Published in final edited form as:

Sci Total Environ. 2008 November 15; 406(1-2): 180–189. doi:10.1016/j.scitotenv.2008.07.017.

Role of Soil-derived Dissolved Substances in Arsenic Transport and Transformation in Laboratory Experiments

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Abstract

Dissolved substances derived from soil may interact with both soil surfaces and with arsenic and subsequently influence arsenic mobility and species transformation. The purpose of this study was to investigate arsenic transport and transformation in porous media with a specific focus on the impact of soil-derived dissolved substances, mainly consisting of inorganic colloids and dissolved organic matter (DOM), on these processes. Arsenic transport and transformation through columns, which were packed with uncoated sand (UC) or naturally coated sand (NC) and fed with arsenate (As^{V}) or monomethylarsonic acid (MMA) spiked influents, were investigated in the presence or absence of soil-derived dissolved substances. The presence of soil-derived inorganic colloids and/or DOM clearly enhanced As transport through the column, with the fraction of As leached out of column (referring to the total amount added) being increased from 23 to 46% (UC) and 21 to 50% (NC) in As^{V} experiments while 46 to 64% (UC) and 28 to 63% (NC) in MMA experiments. The association of arsenic with DOM and the competitive adsorption between arsenic and DOM could account for, at least partly, the enhanced As movement. Distinct species transformation of As during transport through soil columns was observed. When As^{V} was the initial species spiked in the influent solutions, only arsenite (As^{III}) was detected in the effluents for UC columns; while both As^{III} (dominant) and As^{V} were present for NC columns, with As^{III} being the dominant species. When MMA was initially spiked in the influent solutions, all method detectable As species, As^{III} , As^{V} , MMA, and dimethylarsenic acid (DMA) were present in the effluents for both soil columns. These results indicate that risk assessment associated with As contamination, particularly due to previous organoarsenical pesticide applications, should take into account the role of soil-derived dissolved substances in promoting As transport and As species transformation.

Keywords

Arsenic; Soil-derived dissolved substances; Column experiment; Transport; Transformation

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1. Introduction

Transport and transformation of toxic chemicals in the environment is governed by many physical, chemical, and biological processes. Transport of chemicals through natural porous media (e.g., soils and aquifers) typically occurs through molecular species dissolved in the pore water (Lichtner et al., 1997). Understanding the transport and transformation mechanisms, which are inherent to speciation, nature of minerals and microbes, and characteristics of the dissolved substances present in an aquatic environment, is as essential as the identification of the pollutants. It is well established that Fe and Al oxides and hydroxides have a high affinity to arsenic (As). Many studies have demonstrated that As adsorption on soil is correlated with soil Al and Fe oxides contents (Sakata, 1987; Hartley et al., 2004; Zhang and Selim, 2005). However, studies on the adsorption and desorption of organoarsenicals, such as monomethylarsonic acid (MMA) on metal oxides are very limited (Wauchope and McDowell, 1984; Lafferty and Loeppert, 2005). Influence of natural organic matter (NOM) on As transport and transformation has also been recognized and drawn much attention recently (Redman et al., 2002; Buschmann et al., 2006; Chen et al., 2006). NOM such as humic and fulvic acids may interfere strongly with As adsorption and increase As mobility (Redman et al., 2002). A number of studies have demonstrated strong correlations between organic carbon content and As distribution, suggesting NOM plays an important role in controlling As transport (Kalbitz and Wennrich, 1998; Anawar et al., 2003; McArthur et al., 2004). Dissolved organic matter (DOM), defined herein as dissolved organic material that passes through a filter with a pore size of between ~0.1 and 1 μm , can serve as a means for complexation for trace metals, which can then facilitate metal transport in aqueous systems (Schmitt et al., 2003). DOM competing with the soil matrix for As binding can also facilitate As transport in aqueous systems (Bauer and Blodau, 2006). The effect of NOM on the fate and transport of As on farmland and golf courses is particularly important because soils in these settings are commonly amended with organic matter (Bigelow, 2000), with peat moss as the most common amendment utilized at golf courses. The high organic content of peat moss can affect the transport of As species, including MMA in soils.

