Stability of inorganic arsenic species in simulated raw waters with the presence of NOM


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Abstract Effect of natural organic matter (NOM) on the stability of inorganic arsenic species in simulated raw water was examined at circumneutral pH. An ion chromatography—inductively coupled plasma mass spectrometry system was used for simultaneous determination of As(III) and As(V). A reduction of arsenate (As(V)) to arsenite (As(III)) was observed in the unfiltered simulated raw waters (USW). The As(V) reduction to As(III) did not occur in the simulated waters that passed through a 0.2 μm membrane (FSW). Microorganism activities is probably the major reason causing As(V) reduction in the USW. In the FSW without NOM, As(III) tended to be oxidized into As(V). The addition of 0.036 mM of Fe(II) significantly facilitated the oxidation. The presence of 10 mg/L Suwannee River NOM as C inhibited As(III) oxidation no matter whether Fe(II) existed or not. The experimental results suggest that NOM can mediate distribution of inorganic arsenic species in water, thus it is an important factor controlling the mobility and toxicity of arsenic in drinking water.

Keywords As(III); As(V); Fe(II); NOM; oxidation

Introduction
Arsenic is a human carcinogen that attacks multiple sites in the human body (Smith et al., 2000; LaGrega et al., 2001). In order to reduce the potential risks that arsenic may cause to human health, the World Health Organization recommended a maximum arsenic concentration in drinking water as 10 μg/L (WHO, 1993). In 2001, the U.S. Environmental Protection Agency adopted the 10 μg/L standard for arsenic in drinking water, replacing the old standard of 50 μg/L (USEPA, 2001). Based upon the latest data and statistics, it is estimated that around 40 million people in Bangladesh are at risk of chronic arsenic poisoning (Karim, 2000). Arsenic in source drinking water originates naturally from the weathering arsenic–containing rocks and soils. It exists in water primarily as oxyanions of trivalent arsenite, (As(III)), or pentavalent arsenate, (As(V)) (Smedley, et al., 2002). As a contaminant in water, As(III) is more problematic than As(V) since As(III) is more toxic and more mobile than As(V) (Viraraghaven et al., 1999). Because of the variation in toxicity and removal efficiency between As(III) and As(V) (Jiang, 2001), knowledge on the speciation distribution in drinking water is essential.

The inorganic arsenic species are unstable in natural waters due to the transformation between As(III) and As(V). The stability of As(III) and As(V) in aquatic environment has been reported to be dependent on water pH, redox potential, the presence of microbes, and the presence of precipitating metals such as Mn and Fe (Spiethoff et al.,...
In oxic waters, As(III) tends to be oxidized into As(V), while in anoxic and acidic waters, As(V) tends to be reduced to As(III) (Smedley et al., 2002). The redox reactions between As(III) and As(V) can be facilitated or inhibited by the presence of microbes or metals in water (McCleskey, 2004). For example, 500 μg/L of As(III) in a simulated groundwater was found to be almost completely oxidized into As(V) within 100 min at pH 7.8–8.0 with several additions of 2 mg/L Fe(II), whereas the same amount of As(III) in the same simulated water could keep its redox speciation for weeks if Fe(II) was not added (Hug et al., 2001). Though extensive studies have been conducted on the stability of arsenic in various water samples, accurate determination of arsenic redox speciation in a specific natural water remains difficult as many other factors that may affect arsenic stability have not been considered in previous studies. For instance, little information is available on how natural organic matter (NOM) affects the stability of As(III) and As(V) in water.

