Preservation of Inorganic Arsenic Species in Groundwater

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Preservation of Inorganic Arsenic Species in Groundwater

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The objective of this research was to develop a robust preservation method for stabilizing inorganic As(III/V) species in synthetic and actual groundwaters. Ethylenediaminetetraacetic acid (EDTA), H_2SO_4, H_3PO_4, and EDTA−acetic acid (HAc) were evaluated in synthetic groundwater containing 3 mg/L Fe(II) in the pH range 6.5−8.4 and Eh range −100 to +200 mV at room temperature. In the absence of strong UV light, only EDTA−HAc was found to be an effective preservative under all the experimental conditions tested. A total of 89 samples (including 16 samples in triplicate) from 55 drinking water wells in Minnesota, California, and North Dakota were preserved with a combination of EDTA−HAc and speciated to evaluate its effectiveness for preserving inorganic arsenic species in actual groundwater samples. The preserved and field-speciated samples were repeatedly speciated and analyzed in the laboratory for up to 85 days after collection. Field-speciated As(III) concentrations were compared with the As(III) concentrations in the preserved samples. The results were highly correlated (slope 0.9773, $R^2 = 0.9986$), which indicates that during sample transportation and storage the distribution of arsenic species did not change for samples preserved with EDTA−HAc.

Introduction

Inorganic arsenic (As) is considered a human carcinogen with multiple sites of attack (*1*, *2*), and a common source of arsenic is contaminated drinking water, which has emerged as a global problem during the last decade (*3*). In groundwater, only inorganic arsenite, As(III), and arsenate, As(V) are significant. Due to a variation of removal efficiency of As(III) and As(V), a knowledge of their individual concentrations in drinking water is essential.

Arsenic species tend to be unstable in natural water with stability depending on the redox condition, pH, the presence of precipitating metals such as Fe(II/III), background ions, the presence of organic matter, and microbial activity. The ability to reliably preserve the native distribution until the sample can be analyzed in the laboratory is, to date, controversial. Acidification is a widely used protocol to preserve the As species in water samples. Feldman (*4*) demonstrated that ascorbic acid could preserve the As species over an 18 day period. However, Edwards et al. (*5*) reported that neither 0.1% ascorbic acid nor 0.05 M HCl was effective for preserving the inorganic arsenic species in natural waters. Cheam and Agemian (*6*) preserved the As species in deionized and natural waters at room temperature in polyethylene or Pyrex bottles with 0.2% (v/v) H_2SO_4, while Edwards et al. (*5*) used 0.05 % (v/v) H_2SO_4 as an effective preservative for the

inorganic arsenic species. HNO_3 and HCl were not effective, because, in the presence of 0.1% HNO_3 or HCl, oxidation of As(III) to As(V) could not be retarded (*7*, *8*).

Many researchers have reported problems with the preservation of As species in iron-rich waters. According to Aggett and Kriegman (*9*), samples should be preserved at pH 2.0 to prevent the precipitation of iron and the coprecipitation of arsenic. They also recommended preserving samples at lower temperature (0 °C). Borho and Wilderer (*10*) concluded that through the addition of HCl (pH < 2) and a great surplus of Fe(II) the As(III) concentration could be kept constant for at least 1 week even in oxygen-saturated Fe(III)-containing samples. The same observation was reported by McCleskey et al. (*11*). Bednar et al. (*8*) evaluated the efficiencies of H_2SO_4, HNO_3, HCl, and ethylenediaminetetraacetic acid (EDTA) as preservatives for arsenic-containing reagent waters, with and without 1 mg/L Fe(III) in the presence or absence of ambient light at room temperature. None of the mineral acids could maintain the distribution of As species in the dark or in the ambient light. However, EDTA alone could preserve the As species in opaque bottles without lowering the pH. In contrast, Gallagher et al. (*12*) reported that pH lowering to 3.2 with acetic acid was required when using EDTA for As species preservation in the presence of Fe(III). It is important to note that in most of the As preservation studies reagent-grade water without typical background composition was used (*7*, *8*, *10*, *12*). Furthermore, in most of the cases, Fe(III) was used to establish the influence of iron on As species preservation. It is more reasonable to use Fe(II), because it is often found in As(III)-contaminated groundwater, whereas dissolved Fe(III) is not found because of its insolubility.

In view of numerous possible influences on arsenic speciation during sampling and storage and conflicting literature reports on the effectiveness of preservatives, it was the objective of the present study to evaluate the abilities of the commonly used preservatives—EDTA, EDTA−acetic acid (HAc), H_2SO_4, and H_3PO_4,—to maintain the distribution of inorganic As species for at least 30 and possibly 85 days, in Fe(II)-containing synthetic waters with typical background composition at different pH and redox conditions (Eh) and in the presence of UV light. The best preservative for the synthetic groundwaters proved to be the mixture of EDTA−HAc, reported by Gallagher et. al. (*12*, *13*), and it was tested on actual groundwaters from around the Unites States. The effectiveness in preserving the distribution of inorganic As species was determined by comparing the results from immediate field speciation with subsequent laboratory speciation tests over periods up to 85 days.