Studies on transport and transformation of As are complicated by the fact that As is present in oxyanion forms and it readily undergoes transformation between species. Transformation of As has important implications because different As species have different sorption and toxicological characteristics. For example, arsenite (As^{III}) is often considered the more mobile and toxic species than arsenate (As^{V}) and thus more problematic regarding contamination of natural waters (Masscheleyn et al., 1991; Tamaki and Frankenberger, 1992). Microbial activity may cause oxidation of As^{III} to As^{V} or reduction of As^{V} to As^{III} (Mukhopadhyay et al., 2002; Jackson et al., 2003; Oremland et al., 2004; Oremland et al., 2005). These inorganic As forms can also be biomethylated by certain microbes to gaseous arsines or to MMA and dimethylarsenic acid (DMA), while other microbes can demethylate organic forms to inorganic species (Sohrin et al., 1997; Pongratz, 1998; Turpeinen et al., 2002).

Recently (USEPA, 2006) organoarsenical pesticides were denied for re-registration, removing the chemical from the U.S. market. Although MMA and DMA are no longer sold for commercial usage, many sites exist which have received organoarsenical applications for many years. Appropriate decision making concerning these sites will rely on knowledge with respect to the fate, transport, and transformation of organoarsenicals following application in the field. Given the lack of information available, this study focused on elucidating the transport and transformation of two As species, inorganic As^{V} and MMA in porous soil using column experiments. This study was proposed based on our previous field

studies (Feng et al., 2005) which suggest that after MMA application leaching and transformation of As species occurred in golf course fields. We set up laboratory column experiments to evaluate the role of soil-derived dissolved substances in As transport and species transformation because we have found that dissolved substances in soil extracts could bind a considerable fraction of As (Chen et al., 2006) and thus were expected to affect As transport. The selection of MMA and As^V was based on the fact that MMA was widely used as herbicide and inorganic As^V is the major degradation product of the MMA application (Feng et al., 2005).

2. Experimental Section

2.1. Chemicals and Materials

Inorganic As^{III} and As^V individual stock solutions (1000 mg/L) were prepared by dissolving appropriate amounts of sodium metaarsenite (Aldrich) and sodium hydrogen arsenate heptahydrate (Aldrich) in distilled deionized (DDI) water. MMA was obtained as a sodium salt (monosodium acid methane-arsonate sesquihydrate, CH₄AsNaO₃), and DMA was obtained in acid form (dimethylarsenic acid, C₂H₇AsO₂), both from Chem Service (West Chester, PA). Individual MMA and DMA stock solutions (1000 mg/L) were also prepared by dissolving appropriate amounts of solid powder in DDI water. All other chemicals used were analytical grade and were obtained from Fisher (Pittsburgh, PA).

Uncoated sand (plain sand, UC) and naturally coated sand (coated with hydroxy-interlayered vermiculate and Kaolinite, NC) were used as the column packing materials. Both UC and NC are the normal substrates for golf courses putting greens. UC was common quartz sand, light gray or colorless, and did not have clay-sized coatings. NC, 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 ((Mg,Fe⁺⁺,Al)₃(Al,Si)₄O₁₀(OH)₂·4(H₂O)), kaolinite (Al₂Si₂O₅(OH)₄), goethite (FeO(OH)) and gibbsite (Al(OH)₃). Selected soil characteristics were listed in Table 1 and additional characteristics information can be found elsewhere (Snyder, 2003).

