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# Natural Organic Matter Affects Arsenic Speciation and Sorption onto Hematite

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Arsenic mobility in natural environments is controlled primarily by sorption onto metal oxide surfaces, and the extent of this sorption may be influenced strongly by the presence of other dissolved substances that interact with surfaces or with arsenic itself. Natural organic matter (NOM), a prevalent constituent of natural waters, is highly reactive toward both metals and surfaces and is thus a clear candidate to influence arsenic mobility. The objectives of this study were therefore to reveal the influences of diverse NOM samples on the sorption of arsenic onto hematite, a model metal oxide, as well as to reveal influences of arsenic on the sorption of NOM, using conditions and concentrations relevant to natural freshwater environments. Of the six NOM samples tested, four formed aqueous complexes with arsenate and arsenite. The extent of complexation varied with the NOM origin and, in particular, increased with the cationic metal (primarily Fe) content of the NOM sample. In addition, every NOM sample showed active redox behavior toward arsenic species, indicating that NOM may greatly influence redox as well as complexation speciation of arsenic in freshwater environments. When NOM and As were incubated together with hematite, NOM dramatically delayed the attainment of sorption equilibrium and diminished the extent of sorption of both arsenate and arsenite. Consistent with this result, when NOM and As were introduced sequentially, all NOM samples displaced sorbed arsenate and arsenite from hematite surfaces, and arsenic species similarly displaced sorbed NOM from hematite in significant quantities. Competition between NOM and As for sorption thus appears to be a potentially important process in natural waters, suggesting that NOM may play a greater role in arsenic mobility than previously recognized. In addition, in all sorption experiments, arsenite was consistently desorbed or prevented from sorbing to a greater extent than arsenate, indicating that interactions with NOM may also partially explain the generally greater mobility of arsenite in natural environments.

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## I. Introduction

Arsenic is a toxic trace element of great contemporary concern due to its contamination of ground, surface, and drinking waters throughout the world (1–4). Arsenic exists in natural environments primarily as oxyacids of As(V), or arsenate, and of As(III), or arsenite. Arsenate is predominantly anionic at circumneutral pH, while arsenite is uncharged (5). Arsenic mobility in natural systems is controlled primarily by adsorption onto metal oxide surfaces (6–8), involving surface complexation reactions in which the oxygen moiety of the arsenate or arsenite displaces an hydroxyl group on the metal oxide surface to generate an inner-sphere complex (9, 10). The common oxides of iron, aluminum, and manganese appear to be the most important sorbents of arsenic in natural systems (7, 11–13).

Arsenate and arsenite both sorb rapidly and extensively onto a variety of iron and aluminum oxides in clean laboratory systems (11, 14–18), suggesting that the two species might behave similarly in natural systems. However, arsenite is found to be consistently more mobile than arsenate in soils and sediments (19, 20, 61–64), apparently due in part to reduction of sorbent oxides to soluble forms followed by reduction of arsenate to arsenite (1, 8, 19–22). This phenomenon is cause for significant concern given the far greater toxicity of arsenite (23), and additional insight into the underlying mechanisms will be essential to the prediction of risks posed by arsenic and to the design of effective remediation schemes.

Natural organic matter (NOM) is a potentially important factor influencing arsenic biogeochemistry. Operationally defined fractions of NOM known as humic and fulvic acids may interfere strongly with arsenic adsorption under some circumstances (24–26), and arsenic mobility may be increased by NOM present in soil amendments (27), but the parameters governing these effects are not well understood. As the structurally complex product of biomass decomposition, NOM molecules possess unique combinations of functional groups, including carboxylic, esteric, phenolic, quinone, amino, nitroso, sulfhydryl, hydroxyl, and other moieties, the majority of which are negatively charged at neutral pH (28). The chemical and physical behavior of NOM species can vary widely among geographical areas, depending on the biomass of origin and locally active transformation processes, but in general NOM readily forms both aqueous and surface inner-sphere complexes with cationic metals and metal oxides (29–31). Aqueous NOM-metal complexes may, in turn, associate strongly with other dissolved anions, presumably by metal-bridging mechanisms (26), diminishing the tendencies of such anions to form surface complexes. Because NOM is not only potentially reactive toward arsenic but also ubiquitous in natural waters, typically found at concentrations between 1 and 50 mg C/L, its potential influences on arsenic sorption and mobility are great.

NOM is also known to catalyze both oxidation and reduction reactions among chemical species, in part by the quinone-mediated formation of free radicals (32–35). In this way it may serve as an electron shuttle among otherwise kinetically inert redox species (34) and even between microorganisms and metals (36). Because arsenic speciation appears to be an important factor regulating its mobility, this dimension represents another means by which NOM may influence As transport and toxicity.

The purpose of this study was to elucidate NOM influences on As sorption and speciation by examining interactions of six geographically diverse aqueous-phase NOM samples with

arsenate, arsenite, and hematite, a model metal oxide. Because NOM is widespread in soils and sediments (37), NOM is likely to encounter surface sites prior to an influx of contaminating arsenic in many instances. The opposite scenario, in which arsenic-coated metal oxide surfaces are exposed to NOM, may also be important, as in the initiation of passive biotreatment of mine drainage (38, 39). Therefore, NOM was introduced to hematite both before and after arsenic species in sorption experiments. As expected, NOM reactivities toward As and the metal oxide varied with origin, but remarkable consistency was found in their abilities to influence arsenic redox speciation and, in general, to promote arsenic mobility, particularly in the case of arsenite.