Experimental Section

As(Tot) and As(III) Analysis. Arsenic analyses were performed using a Perkin-Elmer flow injection (FI) hydride generation (HG) atomic absorption spectrometer (AAS). Iron was measured by inductively coupled plasma mass spectrometry (ICP-MS).

To determine total arsenic (As(Tot) = As(III) + As(V)) samples were treated with L-cysteine in 2 M HCl and kept for 15 min at room temperature to reduce As(V) to As(III). For the determination of As(III) in the presence of As(V), the carrier HCl solution was replaced by 2 M citric acid/citrate buffer at pH 5.0. The detection limit (DL) measured as 3 times the standard deviation of the blank (*n* =10) was 0.04 μg/L for As(Tot) and 0.096 μg/L for As(III). The accuracy of the As(Tot) method was verified by analyzing six replicates of the NIST Standard Reference Material (NIST 1640, Certified

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Natural Water). The ion-exchange field speciation method using 1.34 mM EDTA and 87 mM HAc preserved samples previously developed for our AwwaRF project (*14*) was used in this study.

Reagents. All reagents were analytical reagent grade. Milli-Q (18 MΩ cm) water was used to prepare all solutions. Primary standards of 100 mg As/L of each species were prepared from sodium arsenite for As(III) and Sodium arsenate for As(V). Citric acid/citrate buffer solution was prepared using 2 M citric acid with pH adjusted to 5.0 using NaOH. Sodium tetrahydroborate solutions supplemented with NaOH were prepared fresh daily. To prepare a representative synthetic groundwater, the following salts were used NaNO₃, NaHCO₃, NaH₂PO₄·H₂O, NaF, Na₂SiO₃·9H₂O, MgSO₄·7H₂O, and CaCl₂·2H₂O (Sigma Chemical or EM Science). Fe(II) solution was prepared from ferrous ammonium sulfate (Fe(NH₄)₂(SO₄)₂·6H₂O) (Fisher Scientific).

Preparation of Arsenic-Containing Synthetic Groundwater at Different pH and Eh Conditions. For laboratory experiments, synthetic groundwater as described in our previous publications (*14, 15*) was used (Supporting Information, Table S1, for the composition of synthetic groundwater). It contained the typical background composition found in groundwaters contaminated with arsenic and used for potable water supplies, and it was chemically stable in the pH 6.5–8.5 range with respect to calcium carbonate as evaluated by the MINEQL+ Chemical Equilibrium Modeling program (*16*). The pH of the synthetic groundwater was adjusted into the range of 6.5–8.4 using dilute HCl and NaOH solutions.

To prepare Fe(II)-containing synthetic groundwater, N₂ was sparged continuously for 1.5 h into a 2.7 L brown glass bottle. After being sparged, freshly prepared Fe(II) solution was spiked into the synthetic groundwater to achieve a final concentration of 3.0 mg/L Fe(II), and then As(III) and As(V) were spiked separately. After 30–45 s, the first 500 mL (approximately) of the synthetic groundwater was used to rinse the sample collection tube, and then 500 mL of the synthetic groundwater was collected in a volumetric flask containing the required amount of preservatives and then transferred into 500 mL plastic sample bottles.

To study the effect of redox potential on the distribution of arsenic species in the synthetic groundwater, the redox potential was set to the required value by sparging mixtures of N₂, H₂, and/or compressed air (*17, 18*), with rates controlled by needle valves. To reduce the redox potential, a mixture of H₂ and N₂ (3:97) was sparged until the Eh value reached −100 ± 10 mV. If the Eh was far below the required Eh, then a mixture of compressed air and N₂ was sparged until the required Eh was attained. The oxidizing Eh value of +200 ± 10 mV was maintained by controlling the ratio of compressed air and N₂ during sparging. After the Eh value was stabilized at a given pH, Fe(II) was spiked under the sparging condition (Eh was readjusted if necessary) and subsequently preserved with one of the preservatives being studied.