In order to prepare soil extracts (SE) to feed the columns, Canadian sphagnum peat moss was mixed (1:9 v/v) with UC or NC to obtain UC plus peat (UCP) or NC plus peat (NCP) soil. Artificial rain water (ARW) and two soil extracts prepared from UCP and NCP were used as column influent solutions. Peat was added to prepare the soil extracts because previous studies showed that the presence of peat greatly enhanced the release of dissolved substances containing Al and Fe from UC and NC soils and dramatically altered the transport and transformation of As (Feng et al., 2005; Chen et al., 2006). The ARW solution was prepared with the following recipe: (NH₄)₂SO₄, 9.25 mg/l; NaCl, 3.86 mg/l; CaCO₃, 2 mg/l; MgSO₄, 1.8 mg/l; KCl, 0.37 mg/l; KH₂PO₄, 0.14 mg/l; NaNO₃, 0.4 mg/l; HNO₃, 0.07 mM; HCl, 0.01 mM (Velthorst, 1993). The soil extracts were prepared by placing UCP or NCP soil (20 g) in a 125 ml Nalgene HDPE bottle (Fisher Scientific) containing 100 ml of ARW. The mixture was subsequently agitated on a rotary platform shaker at 300 rpm for 24 h. Soil particulates were removed by centrifugation at 2800 g for 10 min. The supernatant was then separated and filtered with a Whatman GF/C glass microfiber filter (1.2 μm pore size). The freshly filtered soil extract or ARW was spiked with As species at predetermined concentrations. These solutions were stored in nitric acid washed glass bottles and used immediately as column influent solutions. New influent solutions were generated every fifth day during the column experiments. Selected characteristics of these two soil extracts were illustrated in Table 1. All soils used in this study contain no detectable ARW-extractable As.

2.2. Methods

Continuous-flow Column Experiments—Four sets of column experiments were conducted: 1) UC columns for testing As^V, 2) UC columns for MMA, 3) NC columns for As^V, and 4) NC columns for MMA. Each set of experiment included four columns, two as duplicate testing columns (defined as SE column, S) fed with soil extract and the other two as duplicate controls (defined as control column, C) fed with ARW. Soil extracts derived from UCP and NCP were served as UC and NC soil column influent solutions, respectively. The columns were made of polyvinyl chloride (PVC) pipe with a dimension of 5 cm (i.d.) × 31 cm (length). A glass wool plug was placed at the bottom of the column to prevent leaching of soil particles. All purpose cement (manufactured by OATEY, OH, USA) for PVC was used to coat a thin layer of plain sand onto column inside wall to minimize boundary flow. After adhering a thin layer of sand to the column, all columns were soaked in 10% nitric acid for three days, and then rinsed thoroughly with DDI water before use. Before being packed, soils were cleaned with flowing DDI water in order to remove loosely attached material that may detach during the experiment. The clean soils were oven dried at 60 °C and then packed (~ 800 g) into each column. Prior to delivering the As-spiked influent solution, columns were preconditioned by percolation with 100 pore volumes of ARW to homogenize the composition of ion exchange surfaces and stabilize ionic strength. The columns were then fed with As-spiked solutions through a peristaltic pump (IPC-12, Ismatec, Germany) with a constant flow rate of 90 ml/day. The spiked concentration of As^V or MMA in influent solutions were 100 (for UC column) or 200 µg/L as arsenic (for NC column). Our preliminary experiments indicated that NC soil possesses much higher As adsorption capability than UC, as evidenced by the difference in Langmuir adsorption maximum (27 versus 8.3 mg/kg for As^V). Therefore, influent solution for NC column was spiked with higher As concentration. During the course of experiment, a 5-cm layer of influent solution was maintained over the soil contained in the column. The column effluent was collected from bottom of the column in a polypropylene bottle and pooled for As speciation analysis each day. Bromide ion (Br⁻), applied in the influent solutions at a concentration of 0.6 mM, was used as a nonsorbing tracer to determine the hydraulic characteristics of the columns. The effluent Br⁻ concentration was determined by a Br⁻ selective electrode (Accumet, Fisher Scientific).

pH-Eh monitoring—Both pH and Eh were monitored during the course of the experiments by a pH/ORP controller (Model 3671, JENCO Instruments, INC. San Diego, USA). A MicroProbe glass body pH electrode (Accumet, Fisher Scientific) was placed on top of each column. The probe was inserted into the top layer of the influent solution and served as a pH sensor. The probe was modified in our laboratory so that the KCl-saturated Ag/AgCl reference electrode inside this probe was served as a reference electrode for the Eh monitoring. A customized noble metal electrode (99.95% platinum wire) was inserted into the bottom of each column. The pair of electrodes (platinum working electrode and Ag/AgCl reference electrode) was used for reduction-oxidation potential (Eh) measurements. The Eh was reported relative to the standard hydrogen electrode, meaning that the Eh value was calculated by adding the reference electrode potential to the potential measured by the pH/ORP controller (Patrick and Henderson, 1981; Vorenhout et al., 2004). Two pH/ORP controllers were used for each column, one for Eh monitoring and the other for pH. It should be noted that electrode measurements of Eh can not provide accurate and unique potentials indicative of particular redox couples for the environment investigated here (Stumm and Morgan, 1996). In fact, electrode measurements are unlikely to be stable and thermodynamically meaningful in most surface waters, due to lack of equilibration with certain redox couples, misbehavior of electrodes, and the common existence of mixed potential (Langmuir, 1997).

