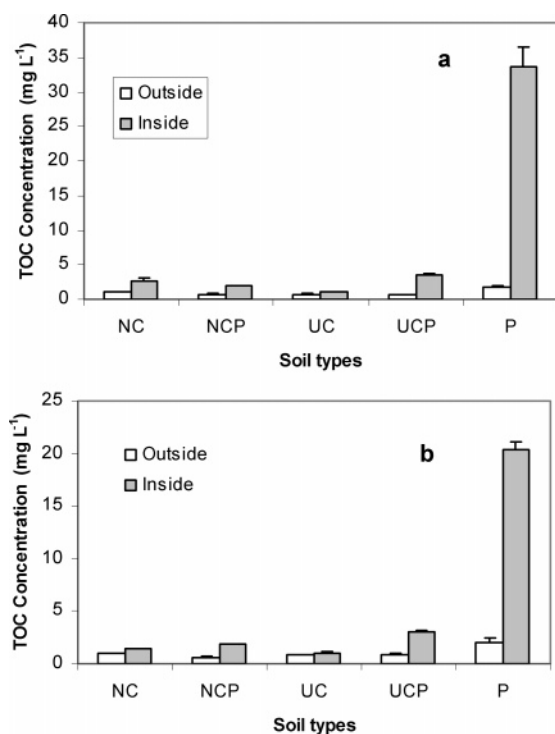


FIGURE 3. DOM concentrations inside and outside 500 Da (a) and 3500 Da (b) dialysis bags after reaching equilibrium. Soil types: UC, uncoated sand (plain sand); NC, naturally coated sand; P, Canadian Sphagnum peat moss; UCP, uncoated sand plus peat (9:1 v/v); NCP, naturally coated sand plus peat (9:1 v/v).

TABLE 1. Estimated Arsenic Fraction Associated with DOM and the Apparent Distribution Coefficients (K_d) of Arsenic between Dissolved (<500 Da) and DOM Associated (500–3500 Da) in Different Soil Extracts after Equilibrium Dialysis

soil extracts	As in dissolved phase (<500 Da), C_i ($\mu\text{g/L}$)	As in associated phase (<500 –3500 Da) ($\mu\text{g/L}$)	DOM between 500 and 3500 Da ($\times 10^{-9}$) (kg)	C_s ($\times 10^9$) ($\mu\text{g/kg}$) ^a	Log K_d (L/kg)
NC	45.0	1.9	18.6	0.03	
NCP	36.2	258	2.33	3.87	7.66
UC	44.0	76.0	0.09	1.14	
UCP	37.7	243	7.28	3.65	7.12
P	24.0	485	199	7.28	6.18

^a The concentration of the "associated As", C_s , in $\mu\text{g/kg}$ was calculated using the amount of arsenic associated with DOM (which was calculated by column 3 times 15 mL) divided by the weight of DOM between 500 and 3500 Da (column 4).

TABLE 2. Some Apparent Distribution Coefficients (K_d) of Arsenate on Different Soil Materials

soil	Log K_d	ref
Olivier loam	~2.1	25
Sharkey clay	~2.3	
Windsor Sand	~2.3	
10 surface soils	0.1–1.8	26
16 Chinese soils	2.2–3.5	27
30 uncontaminated soils	1.1–3.6	28
magnetite crystal	~4.0	29

with As^{V} being the major form both inside and outside the membrane with the presence of peat, while As^{III} predominated for the trials without the presence of peat.