UV Irradiation. To simulate solar radiation in the laboratory, UV light in the range of 320–400 nm was used. It exhibited a spectral composition and intensity similar to sunlight in the spectral region where dissolved iron species absorb the main fraction of light. Two pairs of Philips black lights housed in a specially constructed plywood box (76 × 33 × 61 cm³) were used. The advertised peak maximum for lamp emission spectrum was 365 nm, and the intensity of the incident UV radiation was 80 ± 10 W/m² (photon fluence rate = 244 × 10⁻⁶ mol m⁻² s⁻¹) as measured by a digital ultraviolet radiometer having maximum relative response at 375 nm. During UV irradiation, laboratory air was circulated through the box by a forced-draft fan to maintain the air temperature in the box at 22–24 °C. A maximum of six tightly
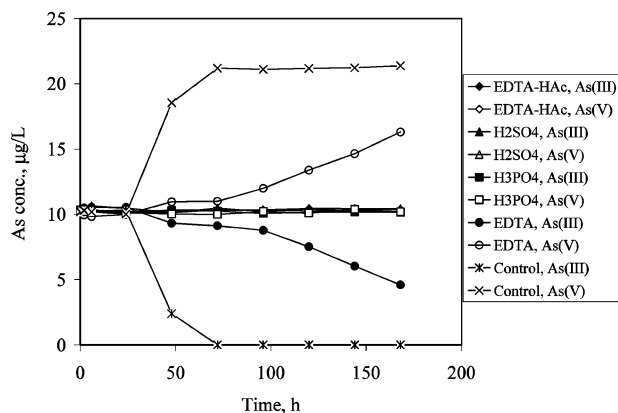

FIGURE 1. Preservation of inorganic As species with EDTA–HAc, EDTA, H₂SO₄, or H₃PO₄ in the synthetic groundwater (initial pH 8.4) having no Fe(II) in brown PP bottles at room temperature. The test solutions initially contained 10 μg/L each of As(III) and As(V).

capped 1 L polyethylene terephthalate (PET) bottles (7 cm in diameter) containing 500 mL of sample were illuminated in the box.

Results and Discussion

Preservation of Arsenic Species in the Synthetic Groundwater without Iron. Initially, both As(III)- and As(V)-containing synthetic groundwaters (pH ≈ 8.4) without iron were preserved with EDTA, EDTA–HAc, H₂SO₄, or H₃PO₄ at room temperature (22–24 °C) in brown propylene (BPP) bottles. The experimental results (Figure 1) indicate that As-(III) and As(V) were stable for 168 h (7 days) when EDTA–HAc, H₂SO₄, or H₃PO₄ was added as a preservative. EDTA alone (resulting pH 6.2) could not preserve the arsenic species for more than 3 days. After 24 h, As(III) was gradually oxidized to As(V), and about 55% As(III) oxidation was observed after 168 h (7 days). When no preservative was added to the synthetic groundwater, As(III) was stable up to 24 h, but within 72 h, 100% of As(III) was oxidized. According to the Eh–pH diagram (*19*), at pH 8.4 and redox potential >+200 mV, As(V) existing as HAsO₄²⁻ is the thermodynamically stable species. Thus, the conversion of As(III) to As(V) in the synthetic water without any preservative was expected. These initial experimental results verified that preservation would be necessary and that EDTA alone was insufficient for preserving the distribution of arsenic species in the synthetic groundwater even in the absence of Fe(II).

Preservation of Arsenic Species in the Synthetic Groundwater with Fe(II). Arsenic-containing synthetic groundwater (pH 8.4) with 3 mg/L Fe(II) was preserved with EDTA–HAc, H₂SO₄, or H₃PO₄ at room temperature (22–24 °C) in BPP bottles. All of the preserved samples remained colorless, but the unpreserved control samples became brownish with time due to the formation of colloidal Fe(III) (hydr)oxides. Initial concentrations of As(III) were measured within 2–3 min of preservation. It was observed that in the presence of Fe(II) at pH 8.4 without preservatives, As(III) was converted to As-(V) much faster (Figure 2) than in the absence of Fe(II) (Figure 1). Within three minutes after addition of Fe(II) in the synthetic water, about 25–35% of the As(III) was converted to As(V), and about 50–60% of As(III) was oxidized within 24 hours. A rapid decrease in As(III) concentration was observed within the first 5 h, and then As(III) decreased slowly with time. According to the literature (*19–21*), at natural pH, Fe(II) in groundwater can be slowly or quickly oxidized upon exposure to air. At pH 8.4, Fe(II) oxidation and Fe(III) (hydr)-oxide formation are much faster than at pH 6.4 (*19–22*). After Fe(III) (hydr)oxides are formed, the oxidation of As(III) to As(V) in the dark becomes very slow (*22*). Recently, Hug
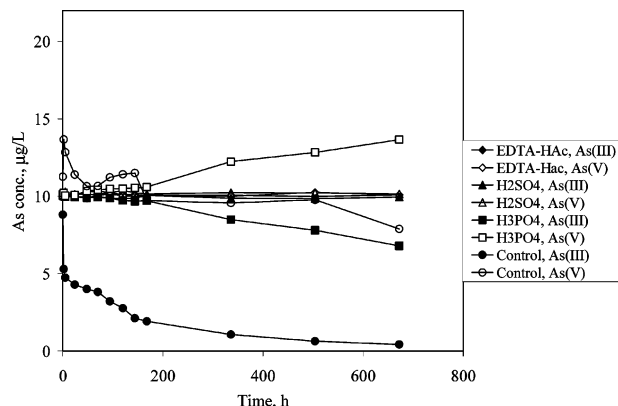
FIGURE 2. Preservation of arsenic species with EDTA−HAc, H₂-SO₄, or H₃PO₄ in the synthetic groundwater (initial pH 8.4) spiked with 3 mg/L Fe(II). Samples stored in brown PP bottles at room temperature. The test solutions initially contained 10 μg/L each of As(III) and As(V).