Arsenic speciation analysis—Arsenic speciation was analyzed on daily basis using a high performance liquid chromatography (HPLC, SpectraSYSTEM P4000 Thermo Separation Products) coupled with hydride generation atomic fluorescence spectroscopy (HG-AFS, Millenium System, PS Analytical, UK) (Chen et al., 2006). Mobile phase (1.5 mM phosphate, pH 5.8) was pumped isocratically at 1ml/min through a Hamilton PRP-X100 polymeric guard and analytical anion exchange columns (Hamilton Company, NV, USA).

Ancillary analysis—Al and Fe in soil extracts and effluent solutions were determined by atomic absorption spectrometer (AAS, Perkin Elmer AAnalyst 600). Soil Al, Fe, and As contents were measured by AAS following open vessel nitric acid digested. DOC was measured by acidifying to pH < 2 with 3N HCl, purging the sample with CO₂ - free air, and analyzing for total carbon using a hot platinum catalyst direct injection analyzer (Shimadzu TOC 5000). Soil total organic matter (TOC) was estimated by the loss of weight on ignition at 550 °C for 5 hours. Soil pH was measured using the method of CaCl₂ extraction by mixing 10 g soil and 20 ml 0.01M CaCl₂ solution (Al-Busaidi et al., 2005).

3. Results and Discussion

3.1. Total As elution

The mobility of As and tracer Br⁻ in the columns under different conditions was evaluated using the ratio of As or Br⁻ concentrations in the effluent vs. those in the influent. A ratio around 1 indicates that the retention/adsorption of As or Br⁻ on the column reached equilibrium. The elution of As and Br⁻ was monitored up to 25 and 16 pore volumes for UC and NC, respectively. The concentration of Br⁻ reached equilibrium shortly after influent application (about 2 pore volumes) for all column experiments (data not shown). Compared to Br⁻, As was more strongly retarded (Figure 1). Distinct differences in As elution were observed depending upon the composition of the influents. With As^V spiked in the influent solution, dissolved substance in soil extract facilitated As transport after 10 pore volumes elution for UC (Figure 1a); the same was true for NC after 8 pore volumes (Figure 1b). Less distinct differences in As concentrations were observed in the effluents from sample and control columns when MMA was spiked in the influent solutions for both UC (Figure 1c) and NC (Figure 1d). Nevertheless, the dissolved substances in the soil extract clearly enhanced transport of both As species. Some irregularity in As leaching pattern was observed at the beginning of the experiments for some columns (e.g. Figures 1a and 1d). Arsenic concentrations in the effluents were increased at the beginning and then decreased after several pore volumes. This could be caused by less well conditioned columns that resulted in preferential flow.

When calculating the fraction of total As leached from the column against total As added in the influent, it was observed again that the presence of soil-derived dissolved substances in influent solutions dramatically enhanced As leaching (Figure 2). Total As input for both As^V and MMA experiments for all columns during the entire experimental period was 480 µg as As. For columns packed with UC, about 46% of the total input inorganic As^V leached from the SE column at the end of experiment while only 23% leached from the control. Similar As leaching trend was observed for NC columns, with 50% of total inorganic As^V leached from the SE column and 21% leached from the control. For influents spiked with MMA, 64 and 46% of total input As leached from SE and control columns packed with UC, respectively, while 63 and 28 % leached from SE and control columns packed with NC. Comparing the leachability of different As species in the same soil columns (Figure 1a vs 1c or Figure 1b vs 1d), MMA showed relatively lower retentions than inorganic As^V regardless the composition of the influent composition.