## II. Materials and Methods

**Materials.** Water samples containing NOM, chosen to represent a variety of geographic origins, were collected from the Rio Negro 80 km NW of Manaus, Brazil (July 2000), the South Fork of the Forty Mile River in Alaska, 141° 45' 14.3 W by 64° 14' 48.3 N (April 2001), a stream in the Michigan Upper Peninsula near Republic, MI (March 1999), Monitoring Well 6 (MW-6) in the Tennessee Park wetland near Leadville, CO (March 1993), the Suwannee River near the Okefenokee Swamp, GA (July, 1995), and the Inangahua River near Lewis Pass, New Zealand (February 1997). Samples were stored for up to 5 years in sealed polyethylene bottles in darkness at 4 °C. Each sample was filtered (0.45  $\mu$ m), diluted to 10 mg C/L to represent a consistent concentration within the range found in many natural waters (40), and brought to 10 mM ionic strength with NaCl prior to use except where specified. The 10 mg C/L concentration corresponded to a 0.14 mM concentration of carboxylic acid functional groups, assuming an average of 1 carboxylic acid group in every six carbon atoms (40). Other than dilution and pH and ionic strength adjustments, NOM samples were used without intentional modification. No NOM isolation or fractionation procedures were used, and no specific efforts were made to alter the NOM redox state.

Colloidal hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) was synthesized by acidic hydrolysis of FeCl<sub>3</sub> followed by collection, washing, and sonication (41), yielding particles 0.2–0.3  $\mu$ m in diameter with a pH<sub>pzc</sub> near 8.6. Sorption site density was estimated at 2.31 sites/nm<sup>2</sup> (41), corresponding to  $6.67 \times 10^{-5}$  mol sites/g hematite or, in a suspension of 300 mg/L hematite, a site concentration of  $2 \times 10^{-5}$  M. This concentration is similar to higher sediment loads found in natural waters (42). X-ray diffraction analysis (Scintag XDS 2000) using Cu- $\alpha$  radiation confirmed the identity of the solid as hematite, and rounding of the baseline spectra indicated the presence of trace amounts of amorphous iron oxides. All chemicals were of reagent grade or higher (Sigma-Aldrich, Fisher Scientific), and ultrapure HCl (GFS Chemicals) was used in all acidifications.

**Arsenic Analyses.** Total arsenic was determined by graphite furnace atomic absorption spectroscopy (GF-AAS) (Perkin-Elmer Analyst 800). Arsenic speciation was determined by a continuous HPLC-ICP-MS system in which aqueous arsenate and arsenite were separated by HPLC (Waters 600) using LC-SAX anion-exchange resin (Sigma-Aldrich) with 12.5 mM ammonium malonate/1% methanol eluent, pH 4.7. Subsequent inline hydride generation (Perkin-Elmer FIAS Chemifold) with cysteine and sodium borohydride reductants and ICP-MS detection (Perkin-Elmer Sciex 6100) (43) allowed detection of arsenic species with a limit of 0.2 ppb and variability of  $< \pm 5\%$ . Organically complexed arsenic was retained on the resin, allowing passage of only “free” arsenic. All samples were stored at 4 °C in darkness and were analyzed within 1 week of sampling. Computations were performed using MassLynx software.

**NOM Characterization.** Prior to dilution, NOM samples were analyzed for metal content by ICP-AES (Perkin-Elmer Optima 4300DV) and for total arsenic by GF-AAS. Total organic carbon was determined by combustion at pH 2 (Shimadzu TOC-5000A) or at pH 3 (OI Corp. Model 1010) for the MW-6 sample to avoid precipitation. FTIR spectra were also collected of all NOM samples, both as liquids concentrated by rotary evaporation and as freeze-dried samples, and are available upon request. Following dilution, acidity of NOM samples was measured by titrating N<sub>2</sub>-purged samples from pH 2.0 to 6.0 with NaOH (0.0954 N) that had been standardized with potassium hydrogen phthalate. Absorption of 254 nm UV radiation was measured spectrophotometrically (Perkin-Elmer Lambda 11), and ionic strength was measured by conductivity with respect to NaCl using a YSI Model 35 conductance meter. Nitrate, phosphate, and sulfate were measured by ion chromatography (Dionex DX-600, AS14A column).

**Aqueous Complexation.** Arsenic species were diluted from stock solutions to reach 1  $\mu$ M final concentrations in 10 mL of diluted NOM (10 mg C/L, pH 6.0). Duplicate solutions were shaken gently (100 osc/min) for 90 h in darkness to prevent photooxidation (44) at  $22 \pm 1$  °C and stored at 4 °C until analysis.

**Arsenic Sorption onto Hematite.** Colloidal hematite and colloidal hematite with presorbed NOM (described below) were suspended using sonication in 10 mL Milli-Q water, pH  $6.00 \pm 0.05$ ,  $I = 10$  mM NaCl, to reach a final hematite concentration of 300 mg/L in acid-washed 50 mL Oak Ridge tubes. After a 30 min equilibration, arsenic species were diluted from stock solutions into hematite suspensions to reach 1  $\mu$ M final concentrations, and suspensions were shaken gently in darkness. For kinetic experiments, tubes were capped loosely to allow gas exchange with the atmosphere, and  $< 1.0$  mL aliquots were periodically removed, centrifuged for 15 min ( $18\,000 \times g$ ), and analyzed for total arsenic by GF-AAS. For equilibrium experiments, tubes were capped tightly to prevent evaporation and incubated for 100 h before centrifugation and analysis of the aqueous phase. For preparation of hematite with presorbed arsenic, suspensions were incubated for 12 h to reach adsorption equilibrium and then centrifuged (3 h at  $6000 \times g$ ) to collect the hematite and sorbed species. A maximum pH change of  $< 0.3$  units occurred during all sorption reactions. All experiments were performed in triplicate at  $22 \pm 1$  °C.

