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Evidence for the Aquatic Binding of Arsenate by Natural Organic Matter−Suspended Fe(III)

KAYLENE RITTER,[†] GEORGE, R. AIKEN,[‡] JAMES F. RANVILLE,[†] MARKUS BAUER,[†,§] AND DONALD L. MACALADY*,[†]

Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado, and U.S. Geological Survey, Water Resources Discipline, Boulder, Colorado

Dialysis experiments with arsenate and three different NOM samples amended with Fe(III) showed evidence confirming the formation of aquatic arsenate−Fe(III)−NOM associations. A linear relationship was observed between the amount of complexed arsenate and the Fe(III) content of the NOM. The dialysis results were consistent with complex formation through ferric iron cations acting as bridges between the negatively charged arsenate and NOM functional groups and/or a more colloidal association, in which the arsenate is bound by suspended Fe(III)−NOM colloids. Sequential filtration experiments confirmed that a significant proportion of the iron present at all Fe/C ratios used in the dialysis experiments was colloidal in nature. These colloids may include larger NOM species that are coagulated by the presence of chelated Fe(III) and/or NOM-stabilized ferric (oxy)hydroxide colloids, and thus, the solution-phase arsenate−Fe(III)−NOM associations are at least partially colloidal in nature.

Introduction

Arsenic is a toxic substance and a carcinogen threatening the drinking water of millions within the Unites States and around the world (*1*−*3*). Hence, understanding the factors influencing its aqueous concentration and mobility is an issue of current concern. An important control on arsenic mobility in natural systems is adsorption to iron and other metal (oxy)hydroxides (*4*−*8*). Natural organic matter (NOM) is ubiquitous to aquatic systems, including those affected by arsenic. Arising from the decomposition of biomass, it is a complex material possessing carboxylic, amino, nitroso, sulfhydryl, hydroxyl, and phenolic moieties (*9*−*11*). It has recently been shown that natural organic matter can influence arsenic adsorption to iron oxides (*12*, *13*). It was found that NOM competes with arsenic for adsorption to iron oxide surfaces (*12*, *13*) and possibly forms aquatic associations with arsenic (*12*). The net result of both of these processes, the latter of which being the focus of this study, is higher concentrations and greater mobility of arsenic in aquatic systems.

Arsenic has two oxidation states relevant to natural environments and is typically present as either arsenite or arsenate, depending upon redox conditions. Arsenite, with pK_a's of 9.2, 12.1, and 13.4, exists as a neutral species in most natural systems. Arsenate has pK_a's of 2.2, 6.9, and 11.5 and thus takes the form of $H_2AsO_4^-$ and/or $HAsO_4^{2-}$ in waters of circum-neutral pH (*14*). The suggestion that arsenate and NOM form aquatic complexes is hence somewhat surprising, as NOM functional groups are also predominantly negatively charged at circum-neutral pH (*9* and refs therein). However, it has been suggested that natural organic matter may associate with anions in solution through bridging mechanisms. The solubilities of transition metal cations such as Fe(III) increase significantly due to complexation with NOM functional groups, such as carboxyls (*15*−*17*). Thanabalasingam and Pickering (*18*) proposed that these cations could then link negatively charged NOM functional groups and inorganic anions in tertiary complexes. Warwick et al. (*19*) provide some evidence for aquatic binding of arsenic by organic matter through ultrafiltration experiments. Lin et al. (*20*) report to have identified arsenate−cation−NOM complexes through dialysis experiments. Though interesting, their results cannot be exclusively attributed to the formation of As−organic matter associations, as the observed arsenic behavior could also be explained by inorganic associations involving dissolved cations present in their system.

Iron and NOM are also known to form colloidal associations, in which the NOM is coagulated by chelating iron cations and/or NOM molecules bind and suspend iron (oxyhydr)oxide colloids in solution (*21*−*27*). NOM−Fe colloids have been reported to be 50−100 nm in diameter (*21*) and hence are considered to be within the dissolved phase, as defined by filtration at 0.45 μm. The iron in these suspended colloids could then provide binding sites for oxyanions such as arsenate. The result for arsenate would then be stable, colloidal As−Fe−NOM associations that may involve As bridging with chelated Fe(III) cations and/or (oxy)hydroxide surface complexation. It has been suggested that such NOM-suspended iron colloidal associations occur with phosphate (*28*), and hence they might also occur with arsenate.

There are many implications of the formation of aquatic associations between arsenate and Fe-bearing NOM. Aside from resulting in greater arsenic concentrations and mobility than would be otherwise predicted in oxide-sorption controlled systems, such associations may influence the bioavailability of arsenic (*29*). Further, there are possible deleterious implications for arsenic treatment processes that are based on the removal of arsenic through adsorption/coprecipitation with iron (and/or aluminum) oxides. We hypothesized that arsenate does form aquatic associations with NOM, occurring via one or both of the discussed mechanisms involving ferric iron. Accordingly, the purpose of this work was to investigate the formation of aquatic associations between arsenate and NOM, and the role of NOM-suspended Fe(III) in such complexes, through dialysis experiments.