3.2. Fe, Al and DOM elution

For UC soil experiments with inorganic As^V spiked in influent, a steady increase in Al concentration in the effluent was observed for SE column (Al: S_{AsV} line in Figure 3a) up to 15 pore volumes. Fe concentration was also increased at the beginning, but remained relatively constant after 3 pore volumes (Fe: S_{AsV} line in Figure 3a). The concentrations of Al after 15 pore volumes and Fe after 3 pore volumes in the effluent were similar to their concentrations in the influent (Table 1), suggesting equilibrium was likely reached. For NC columns, both Fe and Al were strongly adsorbed on SE columns, leaching starting from 6.5 pore volumes (Figure 3b). The concentrations of Fe and Al in the influent of NC column were 21.4 and 20.4 mg/L, respectively (Table 1). The elution results indicated that Fe present in the influent was adsorbed on the soil. Al, however, was rapidly released from soil with time exceeding its concentration in the influent (20.4 mg/L), suggesting further dissolution of Al from the soil in the column. By the end of the experiment, Fe was still far from equilibrium compared to the influent Fe concentration. Some irregular up and down in Fe and Al concentrations in the effluents was possibly attributed to the coagulation of Fe/Al-containing colloids during the transport process. If particles resulted from the coagulation of Fe and Al retained inside the columns, it would cause decrease in Fe/Al concentration in the effluent solution. An abrupt increase in Fe/Al concentration is expected if such particles were eluted from the columns due to hydrodynamic flow. When MMA was spiked in the influent, similar leaching curves were observed for both Fe and Al as that obtained with As^V spiked for both soils (Figure 3c and 3d), indicating As present in the influent did not influence the leaching of Fe or Al. Without the presence of dissolved soil substances in the influent solutions, very little Fe and Al were leached for UC or NC columns (all C_{AsV} and C_{MMA} lines in Figure 3).

DOM (measured as DOC) concentrations in the effluents were increased with time for both UC and NC columns with soil extracts as effluent (Figure 4). The DOC concentrations in the influents used for UC and NC SE columns were 6.4 and 3.0 mg/L, respectively (Table 1). It appears that DOC in the effluents almost reached equilibrium by the end of the experiments for UC while considerable DOC adsorption was observed for NC columns when As^V was spiked. Effluent DOC concentrations were higher when MMA was spiked in the influent compared with As^V spiked. As expected, DOC concentrations changed slightly with time for controls where ARW was used as influent (Figure 4).

3.3. Possible mechanisms of soil-derived dissolved substances affecting As transport

Arsenic transport may be facilitated by dissolved substances in different ways. First, As could bind to Fe/Al colloids and DOM and thus move through the column together with them, resulting in facilitated As transport. Second, the dissolved substances could reduce As adsorption by competing with As for adsorption sites on the soil surface, allowing enhanced leaching of As. Third, DOM in the influents could enhance the dissolution of Fe and Al oxides, which are considered as major components responsible for As adsorption (Fuller et al., 1993; Wilkie and Hering, 1996), from packed soils and thus enhance As transport.

The complexation of As with DOM and Fe/Al colloids present in the soil extracts should play an important role in enhancing As transport. Our previous study (Chen et al., 2006) using membrane equilibrium dialysis using the same soil extracts (UCP or NCP) indicated that the majority of As (As^V or MMA) was associated with soil-derived dissolved substances after 14-day's dialysis, rather than in "free" form (molecular weight, MW < 500 Da). Further dialysis indicated that most of As complexed by dissolved substances was found in the fraction with MW from 500 to 3500 Da. The dialysis results also suggested that the fraction of 500–3500 Da was mainly composed of low MW DOM while the vast majority of the colloidal Fe/Al was present in the fraction with MW larger than 3500 Da.