**NOM Sorption onto Hematite.** Colloidal hematite and colloidal hematite with presorbed arsenic were suspended using sonication to reach 300 mg/L in 10 mL of each diluted NOM sample and incubated with gentle shaking in darkness. For kinetic experiments,  $< 1.0$  mL aliquots were periodically removed, centrifuged for 15 min ( $18\,000 \times g$ ), and analyzed for total organic carbon. For equilibrium experiments, suspensions were incubated for 48 h before centrifugation and analysis of the aqueous phase. For preparation of hematite with presorbed NOM, suspensions were incubated for 12 h to reach adsorption equilibrium and then centrifuged (3 h at  $6000 \times g$ ) to collect the hematite and sorbed species. A maximum pH change of less than 0.3 units occurred during sorption reactions. All experiments were performed in triplicate at  $22 \pm 1$  °C.

**Spectroscopic Analyses.** Attenuated total reflectance Fourier transformed infrared (ATR-FTIR) spectroscopy was performed using 225–500 scans per experiment at a resolution of 4 cm<sup>-1</sup> (Perkin-Elmer Paragon 1000 FT-IR) without smoothing. Colloidal hematite (200  $\mu$ L of a 15 g/L suspension) was dried uniformly onto a ZnSe crystal with a 45° cut and 11 internal reflections, and the crystal was fitted with a flow-through cell (3 mL total volume). Aqueous solutions of arsenic or NOM were then pumped over it at a rate of 1 mL/min; complete mixing was assumed to occur in the cell. Dissolved

TABLE 1. Metal Content of Water Samples

NOM sample	metal content ( $\mu\text{g/L}$ normalized to 1 mgC/L NOM)			
	Fe	Al	Mn	total
Rio Negro	14 (1) <sup>a</sup>	18 (1) <sup>a</sup>	1 (<1) <sup>a</sup>	33 (2) <sup>a</sup>
South Fork	<1 (2)	<1 (1)	1 (<1)	1 (1)
Upper Peninsula Stream	46 (2)	7 (1)	0 (<1)	53 (2)
Monitoring Well 6	685 (16)	13 (<1)	23 (1)	722 (17)
Suwannee River	13 (<1)	8 (<1)	1 (<1)	21 (<1)
Inangahua River	3 (2)	46 (1)	1 (<1)	49 (1)

<sup>a</sup> Mean (standard deviation),  $n = 3$ .

species were not detectable, and all peaks were therefore assumed to originate from species sorbed onto the hematite surface, which remained intact throughout the course of all experiments. Background spectra of hematite and ultrapure water (pH 6,  $I = 10$  mM NaCl) were subtracted from all experimental spectra, and resulting peak heights corresponded to quantities of sorbate associated with the hematite surface (45).

### III. Results and Discussion

**NOM Characterization.** To reveal characteristics of the aqueous NOM samples potentially related to their chemical behaviors, each sample was analyzed for total metal content, of which results for the most abundant (iron, manganese, and aluminum) are shown (Table 1). Previous work has indicated that these metals are virtually completely complexed with the NOM in each sample (30). Samples were also analyzed for total organic carbon, acidity, and UV absorbance at 254 nm (Table 2) as well as major anion content (data not shown). FTIR spectra were taken of concentrated samples (available upon request). Several notable differences among the samples emerged: the sample from Monitoring Well 6 (MW-6) contained by far the greatest total carbon-normalized metal content, at about 700  $\mu\text{g/L}$ , as well as the greatest UV absorbance, greatest total organic carbon, greatest anion content, and greatest acidity of all samples. These features are consistent with its origin in a wetland receiving acid mine drainage. Among the other samples, values for total metal content were all less than 60  $\mu\text{g/L}$ , with the South Fork sample possessing the lowest at 1  $\mu\text{g/L}$ . Carbon-normalized (specific) ultraviolet radiation absorbance at 254 nm (SUVA), commonly used as an indication of aromatic character in NOM samples, varied among the samples from  $\sim 0.03$  to  $\sim 0.09$ . FTIR spectra also showed great variability among samples. Carbon-normalized acidity varied from  $10^{-4.6}$  to  $10^{-6.16}$  equiv/L, and total organic carbon in undiluted samples ranged from 11.8 mg/L for the Inangahua River to 35.0 mg/L for the MW-6 sample. Nitrate, sulfate, and phosphate, anions with potentially competitive behavior toward arsenic oxyacids during sorption (46), were undetectable in all samples except MW-6, which contained nearly 0.4 mg nitrate/mg C and 2.7 mg sulfate/mg C. The NOM set thus provided high variability in UV absorbance, acidity, and eutrophic vs oligotrophic origin, and somewhat less variability in anion and metal content.

**Kinetics of As and NOM Sorption onto Hematite.** Kinetic characteristics of the sorption reactions between As and hematite, between NOM and hematite, and between As and NOM-coated hematite were determined to lend insight into the geochemical significance of these processes. Sorption of arsenate, arsenite, and Upper Peninsula NOM onto colloidal hematite were each rapid, reaching equilibrium within 6 h (Figure 1a). Note that these systems represented an approximate 7-fold excess of NOM carboxylic acid functional groups to sorption sites and an approximate 20-fold excess of sorption sites to arsenic molecules. All concentrations,