NOM is a complex mixture of acidic organic molecules that originates from a variety of natural sources. It is ubiquitous in natural waters and is an essential element controlling the fate and bioavailability of heavy metals in aquatic environment. NOM possesses unique combinations of functional groups, including carboxylic, esteric, phenolic, quinone, amino, nitroso, sulfhydryl, hydroxyl, and other moieties. The hydroquinone moieties within NOM are redox active and may react with inorganic arsenic species or compete with them for oxidants or reductants, and thus thermodynamically or kinetically affect the distribution of As(III) and As(V) in natural waters. Redman et al. (2002) and Ko et al. (2004) reported that NOM affected inorganic arsenic speciation distribution in synthetic raw water at pH 6.0–7.0 after 2–4 day incubation. The effect of NOM on arsenic transformation kinetics was not discussed in their papers.

The primary objective of this study was to investigate the effect of NOM on the stability of inorganic arsenic species in simulated raw waters. An ion chromatography–inductively coupled plasma mass spectrometry (IC–ICP-MS) system was used to simultaneously determine the concentrations of As(III) and As(V) in water. The effect of NOM on the Fe(II) catalytic oxidation of As(III) was also examined.

**Experimental methods**

**Materials**

All chemicals were of analytical grade. Milli-Q water was supplied by the Millipore MR3 water purifier system. Suwannee River NOM (SRNOM), a well characterized NOM, was purchased from the International Humic Substances Society. Sodium arsenite (NaAsO₂, 99%) and sodium arsenate (Na₂HAsO₄·7H₂O, 99%) were obtained from Sigma-Aldrich. Sodium chloride (NaCl, 98%) and ferrous sulfate (FeSO₄·7H₂O, >99%) were purchased from Fisher.

The stock solution of As(III) or As(V) (13.3 mM) was prepared by dissolving a given amount of NaAsO₂ or Na₂HAsO₄·7H₂O in Milli-Q water. The arsenic stock solutions were stored in high density polyethylene bottles, and were kept in a refrigerator at 4°C for up to 6 weeks. The simulated raw water without NOM was prepared by dissolving 0.585 g NaCl in 1 L Milli-Q water. The simulated raw waters with NOM was prepared by mixing 20 mL SRNOM stock solution (500 mg/L as C) with 980 mL simulated water without NOM in order to reach a NOM concentration of 10 mg/L as C. The pH values of the simulated waters were adjusted to 6.0 ± 0.1. Some aliquots of the simulated raw waters were filtered through a 0.2 μm membrane (Gelman FP-Verical) to remove microbes. The unfiltered simulated raw water and filtered simulated raw water are denoted as USW and FSW, respectively.
Experimental procedures

Batch experiments were performed to investigate the stability of arsenic species in simulated raw waters with and without NOM. The stock As(III) and As(V) solutions were diluted with 10 mL simulated raw waters with/without NOM, and were mixed to produce a total arsenic level of 0.4–1 μM. The pH of the mixture was adjusted to 6.0 ± 0.1 using diluted 0.1 M HCl or 0.1 M NaOH. The solutions were then sealed and shaken gently at 100 rpm in the dark to avoid photooxidation. All experiments were performed at room temperature (22°C). Samples were taken at 0.5, 1, 2, 4, 7 d, and were stored in the dark at 4°C till analysis.

To study the effect of NOM on As(III) stability with the presence of Fe(II), the simulated raw waters were mixed with a concentrated Fe(II) solution to prepare solutions containing 0.036 mM Fe(II) (2 mg/L as Fe) right before the addition of As(III). To preserve the arsenic speciation, 50 μL of 2M H₂SO₄ was added into 10 mL of the solutions to lower the pH to less than 2.0.