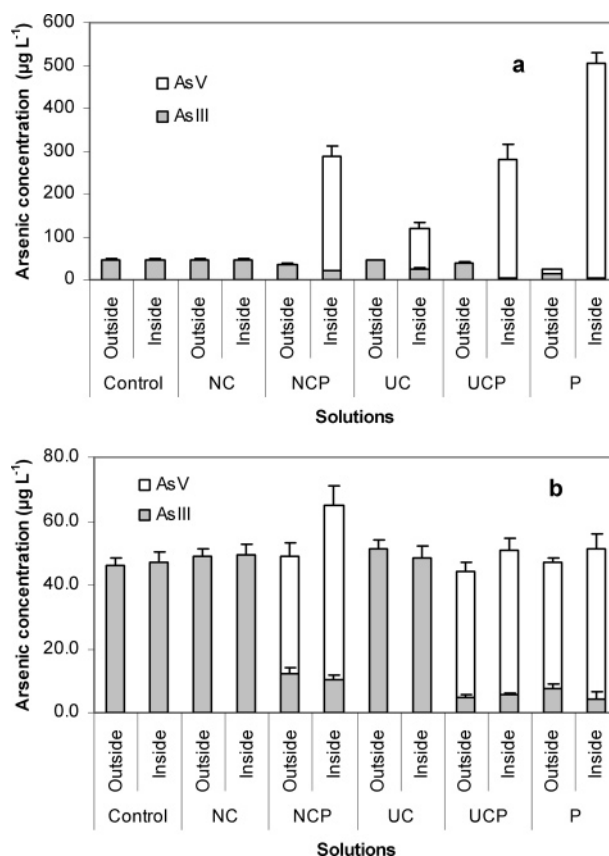


FIGURE 4. Arsenic concentrations with speciation information inside and outside 500 Da (a) and 3500 Da (b) dialysis membranes analyzed by HPLC–HG–AFS after reaching dialysis equilibrium for different soil extracts. Soil types: UC, uncoated sand (plain sand); NC, naturally coated sand; P, Canadian Sphagnum peat moss; UCP, uncoated sand plus peat (9:1 v/v); NCP, naturally coated sand plus peat (9:1 v/v).

Initially, only As^{V} was spiked in the outside solutions. It appears that As tends to remain in As^{V} form when strong interactions between As and the dissolved substances exist. In other words, absence of such interaction promoted transformation of As^{V} to As^{III} . The pH values of the soil extracts ranged from 4.01 to 4.81. The oxidation–reduction potentials (Eh) of the dialysis system using 500 Da membrane were from 519 to 562 and from 338 to 369 mv before and after membrane dialysis, respectively. For the 3500 Da membrane, these values ranged from 519 to 561 and from 309 to 360 mv, respectively. Decreases in Eh values were observed under each experimental condition. According to the pH–Eh diagrams (31), it is unlikely that the reduction of As^{V} to As^{III} was caused by the decrease in Eh during the course of the dialysis. The observed As transformation was possibly mediated by microbial involvement (32). Since our dialysis experiments were not conducted under sterile conditions, microbes could be introduced from reagents, containers, and air to the dialysis system. Particularly the relatively long dialysis time would promote microbial growth at the low As concentration used in this study (33). In order for As to be accessible by microorganisms, As should be present in bioavailable forms in the solutions. Arsenic could undergo two processes in the solutions during the dialysis experiment: association/interaction with the dissolved substances and microbe involved As species transformation. Once arsenate was associated with the dissolved substances (most likely DOM with MW < 3500 Da), it became unavailable or less available for the microbes (34). The strong correlation between As distribution (Figure 1) and As speciation in our study (Figure 4) confirmed the association of As with DOM

with MW from 500 to 3500 Da and suggested that such association strongly affected microbial availability of As. These results were in good agreement with those obtained in a previous field study on golf courses where higher As^{III} concentration was found in the percolate water of NC and UC sands compared with that of peat amended sands (UCP and NCP) (5). The results from the dialysis experiments using NCP soil conducted with the addition of sodium azide (NaN₃) to inhibit microbe growth supported this conclusion. With addition of 0.02% NaN₃ to the outside solution only As^V was detected in both inside and outside solutions after dialysis equilibrium (data not shown). Soils with high Al and Fe oxides content could strongly adsorb arsenate. However, such strong adsorption could be altered by the addition of peat in the soils. The substances derived from peat either covered Al and Fe oxides adsorption sites or became associated with As, which competed with the adsorption of Fe and Al oxides. Both competition with the adsorption site and binding/association by peat-derived DOM will affect As mobility and transformation in the soil-groundwater systems.

Environmental Implications. Understanding the factors affecting As trapping and transport within porous soil media is an important step toward developing comprehensive plans for managing or remediating As contaminated environments. Low soil organic matter content and limited soil water holding capacity are the major natural constraints of dry land cropping on sandy soils. The peat-amended soils are higher in water content, soil organic matter, and total porosity. The treatment consisting of Sphagnum peat moss is considered one of most common soil amendments (35) and this could pose potential environmental problems associated with As contaminated soils. DOM derived from peat could promote the release of Fe and Al oxides and Ca, which in turn would alter the adsorption of As on the oxide surfaces and hence affect the fate and transport of As even though As may not be associated with the released Fe, Al, and Ca-containing colloids. The DOM of certain MW would bind/associate with As present in the soil solutions. Arsenic association with soil-derived substances has two effects on As mobility. On one hand, association could cause facilitated As transport in soils and sediments. On the other hand, such association could change As bioavailability and hence affect microbe-involved As species transformation in real environments. Inorganic arsenite is more toxic than arsenate and more mobile in soil and sediment environments because of its neutral and uncharged molecular state (H₃AsO₃⁰) in common soil/sediment pH ranges (e.g., pH 5–8). Overall changes in As mobility due to binding/association depend on the competition of the two effects. Laboratory batch and column experiments are currently underway to evaluate the effects of major factors controlling As transport and transformation in the soil/water system such as those that occur at golf courses.