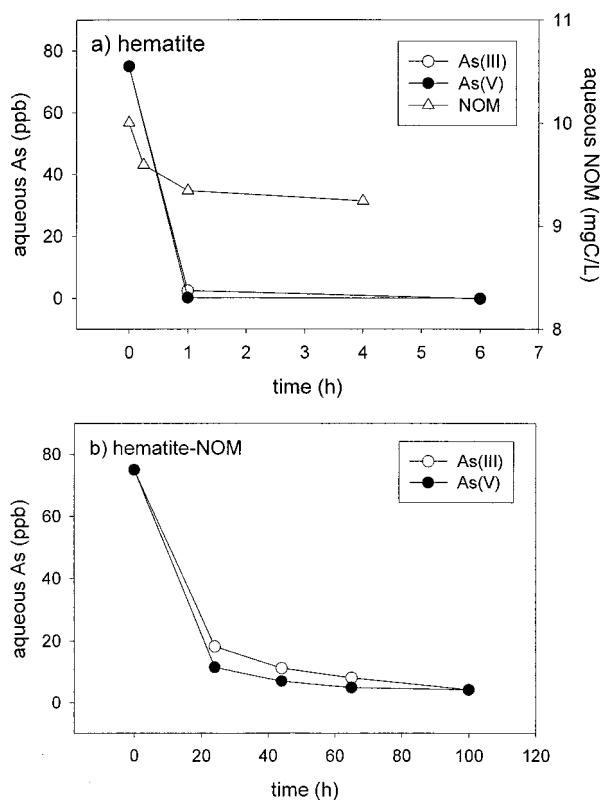


FIGURE 1. Kinetic characteristics of arsenate (1  $\mu\text{M}$ , 74.9 ppb), arsenite (1  $\mu\text{M}$ , 74.9 ppb), and Upper Peninsula Stream NOM (10 mgC/L) sorption onto colloidal hematite (300 mg/L). Hematite was incubated (a) individually with arsenate, arsenite, and NOM and (b) with NOM followed by arsenate and arsenite, each at pH 6.0 and  $I = 10$  mM. Symbols represent the average of triplicate samples, and error bars show the range of data. Error bars that are not visible are smaller than the symbols.

however, were environmentally realistic (40, 42, 47, 48). Based on these data, and on related published data showing rapid arsenic sorption to metal oxides (14, 16, 49, 50), systems incorporating arsenic, NOM, and hematite might be expected to attain sorption equilibrium rapidly. However, preliminary coating of hematite with Upper Peninsula Stream NOM dramatically slowed the attainment of sorption equilibrium by both arsenate and arsenite from less than 6 h to approximately 100 h, with arsenite sorption diminished to a slightly greater extent at early timepoints (Figure 1b).

Kinetics of adsorption are controlled by the availability and accessibility of surface sites (51), the relative charges of the surface and adsorbing species, and the rate of complexation of the dissolved species with surface sites (52). Consequently, the observed extension of equilibration time may have resulted from the following factors: occupation and/or obstruction of a large proportion of sorption sites by the NOM, slowing the rate at which arsenic species encountered favorable sites; coagulation of hematite particles by NOM, further diminishing the number of available surface sites; and possibly, dependence of arsenic sorption on NOM desorption to reveal favorable surface sites. By any mechanism, however, this phenomenon could be quite important in rapidly flowing aquatic systems in which a coating of NOM on solid surfaces could greatly extend the distance over which arsenic species, particularly arsenite, traveled before becoming sorbed.

**Aqueous Complexation of NOM with As Species.** To determine the extent of aqueous complexation of arsenate with NOM, arsenate was incubated with six different NOM samples in batch systems until sorption steady state was



TABLE 2. NOM Characteristics

NOM sample	characteristic			
	pAcidity	SUVA <sub>254</sub> (L/mg/cm)	ionic strength (mM)	NOM concn before dilution (mgC/L)
Rio Negro	5.43 (0.11) <sup>a</sup>	0.037 (0.002) <sup>a</sup>	0.1 (<0.1) <sup>b</sup>	12.5 (0.2) <sup>c</sup>
South Fork	5.04 (0.01)	0.030 (0.002)	0.34 (<0.1)	19.9 (0.3)
Upper Peninsula Stream	6.16 (0.11)	0.053 (0.01)	0.11 (<0.1)	25.3 (0.4)
Monitoring Well 6	4.6 (0.14)	0.089 (0.002)	0.16 (<0.1)	35.0 (0.5)
Suwannee River	5.15 (0.24)	0.043 (<0.001)	0.09 (<0.1)	34.6 (0.5)
Inangahua River	4.76 (0.13)	0.035 (<0.001)	0.08 (<0.1)	11.8 (0.2)

<sup>a</sup> Mean (range of data), *n* = 2. <sup>b</sup> Datum (instrument error), *n* = 1. <sup>c</sup> Mean (standard deviation), *n* = 3.

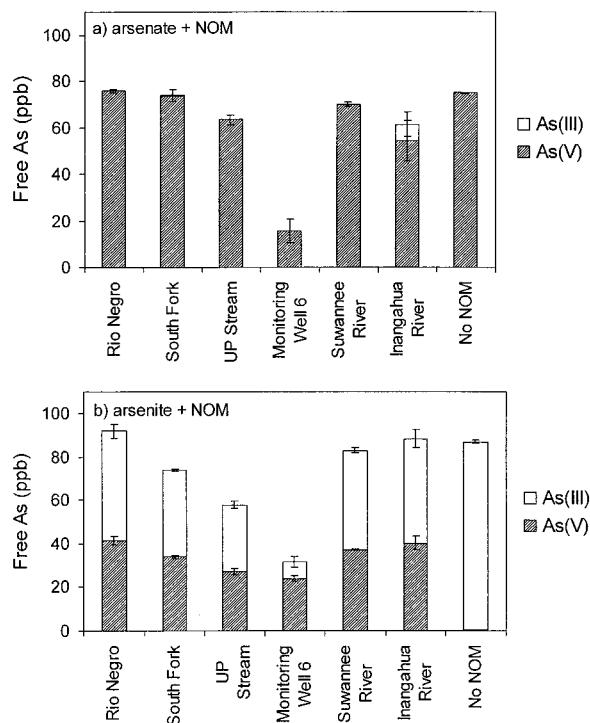


FIGURE 2. Aqueous complexation of NOM with arsenic oxyanions. Aqueous solutions of (a) arsenate and (b) arsenite (74.9 ppb As, 1  $\mu$ M) were incubated with NOM samples (10 mg C/L) for 90 h in darkness, pH 6.0, *I* = 10 mM. Samples from duplicate incubations were analyzed by HPLC/ICP-MS. Error bars show the range of data.