Arsenic analysis

The concentrations of the two inorganic arsenic species were determined simultaneously using an IC–ICP-MS system. Both As(III) and As(V) behave like weak acids in water. The dissociation constants for As(III) and As(V) are 9.29 (Korte and Fernando, 1991) and 2.26 (Perrin, 1982) respectively. Within the pH range of 3.0 to 9.0, As(III) exists primarily as uncharged H₃AsO₃, whereas the predominant species for As(V) include monovalent H₂AsO₄ and divalent HAsO₄²⁻. Therefore, As(III) and As(V) can be separated with an anion exchange column. In this study, a Dionex AS7 column with an AG7 guard column was used to separate As(III) and As(V) in the simulated raw waters. The mobile phases used were 0.5 mM HNO₃ and 50 mM HNO₃. The pH of the two mobile phases were 3.3 ± 0.1 and 1.8 ± 0.1, respectively. The detailed gradient programme for separating As(III) and As(V) was based on Kohlmeyer et al. (2002) and is present in Table 1. An on-line AD25 UV detector was used to monitor the amount of NOM in the sample. The concentrations of the separated arsenic species were detected using a Finnigan Element 2 sector field high resolution ICP-MS (Thermo Electron Corporation). The ICP-MS has a quartz concentric nebulizer and a quartz double pass spray chamber. The sampling and skimmer cones were made of Nickel. The peak areas of different arsenic species in standards and samples were obtained by integrating the ICP-MS signal with time using the software of Matlab 6.5. The detection limit for As(III) or As(V) was 0.2 μg/L, which is equivalent to 0.0026 μM of arsenic. The relative standard deviations for three injections of a sample were within 2%. The retention time shifts for As(III) and As(V) were less than 1.7%.

Table 1 Gradient programme for As(III) and As(V) separation using the Dionex AS7 column with a AG7 guard column

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Phase A (0.5 mM HNO₃, pH 3.3)</th>
<th>Phase B (50 mM HNO₃, pH 1.8)</th>
<th>Pump mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 3.0</td>
<td>100%</td>
<td>0</td>
<td>Isocratic</td>
</tr>
<tr>
<td>3.0 – 4.0</td>
<td>50%</td>
<td>50%</td>
<td>Linear</td>
</tr>
<tr>
<td>4.0 – 9.0</td>
<td>50%</td>
<td>50%</td>
<td>Isocratic</td>
</tr>
<tr>
<td>9.0 – 10.0</td>
<td>100%</td>
<td>0</td>
<td>Linear</td>
</tr>
<tr>
<td>10.0 – 15.0</td>
<td>100%</td>
<td>0</td>
<td>Isocratic</td>
</tr>
</tbody>
</table>
Results and discussion

IC–ICP-MS chromatograms for As(III) and As(V)

Figure 1 presents a typical chromatogram, for the conditions listed in Table 1, of a sample containing As(III) and As(V). The sample contained 0.27 μM (20 μg/L) of each arsenic species and 10 mM NaCl. The chromatogram shows that As(III) and As(V) could be completely separated within 8 min. The retention times for As(III) and As(V) were 1.8 and 6.9 min, respectively. Besides the peaks of As(III) and As(V), there was an additional peak eluted at 10 min. The peak area of the additional peak did not change with the As(III) or As(V) concentration, but it increased significantly as the Cl\(^-\) concentration in the sample was increased from 10 mM to 100 mM. This observation suggests that the additional peak in the chromatogram was caused by \(^{40}\text{Ar}^{35}\text{Cl}^+\) dimer, which is consistent with the literature (Kohlmeyer et al., 2002). The addition of 10–50 mg/L SRNOM as C in the sample neither changed the retention times of the two arsenic species nor produced any other peaks in the chromatogram. No peaks were observed from the on-line AD25 UV detector during the period of analysis, which suggests that SRNOM or its complex with arsenic was retained in the anion exchange column during the separation process.

Arsenic stability in USW or FSW without NOM

The stability of the inorganic arsenic redox species in USW or FSW was examined and the results are presented in Figure 2. The initial total arsenic concentration was 1 μM, with an initial As(III)/As(V) ratio of 1:1. NOM was not present in these simulated waters.