(Chen et al., 2006). Therefore, it was concluded that As was mainly associated with DOM in the UCP or NCP soil extracts where DOM and Fe/Al coexisted. We further estimated that the fraction of free (< 500 Da), Fe/Al colloid-bound (> 3500 Da), and DOM-bound (500–3500 Da) As^{V} would be 12%, 25%, and 63%, respectively, in the NCP soil extracts after 14-day's dialysis. For the UCP soil extracts, the fraction of free, Fe/Al colloid-bound, and DOM-bound As^{V} would be 13%, 10%, and 77%, respectively. The influent solutions used in this column study were not allowed to equilibrate for 14 days (we changed the influents every 5 days), but it is still reasonable to assume a considerable fraction of As was complexed by dissolved substances, in particular low MW DOM. These complexes between As and dissolved substances apparently prevent adsorption of As on solid phase when passing through the columns, resulting in facilitated As transport. In fact, low MW DOM has been recognized to be highly mobile and could influence metal transport in aquifer material (Han and Thompson Michael, 2003). A study on Fe-containing colloids/DOM associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia) has indeed found that As was not associated with colloidal Fe and presented in the form of “dissolved” species with MW less than 1000 Da (Pokrovsky and Schott, 2002). In several other studies about the geochemical controls on As in southeastern United States rivers (Waslenchuk, 1979), it was found that complexes could be formed between As and low MW DOM. Other studies found that As was strongly correlated with DOM concentration in soil percolates or groundwater (Kalbitz and Wennrich, 1998; Anawar et al., 2003).

The competitive adsorption between As and DOM could also contribute to the enhanced leaching of As from the columns. The lower DOM concentration observed in the effluent compared with that in the influent supported the occurrence of DOM adsorption on packed soils (Figure 4 and Table 1). DOM adsorption on the soil surface could scavenge soil adsorption sites for both ‘free’ and ‘associated’ As, causing less As to be adsorbed on the soil and thus more As leached out of the column.

As for DOM-induced dissolution of Fe/Al oxides, we did observe the dissolution of Al oxides for NC columns, but not for UC columns. The retaining of Fe in the influent, rather than dissolution of Fe oxide from the packed soil, was observed for both NC and UC (see 3.2. *Fe, Al and DOM elution* section). These results were contrary to the batch experiments we conducted to prepare soil extracts from UCP and NCP, where the ARW-extractable Fe and Al were substantially increased for both UC and NC with the addition of 10% (V/V) peat (Table 1). Such increase could not be accountable for by the release of Fe and Al from the 10% peat since the contents of both elements were relatively low in the peat. Instead, the sharp increase of Fe and Al in soil extracts from UCP and NCP must be, at least in part, ascribed to the colloids released from UC and NC soil matrices induced by the addition of peat. This DOM-enhanced dissolution of Fe and Al has also been observed in our previous study (Chen et al., 2006). Nevertheless, in the column experiments, dissolution of Al from NC might play a role in the facilitated As transport. However, we are conservative in emphasizing the importance of the DOM-enhanced dissolution of Fe and Al on the observed facilitated As transport under our experimental conditions.

The differences in As^{V} and MMA leachability are consistent with previous studies where inorganic As^{V} was more strongly retained than MMA in the same soil (Di Carlo, 1999; Lafferty and Loeppert, 2005). The differences in soil adsorption coefficients for As^{V} and MMA suggested that MMA was between 4 and 22 times more prone to leaching than As^{V} in low organic carbon soils (Di Carlo, 1999). The reduced adsorption affinity of organoarsenicals could cause increased levels of As to move into groundwater when these species are present.

3.4. Transformation of As species

Rapid transformation between As species was observed during column transport (Figures 5 and 6). With As^V spiked in the influent, only As^{III} was detected in the effluent of UC columns with much higher concentration in SE columns than in controls (Figure 5a). For NC columns, the majority As species present in the effluent was also As^{III} although accountable amounts of As^V were observed at the end of experiments (Figure 5b). With MMA spiked in the influent, all four method detectable As species, As^{III}, As^V, MMA, and DMA were present in the effluents of all columns (Figure 6). For UC experiments, As^V was the dominate inorganic As species in the effluent for SE columns, while As^{III} was the major inorganic As species for controls (Figure 6a). High DMA concentration was observed immediately after the column experiment, indicating that the methylation from MMA to DMA occurred rapidly and extensively (Figure 6c). In fact, MMA, which was originally spiked in the influent, was only account for a small portion of As eluted. The variations in the concentrations of inorganic As species (As^V and As^{III}) (Figure 6a) with time seem reversely corresponding to the changes in the concentrations of MMA and DMA (Figure 6c). It appears that after being introduced into the column MMA was first methylated and then decomposed into inorganic species gradually. When NC soil was used, different As distribution patterns were observed (Figures 6b and 6d). Inorganic As^{III} was the dominant species in the effluent for the SE columns, while little As was eluted for the controls (Figure 6b). Similar to UC columns, concentrations of inorganic and organic As species were reversely correlated. These results suggest that the metabolic products of As in the soils are determined by both the original As species applied in the soil and by the soil characteristics. Generally, the concentrations of all four As species eluted from SE columns were higher than the corresponding control columns.