reached. HPLC-ICP-MS analyses revealed that Upper Peninsula Stream, MW-6, and Inangahua River NOM samples significantly lowered total free arsenic concentrations, indicating that extensive aqueous complexation between the NOM samples and arsenate had occurred (Figure 2a). In contrast, Rio Negro, South Fork, and Suwannee River NOM samples changed the concentration of free arsenic very little compared to controls lacking NOM (Figure 2a). Total As was accounted for by GF-AAS in all samples (data not shown).

An analogous experiment performed with arsenite revealed that significant aqueous complexation again occurred with Upper Peninsula Stream and MW-6 NOM samples (Figure 2b), while Rio Negro and Suwannee River NOM again had little if any effect. In contrast to the results with arsenate, however, South Fork NOM did show significant complexation behavior, while Inangahua River NOM did not. Also in contrast to results obtained with arsenate, every NOM sample significantly altered the redox speciation of the arsenite, with the result that 20–50% of the free arsenic was present as arsenate at the end of the experiment (Figure 2b).

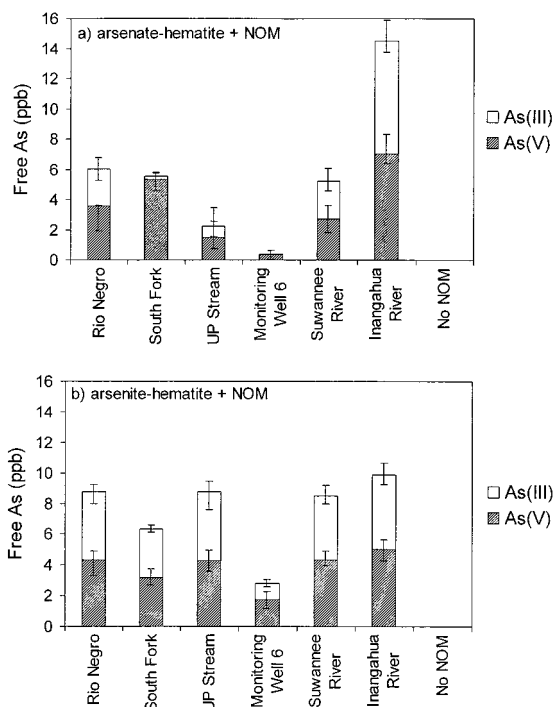
Because the As speciation was changed greatly in the presence of the NOM, it is likely that both As(V) and As(III) were complexed in this experiment, obscuring the capacity

of the NOM samples to form complexes with arsenite alone. Nevertheless, the results are consistent with those obtained with arsenate, indicating that complexation with NOM can proceed to a significant extent with both species. The results also emphasize the great variability in complexation behavior of diverse NOM samples toward arsenic as well as the potentially great impact that exposure to NOM may have on arsenic redox speciation.

**NOM Mediation of As Redox Changes.** While only the Inangahua River NOM reduced As(V), yielding free As(III) (Figure 2a), all of the samples facilitated the oxidation of As(III) to produce free As(V) (Figure 2b). Metals carried within the samples could conceivably have contributed to the redox changes, either directly, as described for Fe and Mn (53–55), or indirectly, using the NOM as an electron shuttle (28, 36). However, the metal contents of the NOM samples showed no apparent relationship to their abilities to facilitate transformation of As species (statistical analyses not shown). Molecular oxygen, which readily oxidizes As(III) under some circumstances (54), was present but was also not likely to have served as the ultimate oxidant due to the minimal As oxidation in control experiments and to the slow kinetics of interactions between O<sub>2</sub> and NOM (28) compared to the time scale of the experiment. NOM structures themselves were thus the most likely redox-active agents influencing the arsenic speciation, acting by means of quinone or other functional groups that had been previously oxidized or reduced in their native environments (28, 36). Notably, the redox activity was both rapid and distributed widely among samples of very different origin and chemical composition.

**Complexation Mechanism.** A ternary complexation mechanism, in which cationic metals mediated the strong association between NOM functional groups and arsenic oxyanions, was one plausible mechanism to explain the observed interactions. To explore the importance of such a mechanism, the metal content of each NOM-containing water sample was compared to the ability of the respective NOM to form aqueous complexes with arsenate. The MW-6 sample possessed both the greatest metal content and greatest complexation activity, while the others showed a similar trend toward increasing complexation activity with metal content. While intriguing, this result was not statistically significant due to the absence of sufficient NOM samples with intermediate metal contents (data not shown). Metal bridging thus appears to be a potential mechanism underlying the association between NOM and arsenic, highlighting the need for additional experiments to define the roles of cationic metals in As–NOM complexation phenomena.