et al. (*22*) reported that several repeated additions of 2 mg/L Fe(II) could oxidize 500 μg/L As(III) at pH 7.8−8.0 in the dark almost completely within an hour. In contrast, the addition of Fe(III) had almost no effect. Our experimental results support these observations regarding the catalytic effect of Fe(II) on As(III) oxidation in the absence of a preservative. Initially, the concentration of As(V) increased due to the oxidation of As(III) in the presence of 3 mg/L Fe(II). However, with time, As(V) concentration decreased due to coprecipitation and sorption of As(V) onto Fe(III) (hydr)oxides. Though at pH 8.4 the adsorption of As(III) onto the Fe(III) (hydr)-oxides is minimal compared with As(V) adsorption, the loss of small amounts of As(III) by adsorption cannot be ignored. However, with a preservative such as, EDTA−HAc, H₂SO₄, or H₃PO₄, the As species were stable at room temperature for a long time. For example, the results in Figure 2 show that EDTA−HAc or H₂SO₄ could preserve the arsenic species up 672 h (28 days) at room temperature without significant changes in their distribution. H₃PO₄ was less effective and could preserve the distribution only up to 168 h (7 days), which agrees with Daus et al. (*19*) who reported that H₃PO₄ could preserve arsenic species in iron-rich water a maximum for 5−6 days at 20 °C.

Low pH and the complexing ability of the acids with iron have increased the stability of arsenic species in the Fe(II)-containing synthetic water. EDTA can form stable iron−EDTA complexes at acidic to neutral pH (*23*). Acetic acid can form

a weak complex with iron; however, Daus et al. (*19*) found that acetic acid alone could only preserve the arsenic species for a few days in iron-rich water.

Effect of UV Illumination on the Stability of Arsenic Species. Preserved and unpreserved samples (500 mL) of synthetic groundwater (pH 8.4) with 3 mg/L Fe(II) in transparent PET bottles were exposed to strong UV light to determine its effect on As(III) stability. Before illumination, As-(III) concentrations were measured, and then the samples were exposed to strong UV light for designated times. As(III) changes as a result of strong UV exposure are shown in Figure 3.

In the absence of UV light, the initially measured As(III) concentration without any preservative was about 25−35% lower than the actual As(III) spiked into the synthetic groundwater (as mentioned before). The initial loss of As(III) was probably due to the rapid oxidation of Fe(II) at pH 8.4, which facilitates As(III) oxidation as illustrated in the reactions for the oxidation of As(III) to As(V) shown in Table 1. Possible oxidants for As(III) oxidation (R11−R17) are generated during the oxidation of Fe(II) by oxygen (R1) and by other oxidants (R2, R3, R6, and R10). The major role for the oxidation of As(III) by the addition of Fe(II) may be the formation of the intermediate superoxides ($O_2^{\bullet-}$) by the reaction of Fe(II) and O_2 (R1). The As(III) oxidation proceeds to As(V) through the intermediate As(IV) state (R11 and R12). Once the intermediate As(IV) species are produced, they are rapidly converted to As(V) by dissolved O_2 (R15). However, in the presence of preservatives, As(III) was stable for 30 days or more in the dark. Fe(II) is more resistant to oxidation because of the low pH (1.8−3.2) and because it forms stable complexes by reacting with EDTA (for FeEDTA log $K=14.33$ (*23*), for H₂SO₄ log $K = 2.25$ (*36*), or for H₃PO₄ log $K = 22.25$ (*36*).

When the unpreserved sample was exposed to UV illumination, about 50% of the initial As(III) was oxidized within 20 min of UV exposure, and then the oxidation rate decreased (Figure 3). However, referring back to Figure 2, in the presence of 3 mg/L Fe(II) and the absence of UV illumination, it took about 2−4 h for 50% oxidation of As(III) under the same experimental conditions. The rapid oxidation of As(III) under UV illumination is presumably due to photolysis of Fe(OH)²⁺ (R18) and production of Fe(II), which is reoxidized back to Fe(III) by oxygen and other oxidants (R1−R3, R5, R6, and R10). Fe(III) recomplexes (R7), and the cycle starts again. Figure 3 also shows that neither EDTA−HAc, H₂SO₄, nor H₃PO₄ could prevent the rapid oxidation of As(III) in the presence of strong UV radiation and Fe(II).
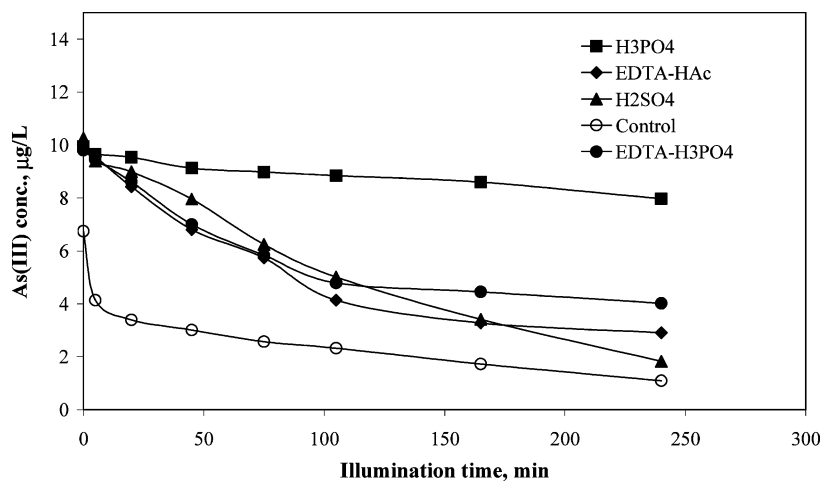