Acknowledgments

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Supporting Information Available

Supplemental table and figure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Tchounwou, P. B.; Centeno, J. A.; Patlolla, A. K. Arsenic toxicity, mutagenesis, and carcinogenesis – a health risk assessment and management approach. *Mol. Cell. Biochem.* **2004**, *255*, 47–55.
- (2) Chen, M.; Ma, L. Q.; Daroub, S. H.; Snyder, G. H.; Cisar, J. L.; Cai, Y. Use and fate of arsenic herbicide in Florida golf courses. In *2003 ASA-CSSA-SSSA Annual Meetings, Abstracts*; CD-ROM, S-11-chen952427-Oral.pdf; Denver, CO, 2003.
- (3) Di Carlo, G. W.; Fuentes, H. R. Potential transport of the herbicides MSMA and arsenate(+5) from golf courses to groundwater in southeastern Florida. In *WEFTEC 2000, Annual Conference & Exposition on Water Quality and Wastewater Treatment*, 73rd, Anaheim, CA, Oct. 14–18, 2000; pp 2938–2965.
- (4) Cai, Y.; Cabrera, J. C.; Georgiadis, M.; Jayachandran, K. Assessment of arsenic mobility in the soils of some golf courses in South Florida. *Sci. Total Environ.* **2002**, *291*, 123–134.
- (5) Feng, M.; Schrlau, J. E.; Snyder, R.; Snyder, G. H.; Chen, M.; Cisar, J. L.; Cai, Y. Arsenic Transport and Transformation Associated with MSMA Application on a Golf Course Green. *J. Agric. Food Chem.* **2005**, *53*, 3556–3562.
- (6) Jackson, B. P.; Ranville, J. F.; Bertsch, P. M.; Sowder, A. G. Characterization of Colloidal and Humic-Bound Ni and U in the “Dissolved” Fraction of Contaminated Sediment Extracts. *Environ. Sci. Technol.* **2005**, *39*, 2478–2485.
- (7) Shafer, M. M.; Hoffmann, S. R.; Overdier, J. T.; Armstrong, D. E. Physical and Kinetic Speciation of Copper and Zinc in Three Geochemically Contrasting Marine Estuaries. *Environ. Sci. Technol.* **2004**, *38*, 3810–3819.
- (8) de Jonge, L. W.; Kjaergaard, C.; Moldrup, P. Colloids and colloid-facilitated transport of contaminants in soils: an introduction. *Vadose Zone J.* **2004**, *3*, 321–325.
- (9) Truitt, R. E.; Weber, J. H. Determination of complexing capacity of fulvic acid for copper(II) and cadmium(II) by dialysis titration. *Anal. Chem.* **1981**, *53*, 337–342.
- (10) Jansen, B.; Mulder, J.; Verstraten, J. M. Organic complexation of Al and Fe in acidic soil solutions. Comparison of diffusive gradients in thin films analyses with Models V and VI predictions. *Anal. Chim. Acta* **2003**, *498*, 105–117.
- (11) Lin, H.-T.; Wang, M. C.; Li, G.-C. Complexation of arsenate with humic substance in water extract of compost. *Chemosphere* **2004**, *56*, 1105–1112.
- (12) Snyder, R. H. Investigation of coated sands and peat for use in golf course putting green construction. Ph.D. Dissertation, University of Florida, Gainesville, FL 2003; p 208.
- (13) Carter, C. W.; Suffet, I. H. Binding of DDT to dissolved humic materials. *Environ. Sci. Technol.* **1982**, *16*, 735–740.
- (14) Kretzschmar, R.; Sticher, H. Transport of Humic-Coated Iron Oxide Colloids in a Sandy Soil: Influence of Ca²⁺ and Trace Metals. *Environ. Sci. Technol.* **1997**, *31*, 3497–3504.
- (15) Swartz, C. H.; Gschwend, P. M. Mechanisms Controlling Release of Colloids to Groundwater in a Southeastern Coastal Plain Aquifer Sand. *Environ. Sci. Technol.* **1998**, *32*, 1779–1785.
- (16) Kaurichev, I. S.; Bazilinskaya, M. V.; Zabolotnova, L. A. Effect of water-soluble organic substances on the availability of iron, aluminum, and silicon of some minerals and rock. *Izv. Timiryazevsk. Skh. Akad.* **1974**, *105*–113.
- (17) Cano-Aguilera, I.; Haque, N.; Morrison, G. M.; Aguilera-Alvarado, A. F.; Gutierrez, M.; Gardea-Torresdey, J. L.; de la Rosa, G. Use of hydride generation-atomic absorption spectrometry to determine the effects of hard ions, iron salts and humic substances on arsenic sorption to sorghum biomass. *Microchem. J.* **2005**, *81*, 57–60.
- (18) Gu, B.; Schmitt, J.; Chen, Z.; Liang, L.; McCarthy, J. F. Adsorption and desorption of different organic matter fractions on iron oxide. *Geochim. Cosmochim. Acta* **1995**, *59*, 219–229.
- (19) Murphy, R. J.; Lenhart, J. J.; Honeyman, B. D. The sorption of thorium(IV) and uranium(VI) to hematite in the presence of natural organic matter. *Colloids Surf., A* **1999**, *157*, 47–62.
- (20) Redman, A. D.; Macalady, D. L.; Ahmann, D. Natural Organic Matter Affects Arsenic Speciation and Sorption onto Hematite. *Environ. Sci. Technol.* **2002**, *36*, 2889–2896.
- (21) Harmsen, J. Identification of organic compounds in leachate from a waste tip. *Water Res.* **1983**, *17*, 699–705.
- (22) Majone, M.; Petrangeli, M.; Papini, P.; Rolle, E. Influence of metal speciation in landfill leachates on kaolinite sorption. *Water Res.* **1998**, *32*, 882–890.
- (23) Kalbitz, K.; Wennrich, R. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Sci. Total Environ.* **1998**, *209*, 27–39.
- (24) Stumm, W. *Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems*; John Wiley & Sons: New York, 1992.