**As–NOM–Hematite Sorption Equilibria: 1a. Competition of NOM with Sorbed Arsenic in Batch Systems.** This experiment represented a scenario in which NOM enters an environment containing As sorbed onto metal oxides, such as might occur in the establishment of a passive remediation system to treat arsenic-contaminated water. Arsenate (Figure 3a) and arsenite (Figure 3b) were allowed to sorb individually onto colloidal hematite, reaching nearly 100% sorption. NOM



**FIGURE 3.** Release of sorbed As species from hematite by NOM. Colloidal hematite (300 mg/L) was incubated for 12h with (a) arsenate or (b) arsenite (74.9 ppb As,  $1 \mu\text{M}$ ), centrifuged ( $6000 \times g$  for 3 h), resuspended in an aqueous solution of NOM (10 mgC/L), and incubated for 48 h to reach adsorption equilibrium in darkness, pH 6.0,  $I = 10 \text{ mM NaCl}$ . Samples from triplicate incubations were analyzed by HPLC/ICP-MS. Error bars show the range of data.

was subsequently introduced and each system was allowed to reequilibrate. Analyses of the aqueous phases showed that NOM caused the release of significant amounts of arsenic into solution, with free As species ranging from 0.5 to 16 ppb ( $0.07\text{--}0.21 \mu\text{M}$ ), representing 6–21% of the total. Control experiments lacking NOM were analyzed for total As by GF-AAS and showed no detectable aqueous arsenic, indicating that the interference of other solution-phase anions with arsenic sorption was not detectable (Figure 3a,b). Sorbed arsenite (Figure 3b) was released to a greater extent than was sorbed arsenate (Figure 3a) by every NOM except the Inangahua River sample, consistent with the generally greater mobility of As(III) in aqueous systems.

Because NOM-arsenic complexes were also present in solution, in proportions similar to those shown in Figure 2a,b, the total amount of As mobilized from the solid surface was actually much greater than that estimated by measurements of free arsenic: analysis of total aqueous arsenate desorbed from hematite by the MW-6 NOM showed that  $\sim 4.1$  ppb of total As was released into solution, compared to the  $\sim 0.5$  ppb that passed through the HPLC column and was designated as “free”. In comparison to the proposed MCL for drinking water of 10 ppb As (56), this total quantity is appreciable, indicating that NOM in water supplies could potentially increase aqueous As to an extent that would affect the compliance of the waters with national standards.

The influences of NOM samples on As redox speciation were again evident, showing very similar patterns in the oxidation of As(III) to those of aqueous complexation experiments (compare Figures 2b and 3b). NOM samples showed much greater tendencies to reduce As(V) in the presence of the hematite, however, with every NOM sample exhibiting As(V)-reducing activity (compare Figures 2a and 3a). Possible explanations for the increased As reduction are that the hematite acted as a surface catalyst or, alternatively,

as an electron-transfer intermediate between reduced NOM moieties and As(V) (57–59). Both scenarios are consistent with the great variability in As(V) reduction among the NOM samples as well as the observation that the only NOM that reduced As(V) in aqueous solution (Inangahua River, Figure 2a) also showed by far the greatest As(V) reduction overall in the presence of hematite (Figure 3a).

NOM samples showed great individuality in their tendencies to mobilize free As into solution in ways generally inversely proportional to their aqueous complexation behaviors toward As. Two samples that had shown the greatest abilities to complex both arsenate and arsenite, MW-6 and Upper Peninsula Stream (Figure 2a,b), for example, released the least free As(V) into solution from the hematite, and MW-6 released the least As(III) (Figure 3a,b), suggesting that much of the desorbed As may have become organically complexed. Conversely, the Inangahua River NOM, which showed only moderate aqueous complexation activity toward arsenate (Figure 2a) and none toward arsenite (Figure 2b), allowed by far the most free As to be released into solution from the hematite (Figure 3a). Other NOM samples that showed little As complexation behavior (Rio Negro, South Fork, and Suwannee River, Figure 2a,b) also tended to cause significant releases of free As from hematite (Figure 3a,b), supporting the hypothesis that desorbed arsenic appeared in free form only when complexation with NOM was weak.

The uniform abilities of NOM samples to mobilize sorbed As, over time scales of at most 2 days in length, is the most striking result of this experiment. Although the extent of As desorption varied widely, each NOM sample desorbed a significant amount of arsenic compared to controls lacking NOM, indicating that NOM may play a significant role in arsenic mobility in natural systems as well.

#### As-NOM-Hematite Sorption Equilibria: 1b. Competition of NOM with Sorbed Arsenic in a Continuous-Flow System.

To provide an additional line of evidence describing NOM interactions with arsenic-coated hematite surfaces, such a system was investigated spectroscopically using ATR-FTIR. After 4 h, stable peaks representing sorbed arsenate appeared in the vicinity of  $870 \text{ cm}^{-1}$  (Figure 4). Reference spectra of 100 mM aqueous arsenate, showing peaks slightly offset (near  $911$  and  $877 \text{ cm}^{-1}$ ) from those of sorbed arsenate due to differences in bond stretching of surface-bound and dissolved arsenate, are provided for comparison. A subsequent rinse of the arsenate-coated surface with deionized water desorbed no detectable arsenic. Upper Peninsula Stream NOM (10 mg C/L) was then passed over the surface. A spectrum of aqueous UP NOM is shown for reference. Significant amounts of NOM sorbed to the surface after 12 h, indicated by peaks near  $1747$ ,  $1558$ , and  $1394 \text{ cm}^{-1}$  that correspond to metal-bound carboxylates, H-bonded phenolic groups, and aromatic C–H stretching, respectively (45, 60). Slight decreases in the sizes of arsenate peaks were noticeable as well. The results of this experiment indicated that prior arsenate sorption onto hematite, even to the extent of surface saturation, still allowed sorption of appreciable NOM onto the surface.