FIGURE 3. As(III) oxidation as a function of time during strong (80 ± 10 W/m²) UV exposure in transparent PET bottles in the initial pH 8.4 synthetic groundwater spiked with 3 mg/L Fe(II) and preserved with EDTA−HAc, H₂SO₄, EDTA−H₃PO₄, or H₃PO₄. The test solutions initially contained 10 μg/L of As(III).

TABLE 1. Relevant Reactions with Rate Constants Involved in the Arsenic Oxidation Process[a]

	reactions	k_n (M^{-1} s^{-1}) or k (M^{-1})	reference
	Iron-Related Reactions		
R1	$Fe(II) + O_2 \rightarrow Fe(III)OH^{2+} + O_2^{\bullet-}$	60 (pH 7.5)	(21)
R2	$Fe(II) + O_2^{\bullet-} + H^+ \rightarrow Fe(III) + H_2O_2$	1×10^7	(24)
R3	$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^-$	1.1×10^6	(25)
R4	$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet}$	$\sim0.01-0.02$	(26)
R5	$Fe(II) + HO_2^{\bullet} \rightarrow O_2 + Fe(II)$		
R6	$Fe(II) + {}^{\bullet}OH \rightarrow Fe(III) + OH^-$	3.2×10^8	(27)
R7	$Fe(III) \rightleftarrows Fe(III)OH^{2+} + H^+$	$pK_a = 2.3$	(28)
R8	$Fe(III)OH^{2+} \rightleftarrows Fe(III)(OH)_2^+ + H^+$	$pK_a = 3.6$	(28)
R9	$Fe(III)OH_2^+ \rightleftarrows Fe(III)(OH)_3^+ + H^+$	$pK_a = 7.9$	(28)
R10	$Fe(II) + CO_3^{\bullet-} \rightarrow Fe(III) + HCO_3^-$	3.6×10^8	(29)
	Arsenic Oxidation		
R11	$As(III) + O_2^{\bullet-} \rightarrow As(IV) + H_2O_2$	3.0×10^6	(22)
R12	$As(III) + {}^{\bullet}OH \rightarrow As(IV) + OH^-$	1.0×10^9 (pH 1–3)	(30)
R13	$As(III) + H_2O_2 \rightarrow As(V) + 2OH^-$	15.3 (pH 10)	(31)
R14	$As(III) + Fe(III) \rightarrow As(IV) + Fe(II)$		
R15	$As(IV) + O_2 \rightarrow As(V) + O_2^{\bullet-}$	1.1×10^9	(32)
R16	$As(IV) + Fe(III) \rightarrow As(V) + Fe(II)$		
R17	$As(III) + CO_3^{\bullet-} \rightarrow As(IV) + HCO_3^-$	1.1×10^8	(32)
	Photolysis and Its Follow-Up Reactions		
R18	$Fe(III)OH^{2+} + h\nu \rightarrow Fe(II) + {}^{\bullet}OH$	4.0×10^{-5} @360 nm	(22)
R19	$Fe(III)EDTA + h\nu \rightarrow Fe(II) + EDTAr$	1.1×10^{-4}	(33)
R20	$EDTAr + O_2 \rightarrow CH_2O + ED3A + O_2^{\bullet-}$	1.0×10^7	(34)
R21	$EDTAr + Fe(III)EDTA \rightarrow EDTAp + Fe(II)EDTA$	1.0×10^5	(35)
R22	$Fe(II)EDTA + O_x \rightarrow Fe(III)EDTA + O_x$	1.0×10^5	(33)
R23	$+HO_2^{\bullet} + O_2^{\bullet-} \rightarrow H_2O_2$	9.7×10^7	(24)

[a] EDTAr stands for the decarboxylated EDTA radical; EDTAp stands for the cationic, oxidized radicals; ED3A stands for ethylenediaminetriacetate; O_x stands for the sum of the concentration of O_2 and other reactive oxygen species.