Experimental Section

NOM Samples. Three different natural organic matter samples were employed: a Suwannee River (SR-WW) whole water, the hydrophobic acid fraction of a Suwannee River water sample (SR-HPOA), and the fulvic acid fraction of a water sample collected in the Everglades (EG-FA). The SR-WW NOM sample, originating from the outlet of the Okefenokee Swamp in Georgia, was collected in April 2002 and was stored in the dark at 4 °C until use. The SR-HPOA and EG-FA water samples were collected and the fractions isolated in 1995 and 1997, respectively. HPOA consists of

* Corresponding author. Phone: (303)273-3610. Fax: (303)273-3629. E-mail: dmacalad@mines.edu.
[†] Colorado School of Mines.
[‡] U.S. Geological Survey.
[§] Permanent address: Limnological Research Station and Department of Hydrology, University of Bayreuth, D-95444 Bayreuth, Germany.

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TABLE 1. Characteristics of the Natural Organic Matter Solutions

NOM	molecular weight (Da)	specific UV absorption (L cm^{-1} (mg C)$^{-1}$)	Fe (μg/L)
SR-HPOA	810	0.044	280
SR-WW	710	0.038	500
EG-FA	700	0.040	(bdl)

TABLE 2. Other Inorganic Constituents of the Natural Organic Matter Samples Present in the Original NOM Solutions (and in the Dialysis Bags after Equilibration)[a,b,c]

NOM	Al	Ca	Cu	Mg	Mn	S	Zn
SR-HPOA	bdl	31.0	24.2	74.8	bdl	61.9	5.37
	(bdl)	(9.32)	(bdl)	(2.47)	(bdl)	(bdl)	(bdl)
SR-WW	72.3	94.2	bdl	73.8	bdl	248	5.77
	(37.3)	(4.68)	(bdl)	(bdl)	(bdl)	(bdl)	(bdl)
EG-FA	bdl	75.8	bdl	42.8	bdl	135	2.80
	(bdl)	(23.7)	(bdl)	(bdl)	(bdl)	(bdl)	(bdl)

[a] All values are in μg/L. [b] bdl = below detection limit. [c] Detection limits in μg/L: Al = 29.6; Ca = 3.40; Cu = 4.70; Mg = 1.57; Mn = 0.759; S = 46.1; Zn = 2.62.

90−95% fulvic acid and 5−10% humic acid, and the HPOA and FA fractions were prepared according to the method described by Aiken et al. (*30*). The whole water sample, SR-WW, was not subject to any fractionation or treatment, other than filtering at 0.45 μm immediately prior to use. The NOMs were characterized according to their molecular weight, specific UV absorption (SUVA) at 254 nm, acidity, and metals content (Tables 1 and 2).

NOM Characterization. SUVA values of the three NOMs were determined by dividing their UV absorbance at 254 nm, measured with a Hatch DR/4000U spectrophotometer, by the dissolved organic carbon (DOC) concentration (*31*). Molecular weights of the NOMs used in this study were obtained by size exclusion chromatography, using a Superdex peptide column (Amersham Pharmacia Biotech), which separates compounds within the approximate MW range of 7−0.1 kDa, coupled to a UV detector set to 254 nm (Dionex), according to the method described by Jackson et al. (*32*).

Reagents. Arsenate stock solutions were made from reagent grade sodium arsenate and adjusted to pH 6 using 0.1 M HNO_3. Fe(III) stock solutions for the dialysis experiments were made with reagent grade $Fe(NO_3)_3{\cdot}9H_2O$ and acidified to pH 2 with 1 M HNO_3. High-purity (18 MΩ) deionized water was used throughout.

Analyses. Arsenic analyses were performed with a Perkin-Elmer Analyst 800 graphite furnace atomic absorption (GF-AAS) spectrometer, with a detection limit of 4 μg/L As (0.05 μM As). Dissolved organic carbon was determined using a Sievers total organic carbon analyzer, model 800, with a detection limit of 80 μg/L (6.67 μM) organic carbon. Total iron and other metals content of the NOM solutions were measured employing a Perkin-Elmer Optima 4300DV ion-coupled plasma atomic emission spectrometer (ICP-AES), with a total iron detection limit of 4 μg/L (0.07 μM). The detection limits of other relevant metals are given in the text. All samples were stored at 4 °C in the dark and were analyzed for As, DOC, and metals within 1 week of sampling.

Dialysis Experiments. Comparable to dialysis studies by Van Loon et al. (*33*) for characterizing radionuclide−NOM complexes, the aquatic binding of arsenate by Fe-bearing NOM was identified through arsenate concentration differences across a dialysis membrane. Ideally, the membrane is chosen such that its pore size allows the passage of arsenate anions but not of the larger NOM or As(V)−Fe(III)−NOM complexes. Hence, in experiments in which dialysis bags are filled with iron-amended NOM solutions and surrounded by an electrolyte solution spiked with arsenate, after a period of equilibration, the formation of As(V)−Fe(III)−NOM associations is indicated by higher total arsenic concentrations inside (arsenate anions + As(V)−Fe(III)−NOM complexes) than outside (arsenate anions only) the dialysis bags.

Arsenate−Fe(III)−NOM Experiments. The dialysis experiments were conducted with Spectra-Por CE (cellulose ester) 1000 molecular weight cutoff (MWCO) dialysis membranes. This pore size was chosen based on arsenate kinetics experiments (described below) because it allowed As equilibration within a reasonable time period, while minimizing NOM bleed through the membrane. All experiments were undertaken at pH 6, 10 mM $NaNO_3$. Acid-cleaned, autoclaved 125 mL borosilicate glass jars with Teflon-lined caps were filled with 95 mL of the 10 mM $NaNO_3$, pH 6 solution. Dialysis bags to be placed in the jars were filled with 5 mL of the appropriate NOM solution and were sealed by tying knots.