#### As-NOM-Hematite Sorption Equilibria: 2a. Competition of As with Sorbed NOM in a Batch System.

The inverse configuration of the previous experiment, representing a scenario in which arsenic enters a NOM-containing soil or sediment, was also of interest due to its relevance to natural environments experiencing an influx of contaminated water. In these experiments, NOM was presorbed onto colloidal hematite, followed by the introduction of arsenate or arsenite. Arsenic remaining in solution following the incubation thus represented As that was prevented from sorbing onto the hematite. As expected, virtually 100% of both arsenate and arsenite sorbed onto the hematite in the absence of NOM (Figure 5 (parts a and b, respectively)). Every NOM sample diminished the ability of arsenate to sorb onto the hematite

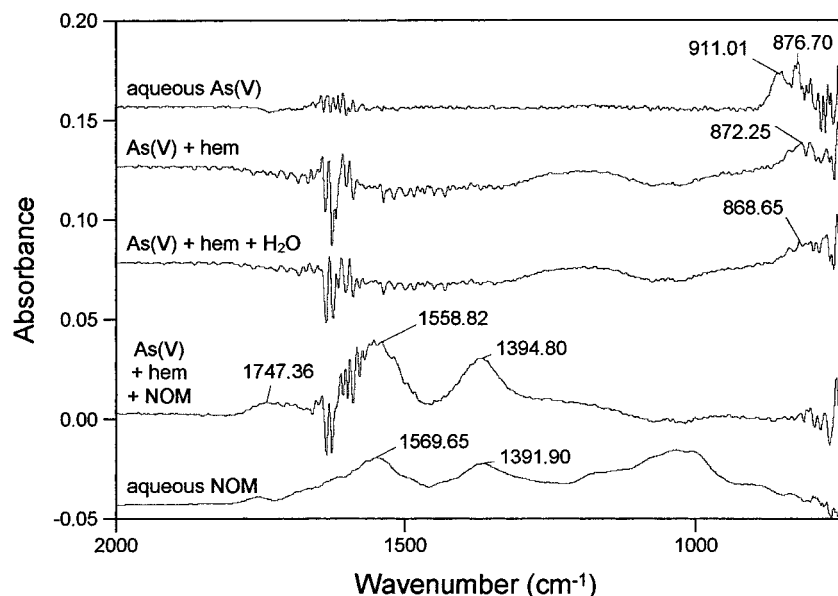


FIGURE 4. Sorption of NOM onto arsenate-coated hematite. Colloidal hematite was dried onto a ZnSe crystal and aqueous arsenate (10  $\mu$ M, pH 6.0,  $I$  = 10 mM NaCl) was passed over it (1 mL/min) until sorption equilibrium was reached (As(V) + hem). The crystal was rinsed with deionized water (As(V) + hem + H<sub>2</sub>O) and then with aqueous Upper Peninsula NOM (As(V) + hem + NOM); aqueous arsenate (100mM) is shown for comparison. Spectra were collected by ATR-FTIR

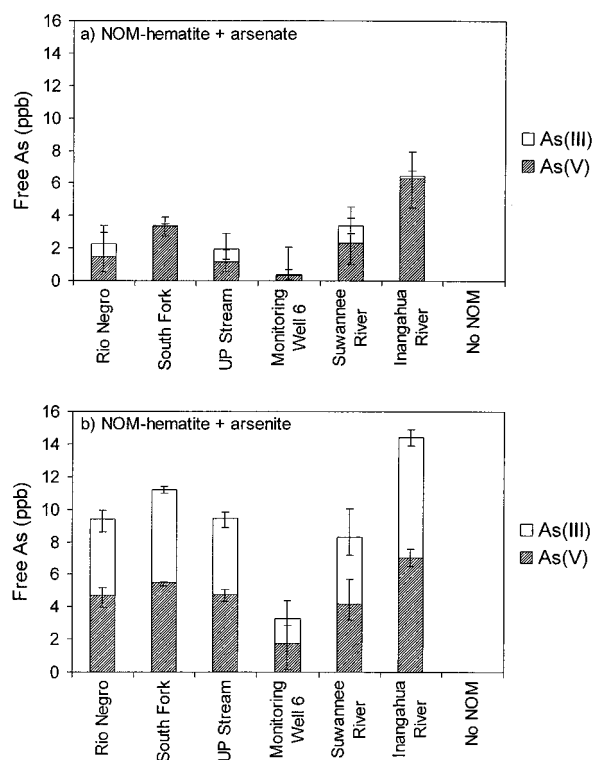


FIGURE 5. Sorption of arsenic species onto NOM-coated hematite. Colloidal hematite (300 mg/L) was incubated with NOM (10 mgC/L) for 12 h, and concentrated solutions of (a) arsenate or (b) arsenite were added to reach final concentrations of 74.9 ppb (1  $\mu$ M) As. Triplicate suspensions were incubated 100 h to reach adsorption equilibrium in darkness, pH 6,  $I$  = 10 mM NaCl, centrifuged, and supernatants were analyzed by HPLC/ICP-MS. Error bars show the range of data.

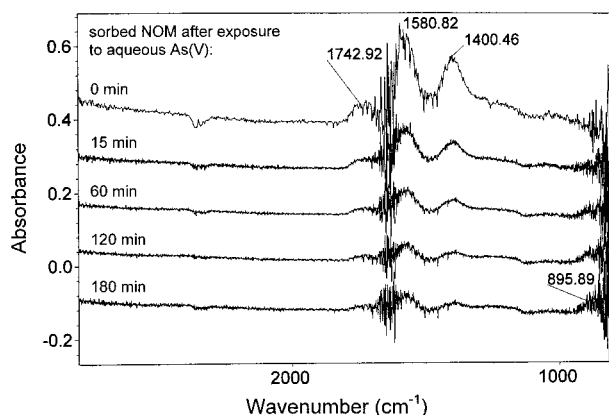
(Figure 5a), causing 0.5–8 ppb free arsenic, or 0.6–10% of the total, to remain in solution. Controls lacking NOM, analyzed for total As by GF-AAS, showed no detectable aqueous arsenic. Importantly, in addition, NOM samples each inhibited the adsorption of introduced arsenite (Figure 5b)

even more effectively than that of arsenate (Figure 5a), with free As in solution ranging from 3 to 14 ppb (4–19% of the total), consistent with the generally greater mobility of As(III) compared to As(V) in natural aquatic systems (19, 20, 61–64).