Although only partially effective, H_3PO_4 was the best preservative in the presence of UV light. Thus, it was studied further by combining it with EDTA in a mixture of 1.34 mM EDTA and 20 mM H_3PO_4. The results shown in Figure 3 suggested that EDTA was playing an important role in the oxidation of As(III) during UV exposure. Within 40 min of exposure, about 32%, 28%, 22%, and 8% of the As(III) were oxidized in the presence of EDTA−HAc, EDTA−H_3PO_4, H_2SO_4, and H_3PO_4, respectively. EDTA forms a soluble complex with Fe(II) and Fe(III), and the Fe(III)EDTA complex goes through photolysis (R19) under the UV illumination to reportedly produce EDTA radicals. These react readily with O_2, resulting ultimately in the formation of CH_2O, ethylenediaminetriacetate (ED3A), and $O_2^{\bullet-}$ (R20). Again, the EDTA radical reacts with Fe(III)EDTA giving rise to another Fe(II)EDTA (R21). The Fe(II)EDTA complex oxidizes to Fe(III)EDTA in the presence of O_2 (R21). The oxidation of As(III) is enhanced by the formation of $O_2^{\bullet-}$ due to photodegradation of Fe(III)EDTA complexes. In the presence of H_3PO_4, the rate of oxidation of As(III) under the UV illumination was comparatively slow. This could be due to the formation of more stable iron phosphates, which were not readily photodegradable under the UV exposure.

The conclusion from the UV experiments is that the oxidation of As(III) to As(V) in the presence of Fe(II) depends strongly on the UV exposure, and no preservative tested could maintain the As(III/V) speciation. Therefore, samples should be preserved in opaque PP bottles to eliminate/minimize the influence of UV light. Alternatively, samples in translucent PP bottles should be stored in the dark until speciated and analyzed.

Preservation of Arsenic Species in the Synthetic Groundwater with Differing Redox Potentials and pH Values. Both redox potential and pH affect the stability of As(III/V) species. Under oxidizing conditions, $H_2AsO_4^-$ is dominant in the pH range of 2.1−7.1, while in the 7.1−11.0 pH range, $HAsO_4^{2-}$ is the dominant species. Under reducing conditions at pH less than about pH 9.2, the uncharged As(III) species, $H_3AsO_3^0$, is dominant. Experiments to determine the effectiveness of three preservatives were carried out at different initial pH and Eh values. The experimental data for the EDTA−HAc
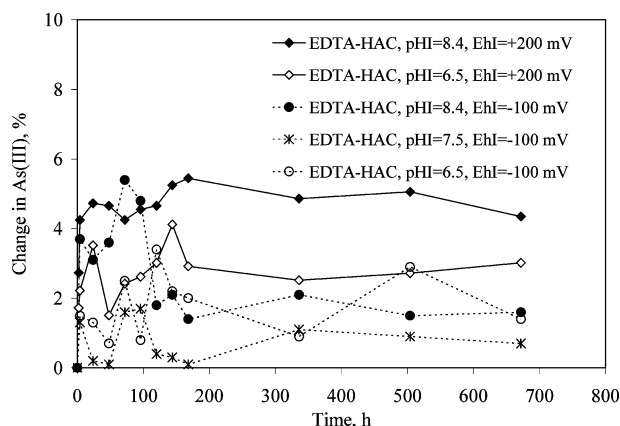

FIGURE 4. Change in As(III) concentration under oxidizing and (initial pH 8.4 and 6.5, Eh +200 ± 10 mV) reducing (initial pH 8.4, 7.5, and 6.5, Eh −100 ± 10 mV) conditions at room temperature up to 672 h (28 days) in the synthetic water containing 3 mg/L Fe(II) preserved with EDTA−HAc. Samples stored in brown PP bottles. The test solutions initially contained 10 μg/L of each As(III) and As(V).

preserved samples with the initial Eh (−100 ± 10 mV) at three different pH values are plotted in Figure 4, which indicates that EDTA−HAc preserved the arsenic species in the synthetic groundwater having the initial pH range 6.5−8.4 at reduced Eh (−100 mV) up to 28 days without any significant change. H_2SO_4 (Supporting Information, Figure S1) could preserve arsenic species at least up to 500 h (21 days) in the synthetic groundwater. But H_3PO_4 (Supporting Information, Figure S1) showed relatively poor performance in comparison with H_2SO_4 and EDTA−HAc. The Eh values of the control sample (without preservative) and samples with H_2SO_4, H_3PO_4, and EDTA−HAc were in the ranges of 105−115, 525−536, 397−412, and 374−389 mV, respectively. The trend for As(V) (not shown) will be opposite that of As(III), because As(V) is calculated as As(Tot) − As(III).