- (25) Zhang, H.; Selim, H. M. Kinetics of Arsenate Adsorption–Desorption in Soils. *Environ. Sci. Technol.* **2005**, *39*, 6101–6108.
- (26) Smith, E.; Naidu, R.; Alston, A. M. Chemistry of arsenic in soils: I. Sorption of arsenate and arsenite by four Australian soils. *J. Environ. Qual.* **1999**, *28*, 1719–1726.
- (27) Jiang, W.; Zhang, S.; Shan, X.-q.; Feng, M.; Zhu, Y.-G.; McLaren, R. G. Adsorption of arsenate on soils. Part I: Laboratory batch experiments using 16 Chinese soils with different physiochemical properties. *Environ. Pollut.* **2005**, *138*, 278–284.
- (28) De Brouwere, K.; Smolders, E.; Merckx, R. Soil properties affecting solid–liquid distribution of As(V) in soils. *Eur. J. Soil Sci.* **2004**, *55*, 165–173.
- (29) Wakui, Y.; Persulesy Anna, E.; Ikeda, T.; Ebina, T.; Onodera, Y.; Suzuki Toshishige, M. Separation and enrichment of arsenic(V) with composite resin beads containing magnetite crystals. *Anal. Sci.: Int. J. Japan Soc. Anal. Chem.* **2005**, *21*, 433–435.
- (30) Wakui, Y.; Ebina, T.; Matsunaga, H.; Suzuki, T. M. Solvent extraction of arsenic(V) with dispersed ultrafine magnetite particles. *Anal. Sci.* **2002**, *18*, 793–798.
- (31) Brookins, D. G. Geochemical behavior of antimony, arsenic, cadmium and thallium: Eh-pH diagrams for 25 DegC, 1-bar pressure. *Chem. Geol.* **1986**, *54*, 271–278.
- (32) Ahmann, D.; Roberts, A. L.; Krumholz, L. R.; Morel, F. M. Microbe grows by reducing arsenic. *Nature* **1994**, *371*, 750.
- (33) Smedley, P. L.; Kinniburgh, D. G. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **2002**, *17*, 517–568.
- (34) Slaveykova, V. I.; Wilkinson, K. J. Predicting the Bioavailability of Metals and Metal Complexes: Critical Review of the Biotic Ligand Model. *Environ. Chem.* **2005**, *2*, 9–24.
- (35) Bigelow, C. A. Sand-based rootzone physical, chemical, and microbial properties as influenced by inorganic soil amendments and sphagnum peat moss. Ph.D. Dissertation, North Carolina State University, 2000.

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