At the environmentally relevant concentrations used, approximate 20-fold excesses of NOM carboxylate groups were present compared to hematite surface sites, with the consequence that simple occupation and/or obstruction of surface sites may have been partially responsible for the observations. However, support for an important role of complexation was provided by analysis of total arsenic prevented from sorbing by the MW-6 NOM: while free arsenic measured only  $\sim$ 0.3 ppb, total arsenic in solution reached over 6.5 ppb, indicating that total As mobilized by the NOM was again much greater than indicated by measurements of free As alone. The levels of free arsenic remaining in solution, unable to sorb onto NOM-coated hematite, showed a very similar pattern among individual NOM samples to the levels of free arsenic displaced from hematite by NOM in the previous batch experiments. In particular, free arsenic was lowest in all sorption experiments using the strongly As-complexing MW-6 NOM (compare Figure 3a,b and Figure 5a,b) and greatest in all cases using the weakly As-complexing Inangahua River NOM (compare Figure 3a,b and Figure 5a,b). The comparability of results between these experiments suggests that the aqueous complexation between NOM and arsenic was sufficiently strong, and/or that the rate of exchange between surface-bound and aqueous species was sufficiently great, that NOM could substantially increase arsenic mobility whether it were introduced into a system before or after the arsenic. In this context, the mechanism for greater inhibition of arsenite sorption may have involved the relative stabilities of sorbed NOM, arsenate, and arsenite species onto hematite as well as the relative stabilities of NOM-arsenate and NOM-arsenite complexes.

Free arsenic again showed redox speciation changes in the presence of NOM. Arsenate reduction occurred in some samples, to a generally greater extent than observed in aqueous systems (compare Figures 2a and 5a) but to a generally lesser extent than that observed when sorbed As was exposed to NOM (compare Figures 3a and 5a). Perhaps,





**FIGURE 6.** Sorption of arsenate onto NOM-coated hematite. Colloidal hematite was dried onto a ZnSe crystal and Upper Peninsula NOM (25.3 mgC/L, pH 5.2,  $I = 10$  mM NaCl) was passed over it (1 mL/min) until sorption equilibrium was reached. Aqueous arsenate (10 mM, pH 6.2) was then introduced (1 mL/min), and spectra were collected by ATR-FTIR after 0, 15, 60, 120, and 180 min.

due to the NOM coating, the hematite's ability to mediate redox reactions between NOM and As was diminished. Arsenite oxidation, however, occurred to virtually the same extents with all NOM samples in both sorption (Figures 3b and 5b) and aqueous complexation (Figure 2b) experiments. Clearly, the oxidation of As(III) by NOM was a much more favorable process than the reduction of As(V), as would be expected in these oxygenated systems. This implies that NOM interference with arsenite sorption may have been tempered by its tendency to oxidize the arsenite to a form that appears to sorb more stably to natural materials and to complex with NOM itself.

**As-NOM-Hematite Sorption Equilibria: 2b. Competition of As with Sorbed NOM in a Continuous-Flow System.** To augment the results observed in batch systems, the fate of the Upper Peninsula NOM was examined spectroscopically in an analogous continuous-flow system.

Adsorption of the NOM onto hematite reached a steady state within 4 h, and after 17 h aqueous arsenate (10 mM) was passed over the NOM-coated hematite film. Spectra revealed rapid removal of adsorbed NOM (Figure 6), indicating that arsenate was causing NOM to be released into solution, presumably by either competition for sorption sites or by aqueous complexation. The diminution of the NOM peak sizes indicates that approximately 60% of the NOM was removed from the hematite over 3 h (45). Though very weak, As peaks seemed also to appear in the  $890\text{ cm}^{-1}$  range. Because the concentration of aqueous arsenate used was quite high, the observed effects are certain to be much smaller in natural environments. Nevertheless, the results are consistent with those of the batch experiments, conducted at environmentally relevant concentrations, and add support to the potential of arsenate to displace sorbed NOM into aqueous environments.

**Geochemical Importance of NOM Interactions with Arsenic.** The collection of experiments presented above reveal several consistent phenomena. First, despite the predominantly anionic character of both NOM and arsenate, aqueous complexation between them does occur to an appreciable extent, possibly through ternary complexation involving cationic metals. Second, NOM and arsenic oxyacids compete strongly with each other for sorption onto hematite at both environmentally representative and higher concentrations tested, and third, diverse NOM samples show pronounced redox activity toward arsenic. Finally, NOM generally interacts with arsenic oxyacids in ways that promote arsenic mobility and especially promote mobility of arsenite relative to that

of arsenate. For natural environments, the implication is that sorption may still be the most important mechanism controlling As mobility in a system, but that NOM can be expected to diminish the strength of this mechanism to an extent that must be taken into account in the prediction of As speciation and mobility. Work with additional metal oxides, additional NOM samples, and additional aqueous conditions will be required to quantify the effects of each of these phenomena under a variety of environmental conditions. Nevertheless, these basic observations suggest that NOM may be a sufficiently important influence on arsenic mobility to warrant its consideration in geochemical models used in contaminant transport prediction and remediation design.

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