The NOM-filled dialysis bags were prerinsed in pH 6, 10 mM $NaNO_3$ solutions for 1 week. In recognition of the large membrane pore size relative to the MWs of the NOMs (Table 1), the purpose of the prerinse was to flush out smaller NOM molecules, thereby avoiding excessive leaching during the course of the experiments. The rinsing solutions were sampled for DOC for mass balance purposes. For consistency, the dialysis bags containing control solutions (no NOM) were also prerinsed.

After completion of the 1 week prerinse, the dialysis bags were placed in the jars. The electrolyte solution in the jars was then spiked with the arsenate stock, resulting in a concentration outside the bags of 90 μg/L (1.2 μM) arsenate in the case of initial SR-HPOA experiments or 720 μg/L (9.6 μM) arsenate for all subsequent experiments. After a 2 week equilibration period, aliquots were taken from the solutions in the jars and in the dialysis bags. These were analyzed for total arsenic, DOC, total iron, and metal content. The 2 week equilibration period was determined based on the kinetics experiments described below.

Preparation of NOM and Fe(III)-Amended NOM Solutions. The SR-HPOA and EG-FA solutions were made by dissolving 10 mg of the freeze-dried material into 100 mL of water, resulting in a concentration of 100 mg NOM/L (or ~50 mg C/L; 4.2 mM C) and were filtered at 0.45 μm. The SR-WW sample (60 mg C/L; 5 mM C) was also filtered at 0.45 μm. All three NOMs were adjusted to pH 6 with 0.1 M HNO_3 and/or 0.1 M NaOH. Note that while iron was below detection in the EG-FA NOM, both the SR-HPOA and the SR-WW had inherent iron contents (Table 1), and all iron concentrations reported henceforth refer to total iron (inherent + added). To make the Fe(III)-amended NOM solutions, the NOM solutions were spiked with the Fe(III) stock solution. In the case of the initial SR-HPOA studies conducted with 90 μg/L (1.2 μM) arsenate, the SR-HPOA was spiked to make 1 mg/L (0.02 mM) Fe(III). The solution was allowed to equilibrate for 24 h, filtered again at 0.45 μm, and the pH readjusted to 6. The second filtration step removed some of the added Fe(III). A portion of the Fe(III) was also leached during the 1 week prerinse period (presumably iron that was associated with bled NOM), resulting in final Fe(III) concentrations measured in the dialysis bags upon completion of the experiment of 0.6 mg/L (0.01 mM) Fe(III). Following the same procedure, the Fe(III)-amended EG-FA and SR-WW NOM solutions used in the experiments with 720 μg/L (9.6 μM) arsenate were spiked to make 5 mg/L (0.09 mM) Fe(III). Filtering removed approximately 1 mg/L (0.020 mM) Fe(III) from the amended EG-FA and 0.5 mg/L (0.009 mM) Fe(III) from the amended SR-WW solution. The final solutions in the dialysis compartments were approximately 2 mg/L (0.04 mM) Fe(III).

Experiments were also undertaken with solutions of SR-HPOA and 720 μg/L arsenate with incremental amounts of Fe(III), in which the final concentrations measured in the dialysis bags were 0.3 mg/L (0.005 mM), 2.4 mg/L (0.04 mM), 6.1 mg/L (0.1 mM), and 11.6 mg/L (0.21 mM) Fe. Ferric iron control experiments (no NOM) were conducted with solutions of Fe(III) prepared following the same procedure (pH 6, 10 mM $NaNO_3$, 0.45 μm filtered), with and without spiking with arsenate. Other control experiments included the pH 6, 10 mM $NaNO_3$ electrolyte solution in the jar and bag, not spiked with arsenate, 10 mM $NaNO_3$ in the jar and bag and spiked with arsenate, and NOM in the bag, 10 mM $NaNO_3$ in the jar, not spiked with arsenate. No attempt was made to keep solutions from laboratory light.

It is noted that NOM, Fe, and As(V) are both abiotically and bacterially mediated redox active (*13*, *34* and refs therein). Hence, even though the solutions were initially oxygenated and exposed to the atmosphere during the experiments, it is possible that a small fraction of the iron and arsenic initially added as ferric iron and arsenate may have been reduced to arsenite and ferrous iron. However, this does not detract from the validity of the experimental method nor the evidence they provide for the aquatic interactions under study; it simply means that a fraction of the arsenic and/or iron involved in the aquatic interactions may have been present in reduced form.

Arsenate Kinetics Dialysis Experiments. The purpose of the kinetics experiments, conducted with 500, 1000, 2000, and 3500 MWCO Spectra-Por CE membranes, was to select an appropriate MWCO membrane for use in the NOM−arsenate and NOM−arsenate−Fe(III) experiments and establish the time required to reach arsenic equilibrium across the dialysis membrane. A similar procedure was followed as described above, except the dialysis bags were filled with the electrolyte solution (10 mM $NaNO_3$, pH 6) rather than NOM, and sampling occurred on an hourly, daily, and weekly basis, up to a total period of 1 month.