The fast As species transformation could be facilitated by a number of abiotic and/or biotic factors. Redox potential (Eh) and pH are two of the most important factors controlling As speciation. The pH of the effluent for all columns remained relatively constant throughout the experiment, about 4 for controls and 4 to 6 for samples (data not shown). Under these pH conditions, conversion of As^V to As^{III} would only happen when Eh drops approximately below 300 mV (pH 4) to 100 mV (pH 6) at respective pH according to the inorganic As pH-Eh diagram (Brookins, 1986). The Eh for UC soil using As^V-spiked influent (Figure 7a) was around 600 mV at the beginning for both sample and control columns and dropped to ~ 450 mV after 5 pore volumes and remained constant for the rest of experimental period. The Eh for UC soil using MMA-spiked influent (Figure 7a) was also slightly decreased after several pore volumes for all columns, then remained constant for control, but gradually increased for SE columns until reached the value at the beginning of experiment (~ 600 mV). For NC columns, Eh remained constant around 600 mV for control columns, while dropped gradually for samples (Figure 7b). By the end of experiment, the Eh for SE columns dropped to 200 and 100 mV for influent spiked with As^V and MMA, respectively. Dramatically dropping in Eh could partially be the reason why As^{III} was the major As species for NC columns when the influent was spiked with either As^V or MMA. The relatively high Eh during the entire course of experiment could account for the predominance of As^V in the effluents from UC columns when MMA was spiked.

In addition to Eh changes, the transformation of As was influenced by other factors. This can be supported by the fact that As^{III} was formed in the As^V spiked experiments using UC soil where Eh remained relatively high. As^{III} appeared even at the beginning of experiment where Eh changes were not observed (Figure 5a vs Figures 7a). This finding is also supported by the fact that As^{III} increased to the maximum at 10 pore volumes and then declined with time in the experiments using NC soil with As^V spiked to the influent (Figure 5b), which did not match the Eh profiles (Figure 7b). Microbe-involved processes appeared to play a role in controlling the reduction of As^V to As^{III} as well as methylation of MMA to

DMA. The decrease in Eh may be caused by the growth of microorganisms that metabolize the natural organic matter present in the soil/water system. Decreases in DOC concentrations in effluents compared to influents during the entire experimental period could be partially attributed to the consumption by microorganism growth, especially for UC columns.

Microorganisms that express As resistance genes are able to withstand high concentrations of As^V through the intracellular reduction of As^V and the subsequent excretion of As^{III} into the surrounding media. It is thought that this pathway may function in aerobic as well as anaerobic environments (Newman, 1998; Macy et al., 2000) and may contribute to apparent nonequilibrium conditions where As^{III} has been often observed in oxic surface waters (Cullen and Reimer, 1989). Although it is likely that bacteria in soil, especially at As-contaminated sites, possess As detoxification pathways, the literature about the effect of aerobic As^V-reducing bacteria on As behavior in soils is very limited (Macur et al., 2001). Biomethylation of As is frequently suggested to act as a detoxification method for microbes. Field studies for As transport and species transformation associated with monosodium methanearsonate (MSMA) application on golf course green revealed microorganism-mediated processes were likely involved in As transformation (Di Carlo and Fuentes, 2000; Feng et al., 2005). This study showed that As species conversion in soil columns can be associated with microbial activities. High concentrations of DMA were observed in column effluent after MMA application to soil columns. The fast methylation of MMA to DMA confirmed the involvement of microorganisms in As species transformation in soil columns. It is notable that no effort was made to measure further methylation products, although further methylation of DMA is possible.