Figure 2 Stability of As(III) and As(V) in (a) USW and (b) FSW. Error bar represents the relative error for duplicate samples. Total arsenic concentration, 1 μM; Initial As(III)/As(V) ratio, 1:1; pH, 6.0
**Figure 2(a)** shows the concentration change of As(III) and As(V) in the USW with time. The concentration of As(III) increased gradually in USW. The increase of As(III) was in accompany with the decrease of As(V). The sum concentration of the two arsenic species remained unchanged within 7 d, suggesting that As(V) was gradually reduced to As(III). The standard reduction potentials of As(V)/As(III) couple for various species in water are listed in Equations 1–4 (Santhanam and Sundaresan, 1985). Under the experimental conditions, the major species of As(III) and As(V) species are $\text{H}_3\text{AsO}_3$ (equivalent to $\text{HAsO}_2$) and $\text{H}_2\text{AsO}_4^-$, respectively. The $E^0$ (As(V)/As(III)) at pH 6.0 can be obtained from the Nernstian Equation 2, which is 0.139 V. Since the initial ratio of As(V) to As(III) was 1:1, the redox potential of As(V)/As(III) should be 0.139 V under the experimental conditions. According to Eq.5, the standard potential of $\text{O}_2/\text{H}_2\text{O}$ is $(1.229 - 0.059 \text{pH})$, which equals to 0.875 V at pH 6.0. Considering the concentration of dissolved oxygen, which was found to vary from 4.7–3.3 mg/L in the simulated waters, the redox potential of $\text{O}_2/\text{H}_2\text{O}$ should be within the range of 0.818–0.816 V, which is more positive than that of As(V)/As(III). The thermodynamic calculation indicates that the reduction of As(V) to As(III) would be unlikely unless some reducing agents existed in the USW.

The stability of As(III) and As(V) in FSW is presented in **Figure 2(b)**. Contrary to the result obtained in the USW, As(III) tended to be oxidized to As(V) in the FSW instead of the reduction of As(V) to As(III) (**Figure 2(a)**). The gradual oxidation of As(III) to As(V) is not surprising according to the aforementioned thermodynamic calculation. The dissolved $\text{O}_2$ in the simulated waters should be responsible for the oxidation of As(III) to As(V) in FSW.

The comparison of **Figures 2(a) and 2(b)** suggests that the reducing agents existing in the USW could not pass through the 0.2-μm membrane. The reduction of As(V) to As(III) in deionized water was also reported in Hall et al. (1999), in which microorganism activities were considered to be the major reason for the As(V) reduction. Our results appear to support this hypothesis because almost all the microbes in water can be removed by a 0.2 μm membrane. Another explanation for the observed As(V) reduction in the USW could be the presence of granular activated carbon (GAC), which is used in the Millipore water purifier system for removing organic impurities. Accordingly, the effect of GAC on As(V) stability in the FSW was examined. No As(III) was detected after the solution of 1 μM As(V) was mixed with 2 mg/L of GAC for 7 d (data not shown). The total concentration of arsenic in solution, however, decreased significantly with the presence of GAC, suggesting that the GAC could adsorb arsenic in the solution. The result suggests that GAC might not be the major reason for the reduction of As(V) to As(III) in the USW. Further experiments regarding the adsorption capability of GAC to As(III) is needed to confirm this.
Effect of NOM on stability of inorganic arsenic species in FSW

The stability of the two inorganic arsenic species in the presence of 10 mg/L SRNOM as C was examined. To avoid the interference from microbes and/or other possible reducing agents in the Milli-Q water, the FSW was used in all experiments. The results are presented in Figure 3.

With the presence of 10 mg/L SRNOM as C, the concentrations of As(III), As(V), and total arsenic in the simulated raw waters did not change within 7 d, which is different from the results obtained in FSW without NOM (Figure 2(b)). The comparison of Figures 4 with Figure 2(b) suggests that SRNOM tended to inhibit As(III) oxidation.