With the exception of the arsenic kinetics and preliminary SR-HPOA experiments, which were conducted in duplicate, all experiments were conducted in triplicate, with error bars depicting 1 standard deviation from the mean. The error bars for the kinetics experiments represent the range of the data, and individual replicate data are shown for the initial SR-HPOA experiments, with the error bars showing 1 standard deviation of triplicate instrument analyses.

Fe(III)-Amended NOM Sequential Filtration Experiments. To ascertain the nature of the ferric iron amended to the NOM solutions (colloidal vs noncolloidal chelated cations), sequential filtration experiments were conducted with the SR-WW NOM at two different dilutions: 10 mg C/L (0.08 mM C) and 40 mg C/L (3.3 mM C). The SR-WW NOM was diluted from its original concentration of 60 mg C/L (5 mM C). The samples were spiked with the stock solution to make 5.5 mg/L (0.1 mM) Fe and 0.28 mg/L (0.005 mM) Fe. The pH was adjusted to 6 with NaOH. The samples were allowed to equilibrate for 5 h. Aliquots were then taken and filtered at 0.45 μm and then at 0.1 μm. Prior to filtering, and after each filtering step, samples were taken for analysis of total iron.

Results and Discussion

Arsenate Kinetics Dialysis Experiments. It was found that an equilibration time of 2 weeks was required to reach $[\text{arsenate}]_{\text{bag}} = [\text{arsenate}]_{\text{jar}}$ for the Spectra-Por CE 1000 MWCO dialysis membrane (Figure 1A), and this membrane pore size was chosen for use in the arsenate−NOM experiments. Equilibrium was not reached with the 500 MWCO membrane after 1 month, and hence it was not suitable for the intended experiments. The 2000 and 3500 MW membranes reached equilibrium in a slightly shorter time than the 1000 MWCO membrane. However, there was concern that these pore sizes would permit excessive passage of the NOM. The 2 week equilibration time required for the 1000 MWCO membrane and lack of equilibrium after 1 month with the 500 MWCO membrane, despite the small size of the arsenate oxyanion relative to the membrane pore dimensions, can be attributed to electrostatic effects. The rate of diffusion of across Spectra-Por CE membranes decreases with increasing negative charge on the species, presumably due to repulsion between the diffusing anion and negatively charged membrane surface groups (*35*).

Arsenate−NOM Aquatic Associations: Initial SR-HPOA Experiments. The results of the initial dialysis experiments conducted with SR-HPOA, 90 μg/L (1.2 mM) arsenate, and 0.6 mg/L (0.01 mM) Fe(III) are summarized in Figure 1B. Arsenic equilibrium in the control experiments (no NOM) was reached in 2 weeks, as predicted by the kinetics experiments. In contrast, the concentration of arsenate in the dialysis bags containing SR-HPOA was approximately 6% greater than the concentration in the surrounding jar solution. Experiments in which the equilibration time was extended up to 4 weeks (data available upon request) showed no further mobilization of arsenate into the dialysis bags, indicating that, as with the arsenic-only experiments, the 2 week period was adequate to reach arsenic equilibrium in the presence of the NOM. There is also partitioning of the As (V) into the dialysis bags when the SR-HPOA was amended with Fe(III) for a total concentration of 0.6 mg/L (0.01 mM) Fe(III). Noting that the SR-HPOA has an inherent iron content of 280 μg/L (5.1 μM) Fe (Table 1), and a final concentration measured in the dialysis bags of 80 μg/L (1.5 μM) Fe, the results of these experiments were consistent with the aquatic binding of arsenate by NOM with ferric iron acting as an intermediary.

Formation of Arsenate−Fe(III)−NOM Aquatic Associations with EG-FA and SR-WW. Experiments were conducted with SR-WW and EG-FA to determine if the aquatic binding of arsenic would occur with a broader range of organic matter samples and to further evaluate the role of Fe(III). A higher arsenate concentration of 720 μg/L (9.6 μM) arsenate was used, in anticipation of greater arsenate partitioning due to the higher levels of Fe(III) employed in these studies. It was found that elevated concentrations of arsenate in the dialysis bags relative to that of the surrounding solutions also occurred in the experiments conducted with SR-WW and EG-FA (Figure 2A). However, analysis of the bag and jar concentrations for EG-FA and SR-WW via a Student *t*-test revealed that, at the 95% confidence level, only the SR-WW bag and jar arsenate concentrations were statistically different, while the EG-FA data were not. The results were consistent with the importance of iron in the aquatic binding of arsenate by NOM, as the SR-WW had an inherent iron concentration of 500 μg/L (9.1 μM) Fe and a final concentration in the dialysis bags of 100 μg/L (1.8 μM) Fe, while Fe was below detection in the EG-FA sample (Table 1). Amending the NOMs with approximately 2 mg/L (0.04 mM) Fe(III) resulted in significantly more arsenate in the dialysis bags for both NOM samples, confirming the role of the transition metal in arsenate−NOM interactions (Figure 2B).