Similar experiments were carried out to determine the stability of As species under oxidizing conditions in the synthetic groundwater having an initial Eh value of +200 ± 10 mV at two different initial pHs (8.4 and 6.5). Samples were

TABLE 2. Utilizing LLS estimates of As(III) Concentrations in Drinking Waters Collected in Triplicate from Minnesota, California, and North Dakota To Predict As(III/V) Stability with Time

sample (final day, times analyzed[a])	Fe (mg/L)	As(Tot) at day 0 (μg/L)	As(III) at day 0 (μg/L)	As(V) at day 0 (μg/L)	slope of least-squares equation (μg/L/h)	change in As(III) concentration (μg/L)[b]	% As(III) at final day vs % As(III) at day 0
Minn-1 (85, 7)	1.08	15.3 ± 0.1	10.7 ± 0.0	4.5 ± 0.1	$m = 1.2 \times 10^{-4}$	−0.15 ± 0.1	104 ± 0.6
Minn-2 (73, 6)	4.12	90.5 ± 0.1	71.4 ± 0.4	18.5 ± 0.9	$m = 4.6 \times 10^{-4}$	−0.07 ± 0.8	100 ± 0.5
Minn-3 (72, 6)	3.17	56.3 ± 0.3	52.1 ± 0.1	3.9 ± 0.1	$m = -1.1 \times 10^{-4}$	+0.63 ± 0.3	98 ± 0.4
Minn-4 (69, 6)	2.67	96.4 ± 0.7	88.1 ± 0.4	8.3 ± 0.3	$m = 7.7 \times 10^{-4}$	+0.13 ± 0.4	100 ± 0.6
Minn-5 (65, 6)	1.32	9.8 ± 0.1	9.2 ± 0.0	0.6 ± 0.1	$m = -4.0 \times 10^{-5}$	+0.2 ± 0.0	97 ± 1.0
Minn-6 (64, 6)	1.44	66.9 ± 0.4	43.2 ± 0.3	23.7 ± 9.1	$m = 5.2 \times 10^{-4}$	+0.5 ± 0.3	98 ± 2.1
Minn-7 (30, 5)	3.24	39.5 ± 0.1	36.4 ± 0.3	3.1 ± 0.3	$m = -1.1 \times 10^{-3}$	+0.93 ± 0.3	95 ± 0.9
Minn-8 (58, 6)	0.17	4.9 ± 0.2	4.6 ± 0.1	0.4 ± 0.1	$m = -2.5 \times 10^{-5}$	−0.03 ± 0.2	104 ± 4.7
Minn-9 (56, 6)	4.64	52.4 ± 0.4	46.6 ± 0.9	5.8 ± 1.2	$m = 1.0 \times 10^{-4}$	−0.07 ± 0.8	101 ± 1.2
Minn-10[c] (57, 6)	1.48	47.9 ± 0.3	41.3 ± 0.8	6.6 ± 0.6	$m = 1.4 \times 10^{-2}$	−18.4 ± 0.7	80 ± 1.8
Minn-11 (57, 6)	1.23	12.1 ± 0.5	10.3 ± 0.3	1.8 ± 0.5	$m = 3.0 \times 10^{-4}$	−0.13 ± 0.3	99 ± 0.6
Calif-1 (57, 6)	0.25	25.5 ± 0.3	19.5 ± 0.6	5.4 ± 0.2	$m = 5.0 \times 10^{-4}$	+0.4 ± 0.3	95 ± 0.7
Calif-2 (57, 6)	0.48	13.9 ± 0.3	4.1 ± 0.6	9.9 ± 0.1	$m = -4.6 \times 10^{-5}$	−0.1 ± 0.1	100 ± 2.5
Calif-3 (57, 6)	0.35	18.3 ± 0.3	7.2 ± 0.6	11.1 ± 0.2	$m = -1.3 \times 10^{-4}$	0.1 ± 0.1	99 ± 2.4
Calif-4 (57, 6)	0.29	16.1 ± 0.3	14.9 ± 0.5	1.2 ± 0.1	$m = -8.3 \times 10^{-5}$	+0.9 ± 0.1	93 ± 2.7
Dako-1 (32, 5)	0.78	12.3 ± 0.3	11.5 ± 0.6	0.8 ± 0.3	$m = -1.1 \times 10^{-3}$	−0.4 ± 0.2	96 ± 1.3

[a] Number of times sample analyzed during total number of days preserved. The resulting concentrations were used in the LLS calculation [b] Change in As(III) concentration = As(III) concentration at the final day − As(III) concentration at $t = 0$. [c] On the basis of its odor, the sample contained sulfide.