NOM possesses unique combinations of functional groups, including carboxylic, esteric, phenolic, quinone, amino, nitroso, sulfhydryl, hydroxyl, and other moieties. The hydroquinone moieties within NOM are redox active and may react with As(V) or O₂, and thus thermodynamically or kinetically inhibited the oxidation of As(III) to As(V) in the simulated raw waters. Since the oxidation of As(III) to As(V) without NOM was mainly due to dissolved oxygen in water, the inhibited As(III) oxidation in the presence of NOM indicates that NOM seems to undergo oxidized degradation under our experimental conditions.

As(III) stability in presence of NOM and Fe(II)

Fe(II) is a common component in natural waters. It is also an essential element controlling the speciation transformation between As(III) and As(V) in aquatic environment. Upon exposure to air or oxygen, the presence of Fe(II) can significantly accelerate the oxidation of As(III) to As(V) (Hug et al., 2001; Samanta and Clifford, 2005). Among the limited publications regarding Fe(II) facilitated oxidation of As(III), few of them have shown the role of NOM during this process. Accordingly, the stability of As(III) in the presence of Fe(II) with and without NOM was examined, and the results are presented in Figure 4. The FSW was used in these experiments.

Figure 4(a) shows As(III) stability with and without Fe(II) in the FSW that did not contain NOM. No matter whether Fe(II) was present in the simulated waters or not, the concentration of As(III) decreased with time. In the absence of Fe(II), As(V) concentration increased with time, and the total concentration of the two arsenic species did not change. It suggests that As(III) was transformed to As(V). After 4 d, about 14% of As(III) was oxidized into As(V) in the FSW. In the presence of Fe(II), As(V) concentration initially increased with time and then decreased after 2 d. About 0.1 μM of As(V)
was detected in the FSW by the end of the 2-d incubation. The detected As(V) was equivalent to 25% of the initial amount of As. The results suggest that Fe(II) facilitated the oxidation of As(III) in the FSW. The catalytic effects of Fe(II) on As(III) oxidation in natural waters have been reported in the literature (Hug et al., 2001). Figure 4(a) also suggests that the total concentration of As(III) and As(V) decreased gradually in the NOM-free FSW that contained Fe(II). A similar phenomenon was also observed by Samanta and Clifford (2005). They ascribed the mass loss of the total inorganic arsenic in solution to the adsorption of As(V) onto iron hydroxide, which was formed when Fe(II) was oxidized into Fe(III). In our experiments, all the samples were acidified to pH < 2.0 using 2 M H₂SO₄. The formed iron hydroxide would be dissolved under such an acidic condition, and the As(V) attached to the iron hydroxide surface would be re-dissolved into the solution. It seems unlikely that the gradual loss of arsenic was caused by the adsorption of As(V) by iron hydroxide. One possible explanation for the observed mass loss of As(V) and the total inorganic arsenic (As(III) + As(V)) after the 2-d incubation is that As(V) and Fe(III) reacted to formed new compounds that has very low solubility even at low pH values. The new compounds could be crystalline sorodite (FeAsO₄·2H₂O) and/or amorphous FeAsO₄·xH₂O.

Figure 4(b) shows As(III) stability with and without Fe(II) in the FSW that contained 10 mg/L SRNOM as C. In the absence of Fe(II), almost no As(III) was oxidized into As(V) after 4 d. The addition of 0.036 mM of Fe(II) slightly accelerate As(III) oxidation. When Fe(II) was present in the simulated waters, the concentration of As(V) initially increased with time and then decreased after the 2-d incubation. The trend for the change of As(V) concentration with time is similar with that obtained in the NOM-free FSW (Figure 4(a)). Maximum As(V) concentration detected in the FSW that contain NOM and Fe(II) was 0.068 µM, which is equivalent to 17% of the initial As concentration. The experimental results suggest that the catalytic effect of Fe(II) on As(III) oxidation was smaller in the presence NOM compared to that in the absence of NOM. NOM has strong complexation capability with various types of metals. The complexation between NOM and Fe(II) may inhibit Fe(II) oxidation to Fe(III) and therefore inhibit the oxidation of As(III) to As(V).

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