Arsenate mass balances were 100% (±8%) for the experiments with all three NOMs (Figure 3), with data shown for the iron-amended SR-WW and EG-FA experiments (~2 mg/Fe(III)), as well as for the SR-HPOA experiment with 2.5 mg/L (0.05 mM) Fe(III) that is discussed below. The DOC mass balances were 100% (±10%) and show that the 1 week prerinse successfully flushed out a significant portion of the smaller NOM molecules, which amounted to roughly 35−50% of the total initial DOC. A further 12−20% of the initial DOC concentration passed through the bags to the surrounding jar solution during the course of the 2 week

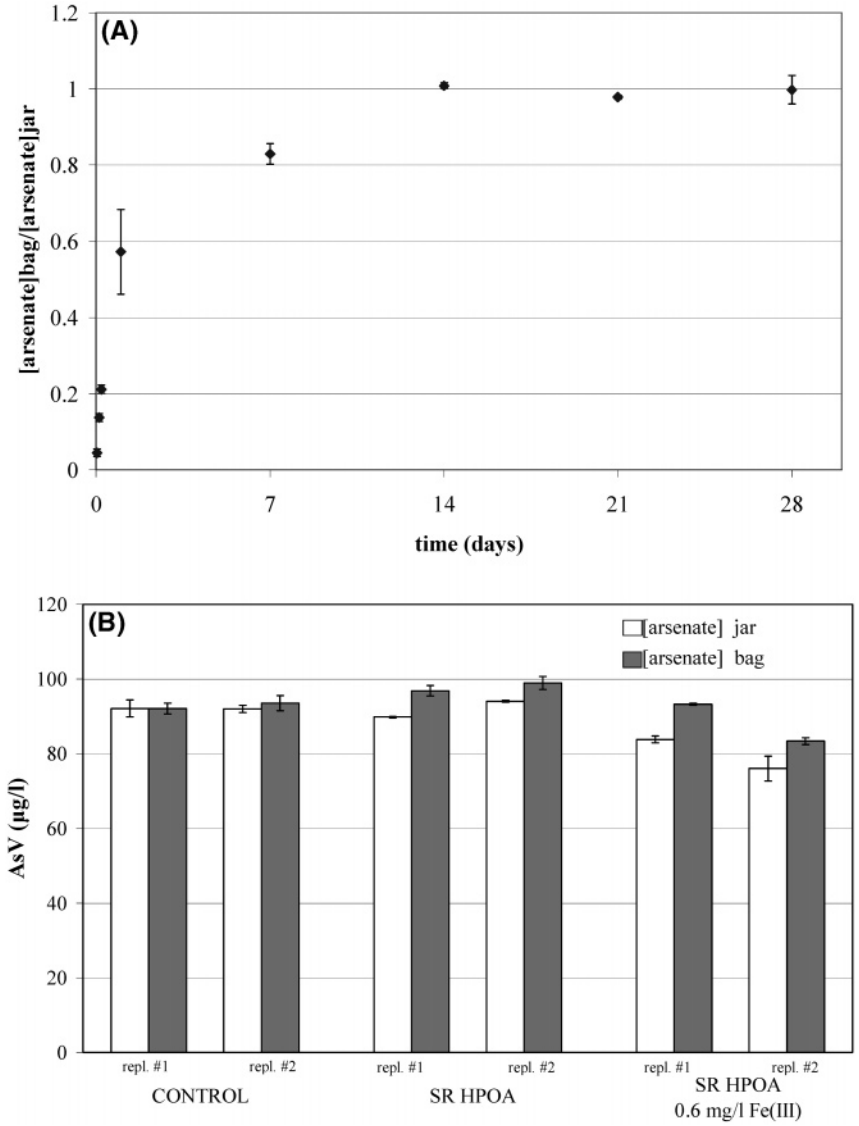

FIGURE 1. (A) Diffusion kinetics of arsenate for the 1000 MWCO Spectra-Por CE dialysis membrane. Fourteen days were required to reach $[arsenate]_{bag} = [arsenate]_{jar}$. The error bars show the range of data. (B) The results of dialysis experiments conducted with SR-HPOA, 90 μg/L arsenate, and 0.6 mg/L Fe.

equilibration period (Figure 4A). Hence, the prerinsing effectively minimized the amount of leaching that occurred during the 2 week equilibration period, and the leaching that did occur was not significant enough to inhibit the experiments. Final NOM concentrations in the dialysis bags were approximately 20 mg C/L (1.7 mM C), and 0.3 mg C/L (0.03 mM C) in the jars (Figure 4A). The Fe(III) mass balances show that there were low levels of iron measured in the jars at the completion of the 2 week equilibration period (SR-HPOA = 24 ± 10, EG-FA = 13 ± 8, and SR-WW = 42 ± 16 ppb). However, these values are within experimental uncertainty of the iron level in the jar blank of 19 ± 9 ppb (no iron, no As(V), no NOM added) and, hence, are comprised mainly iron from the background electrolyte, only a small fraction resulting from leakage from the dialysis bags during the course of the experiments (Figure 4B). While the presence of low levels of both iron and NOM in the jars may have resulted in the binding of a small fraction of the arsenate outside of the dialysis bags (rather than inside as intended), this would have had only a minimal effect on the experiments. The average Fe(III) content of the jars was 0.05 μmol of Fe(III), assuming the iron was complexed to NOM, and on the basis of the relationship between iron concentration and complexed arsenate given below, this would result in a maximum of 0.009 μmol of arsenate bound by Fe(III)−NOM, or 1% of the average arsenate content of the jars of 0.84 μmol of As. The worst case scenario, with SR-WW, assuming a jar Fe(III) level 1 standard deviation above the mean would involve less than 3% error.