4. Conclusions

Laboratory column experiments indicate that dissolved substances derived from natural soils, particularly peat, can facilitate As transport through the porous media. Direct complexation of As with inorganic colloids and DOM and competitive adsorption on soil surface of DOM with As could account for the facilitated As transport by soil-derived dissolved substances. Rapid species transformation of As during column transport was clearly observed. With As^V spiked in influent solution, As^{III} was the only (for UC column) or dominant (for NC) species in the column effluent. When MMA was spiked in influent solution, all method detectable As species, As^{III}, As^V, MMA, and DMA were present in the effluents for both soil columns. In addition to pH and Eh, microbial processes played an important role in species transformation of As.

Acknowledgments

This study was partially supported by NIEHS ARCH (S11 ES11181) and NIH-MBRS (3 S06 GM008205-20S1) programs. We thank George Meichel for his assistance in modifying the electrodes and setting up the column experiments. We thank two anonymous reviewers for their valuable suggestions and comments. This is contribution # XXX of Southeast Environmental Research Center at FIU.

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Figure 1.

Total As elution with time from UC and NC columns. (a) UC column, influent spiked with As^V; (b) NC column, influent spiked with As^V; (c) UC column, influent spiked with MMA; (d) NC column, influent spiked with MMA. The influent As concentrations were 100 and 200 µg/L for UC and NC, respectively. S_{AsV} and S_{MMA} stand for columns that were eluted with soil extracts spiked with As^V and MMA, respectively. C_{AsV} and C_{MMA} stand for columns that were eluted with ARW initially spiked with As^V and MMA, respectively. Each data point was the average of the results from the duplicated columns.

Figure 2.
Fraction of total As eluted from soil columns during the experiments

Figure 3. Concentrations of Fe and Al in the column effluents. (a) UC columns, influent spiked with As^V; (b) NC columns, influent spiked with As^V; (c) UC columns, influent spiked with MMA; and (d) NC columns, influent spiked with MMA.

Figure 4. DOC concentrations in the effluents from (a) UC columns and (b) NC columns.

Figure 5. Arsenic speciation profiles in the effluents from (a) UC and (b) NC columns with As^{V} as the initially spiked As species in the influents.

Figure 6.

Arsenic speciation profiles in column effluents for MMA spiked experiments. (a) inorganic As species in UC columns; (b) inorganic As species in NC columns; (c) organoarsenicals in UC columns; and (d) organoarsenicals in NC columns. The influents were spiked with MMA at As concentration of 100 $\mu\text{g/L}$ for UC and 200 $\mu\text{g/L}$ for NC, respectively.

Figure 7.
 Eh profiles in the effluents from (a) UC columns and (b) NC columns.

Table 1

Characteristics of the soils used for packing columns and soil extracts

Soil ^a	pH	CEC (cmol/kg)	TOC (%)	Fe (mg/kg)	Al (mg/kg)	As (µg/kg)
UC	4.5	0.2	0.01	37.1	54.2	72.3
NC	4.8	4–5	0.02	331	216	51.3

Soil extract ^b	pH	DOC (mg/L)	Fe (mg/L)	Al (mg/L)	As (µg/L)
UCP	4.2	6.4	2.18	11.56	<0.02
NCP	4.5	3.0	21.40	20.41	<0.02
UC	4.6	1.0	0.24	0.58	<0.02
NC	4.8	2.0	0.06	0.24	<0.02
P	4.0	35.6	0.76	0.59	<0.02

^a : Uncoated (UC) and naturally coated (NC) sand were used for column packing.

^b : Soil extracts were prepared by extracting 20 g of soil with 100 ml of artificial rainwater. UCP or NCP soil was prepared by adding Sphagnum peat moss (P) to UC or NC (1:9 v/v). Soil extracts of UCP and NCP were used as feeding solution to UC and NC columns, respectively. Soil extracts of UC, NC, and P were also included in the table in order to show the differences between UCP and UC (or NCP and NC) soil extracts.