Complexation of Arsenate by HPOA Amended with Incremental Levels of Fe(III). The importance of Fe(III) in the aquatic association of arsenate with NOM was further delineated when experiments were conducted with SR-HPOA to which was added incremental amounts of Fe(III). Figure 5 shows that within the wide range of iron concentrations used here, there was a strong linear relationship (r^2 = 0.97) between the total Fe(III) content of the NOM and the amount of complexed arsenate. Figure 5 includes data from the Fe-amended EG-FA and SR-WW NOM experiments. These combined results strongly indicate that it is the iron content of the NOM that is critical to its ability to bind arsenate, with little evidence to support aquatic interactions of arsenate with NOM that do not involve iron. Instead, the lack of aquatic interactions between arsenate and EG-FA (iron below detection), and the fact that the linear relationship shown in Figure 4 passes near the origin, both suggest that

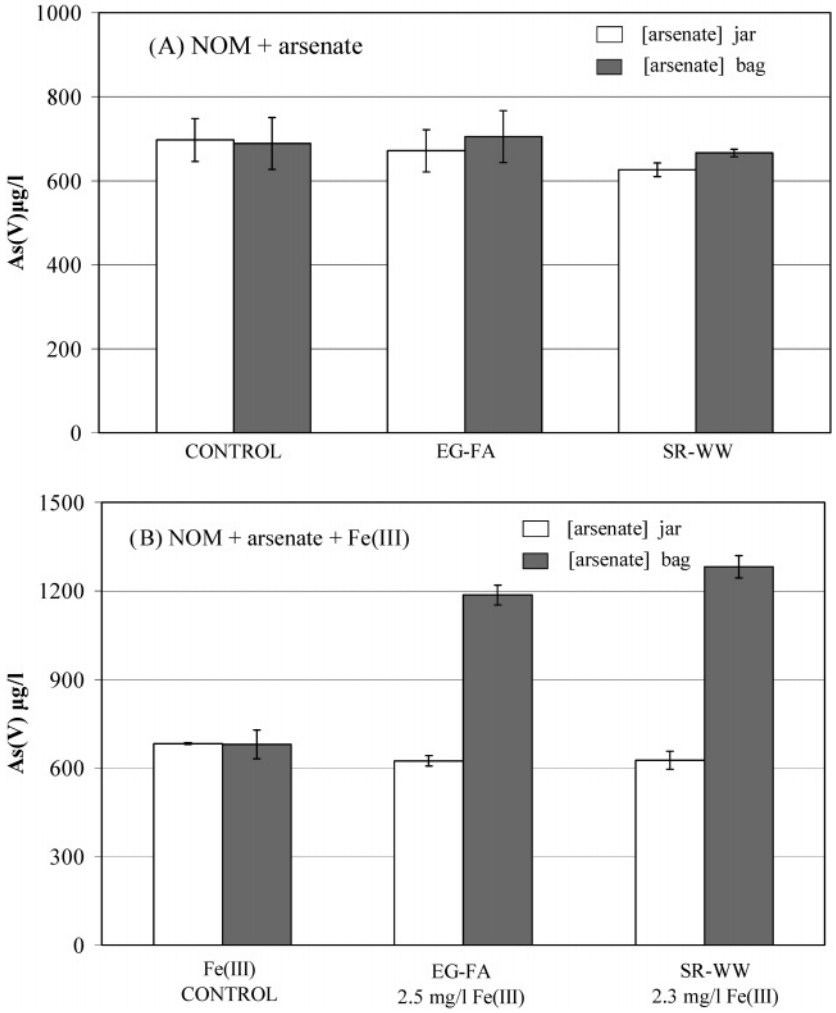

FIGURE 2. (A) Results of dialysis experiments with EG-FA and SR-WW, showing an increase in arsenate in the bag relative to that of the solution in the jar when NOM was in the bag. Control = no NOM. (B) Effect of amending the NOMs with Fe(III). Fe(III) control = Fe(III) in the dialysis bag but no NOM (the initial solution was 5 mg/L Fe(III), but the final concentration in the bag was much lower, see Figure 5).

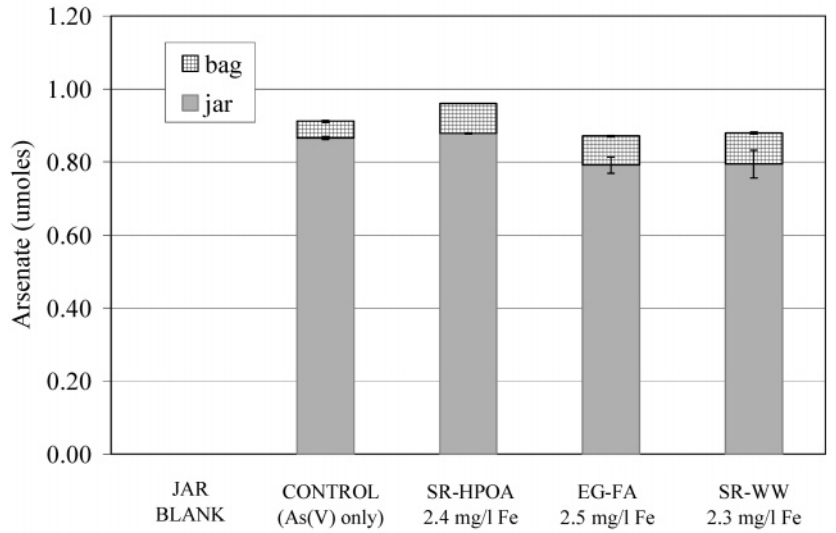

FIGURE 3. Arsenate mass balance for the dialysis experiments conducted with the three NOMs and ~2 mg/L Fe(III). The total arsenate added was 0.96 μmol. Control = no NOM. The jar blank = no added arsenate, Fe(III), or NOM and no dialysis bag.

aquatic interactions of arsenate and NOM are not significant in the absence of iron.

The possibility that the increased concentration of arsenate measured in the dialysis bags was due to the formation of inorganic Fe(III)−arsenate associations is largely discounted by the results obtained in the control experiments. In the Fe(III) controls (no NOM), no increase in arsenic in the dialysis bags occurred relative to that of the surrounding

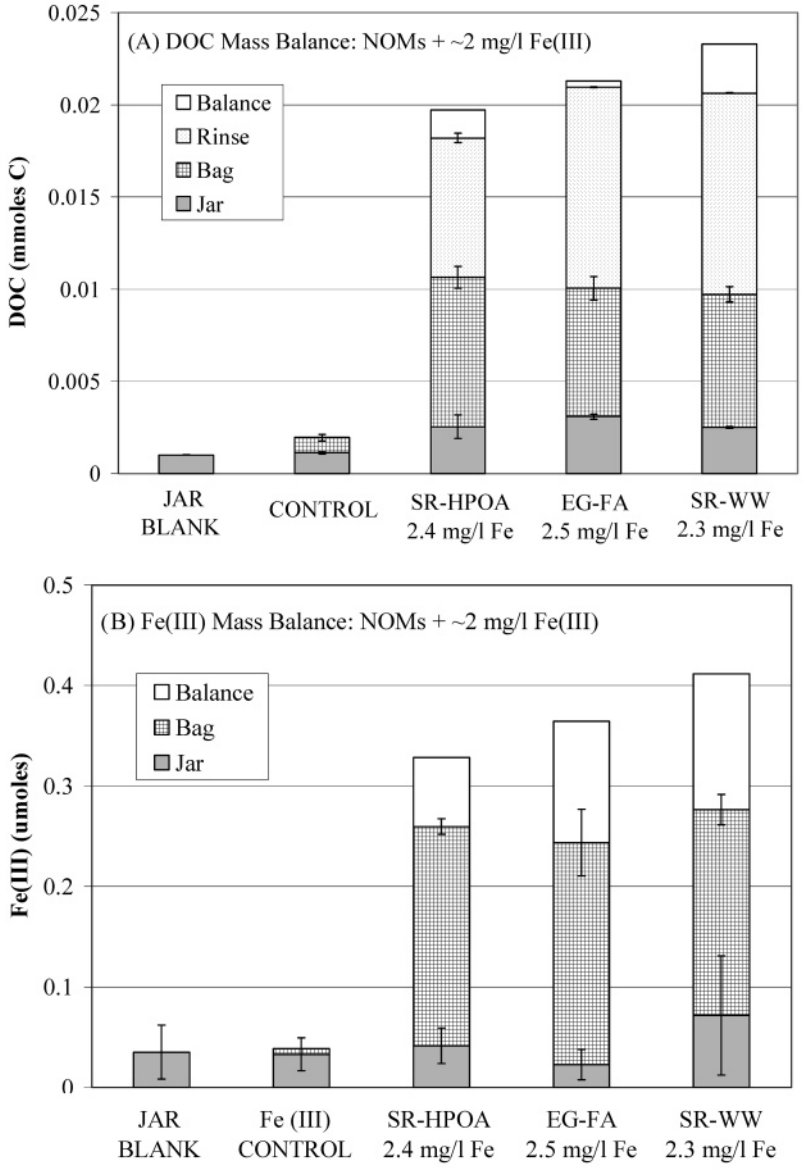

FIGURE 4. (A) DOC mass balance for the dialysis experiments conducted with the three NOMs and ~2 mg/L Fe(III). Control = no NOM. (B) Fe(III) mass balance for the same experiments. Fe(III) control = no NOM and an initial solution of 5 mg/L Fe(III). The balance of the Fe(III) is assumed to have leached from the bags during the 1 week prerinse, presumably associated with the smaller NOM molecules that were also flushed from the bags during the prerinse. For both graphs, the jar blank = no added arsenate, Fe(III), or NOM and no dialysis bag.

solution (Figure 2). When the control solutions were made, there was visible iron precipitation upon adjusting the pH to 6, consistent with the low solubility of ferric iron above pH 3.5 (*36* and refs therein). Subsequent filtration at 0.45 μm then removed most of the Fe(III) from solution, as indicated by the total Fe measured in solution (Figure 4B). Hence, at the pH of these experiments, and in the absence of NOM, dissolved Fe(III) is largely absent from the solution phase, and as such, inorganic Fe(III)−arsenate cannot account for the observed aquatic complexation of arsenate. Instead, the data are interpreted as follows: the NOM served to suspend the added Fe(III) in solution, through the formation of noncolloidal NOM−Fe complexes and/or through colloidal Fe(III)−NOM interactions. The NOM-suspended iron then served as binding sites for the arsenate, resulting in the formation of dissolved, noncolloidal As(V)−Fe(III) cation−NOM complexes and/or NOM-suspended Fe(III)−arsenate colloidal associations. Hence, both the NOM and the Fe(III) have a critical role to play, and both are necessary components for the aquatic binding of arsenic observed in our system.

Nature of the Arsenate−Fe(III)−NOM Association. Sequential filtration experiments revealed that even at the lowest molar ratio of Fe/C of 0.001, 23% of the dissolved iron (i.e., iron in solution after filtration at 0.45 μm) was present as colloids between the size range of 0.1 and 0.45 μm (Table 3). Note that the total fraction of colloidal iron may have been even larger, due to the possible presence of colloids smaller than 0.1 μm in diameter. At the upper Fe/C molar ratio of 0.12, upward of 84% of the dissolved iron was present within the 0.1 and 0.45 μm size fraction. Hence, while the possible presence of noncolloidal ferric cations chelated to NOM molecules cannot be discounted in our system, a significant proportion of the iron is colloidal at all Fe/C ratios. The suspension of colloidal iron by NOM has been demonstrated by numerous authors, including Pullin and Cabaniss (*21*), who showed that at an Fe/C ratio of 0.024, roughly 35% of the Fe(III) suspended by a Suwannee

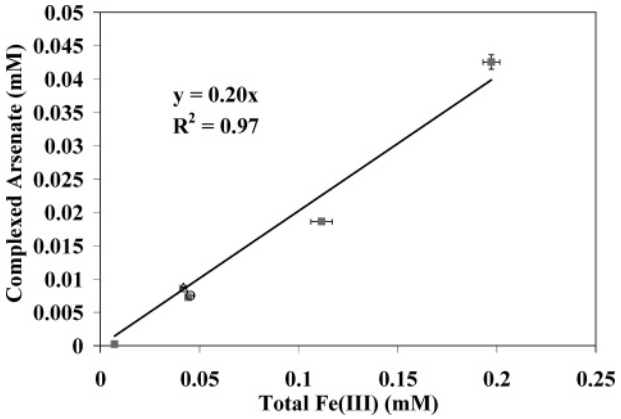

FIGURE 5. Complexed arsenate concentration in the dialysis bags as a function of the Fe(III) content of SR-HPOA (squares). For comparison, the EG-FA + 2.5 mg/L Fe (open circle) and the SR-WW + 2.3 mg/L Fe (open triangle) are also plotted.

TABLE 3. Results of the Sequential Filtration Experiment with SR-WW at Two Different Dilutions (10 and 40 mg C/L) and Two Different Concentrations of Amended Ferric Iron (0.1 and 0.005 mM Fe(III))[a]

	Initial Amount of Iron Added: 100 μM Fe(III) Fe(III) measured in solution (μM)				
organic matter content	unfiltered	0.45 μm	0.1 μm	Fe/C mol ratio	% of Fe(III) filtered between 0.45 and 0.1 μm
0 mg C/L	66.1	0.18	0		
10 mg C/L	82.9	61.0	9.75	0.12	84
40 mg C/L	82.9	73.4	36.4	0.03	50

	Initial Amount of Iron Added: 5 μM Fe(III) Fe(III) measured in solution (μM)				
organic matter content	unfiltered	0.45 μm	0.1 μm	Fe/C mol ratio	% of Fe(III) filtered between 0.45 and 0.1 μm
0 mg C/L	1.86	0.32	0.11		
10 mg C/L	3.79	3.43	2.39	0.006	30
40 mg C/L	4.89	4.00	3.07	0.001	23

[a] $n = 1$.

River fulvic acid NOM sample was present in the colloidal size range.

Dzombak and Morel (*37*) summarize data showing that ferrihydrite colloids at pH's near 6 have densities of type 2 surface sites capable of complexing cations, oxyanions such as arsenate, and neutral species such as arsenite, in the range of 0.1−0.2 mol of sorption sites/total mol of Fe. The slope of the graph shown in Figure 5 is 0.2. Hence, our data are consistent with arsenate binding through adsorption to NOM-suspended iron oxide colloids, if it is assumed that all of the iron in the system is present as ferrihydrite colloids and that all available iron surface sites are occupied by arsenic. While this is possible, it is not likely, as a fraction of the sites would be by necessity occupied by NOM moieties suspending the colloids, and it is likely that at least a small percentage of the iron in our system is not colloidal. Alternate forms of As−Fe−NOM interactions are also consistent with our results. Clearly, a significant fraction of the iron is colloidal. However, the issue of whether these colloids are dominantly NOM-stabilized (oxy)hydroxides or formed by Fe(III)-induced coagulation of NOM is unresolved, and the constancy of the ratio of complexed arsenate to iron through a wide range of iron concentrations (Figure 5) suggests that the latter may be more important in our system. If this is the case, then arsenate chelation by ferric cations entrained within the coagulated NOM may be the dominant arsenate binding mechanism.

While the exact nature of arsenic binding by NOM-suspended Fe(III) is not yet fully characterized, and is worthy of further study, the results of this work are nonetheless striking, as they have clearly established the formation of aquatic complexes between arsenate and natural organic matter. The work has further shown the critical role that ferric iron plays in the aquatic association and the importance of stable colloidal moieties in these systems. The dominant effect of iron, independent of the NOM sample employed, suggests a broader role of Fe (and perhaps Al (*38*)) in other studies of binding of species such as arsenite (*13*) and Sb (*39*) to solution-phase NOM.

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