preserved as before. The results are presented in Figure 4, which indicates that EDTA−HAc could preserve the arsenic species at least up to 21 days, but neither H_3PO_4 nor H_2SO_4 could maintain the distribution of As species within 10% of the initial value (Supporting Information, Figure S2). The distribution was shifted almost instantaneously from As(III) to As(V) in the presence of H_3PO_4 or H_2SO_4. The As(III) oxidation rate was very fast for the first few hours, but after 24 h very little oxidation occurred. When H_3PO_4 was used as a preservative, the final pH and Eh became ∼2.0 and ∼450 mV, respectively. Under these conditions, both As(III) and As(V) presumably formed the thermodynamically favored As(III), $H_3AsO_3^0$, and As(V), $H_2AsO_4^-$, species, respectively. In the presence of dissolved oxygen, As(III) gradually oxidizes to the thermodynamically favored As(V) species. In the presence of H_2SO_4, the final pH and Eh were ∼1.8 and ∼550 mV, respectively. Under these conditions, As(V), H_3AsO_4, was the expected species, and As(III) was not stable in the oxygenated water, but in the case of EDTA−HAc (pH 3.2 and Eh ∼380 mV), As(III) had moderate stability according to Eh−pH consideration (*19*). Moreover, EDTA formed a stable iron−EDTA complex, which presumably prevented Fe(II) from catalyzing the oxidation of As(III) in the oxygen-saturated water. These presumptions were confirmed by our experimental data, which showed that EDTA−HAc preserved the arsenic species efficiently. Although the As(III) concentration immediately after sampling was slightly lower than the originally spiked As(III) concentration, the concentrations of As(III) and As(V) were within the ±10% change used to demonstrate successful preservation.

Preservation and Speciation of Arsenic Species in Field Samples. To study the efficiency of EDTA−HAc—the best preservative based on lab tests—field samples were collected directly into 250 mL precleaned brown PP bottles (in a few cases translucent PP bottles), which contained the required amount of preservatives. Samples from 48 Minnesota wells (including 11 samples in triplicate), 4 Southern California wells (all in triplicate), and 3 North Dakota wells (all in triplicate) were collected in bottles containing the EDTA−HAc preservative. Portions of all of these samples were preserved and immediately speciated in the field using a chloride-form anion-exchange resin column (*14*). Preserved and field-speciated samples were shipped to our laboratory without refrigeration by overnight mail service. Samples were received within 27−54 hours of collection and analyzed on the day of receipt. If the distribution of the As species had changed during transportation, then it could be identified
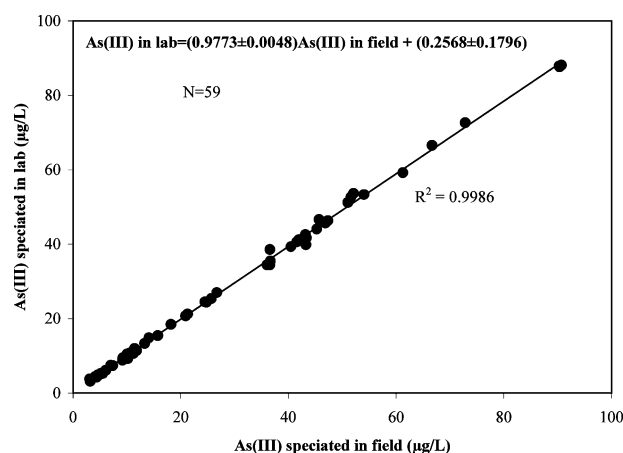

As(III) in lab=(0.9773±0.0048)As(III) in field + (0.2568±0.1796)

N=59

$R^2 = 0.9986$

FIGURE 5. Correlation between As(III) measured in the laboratory by differential −pH hydride generation on the day it was received and As(III) determined from immediate field-speciated samples collected from 51 different sources.

by comparing the concentration of field-speciated As(III) with the As(III) concentration in the preserved samples measured in the laboratory. Figure 5 shows the correlation between the field-speciated As(III) and laboratory-speciated As(III) results, which are highly correlated (slope 0.9773, intercept 0.257, and $R^2 = 0.9986$). So, it was concluded that EDTA−HAc could preserve the As(III/V) distribution in groundwaters for at least 1−2 days of transportation and storage.

After the lab speciation tests on the samples stored for 1−2 days, all of the preserved samples were stored at 22−24 °C in the dark for at least 30 days from the date of collection, and the triplicate samples were stored for up to 85 days. The linear least-squares (LLS) equation was calculated from multiple data points for As(III) in the preserved samples stored for at least 30 days, considering the field-speciated As(III) ($t = 0$) as the initial As(III) concentration. The slope of the line is an estimate of the conversion rate of As(III) to As(V) or vice versa over the study period. Negative slopes indicate oxidation to As(V) and positive slopes indicate reduction of As(V) with time. A zero slope indicates neither oxidation nor reduction. Table 2 presents As(III/V) stability data on 16, triplicate EDTA−HAc preserved samples from Minnesota, California, and North Dakota. These samples, which contained iron in the range of 0.17−4.64 mg/L, were monitored for 32−85 days.

Table 2 indicates that, even at high levels of iron, EDTA−HAc could preserve the distribution of As species for more than 30 days. The LLS slopes for As(III) during the preservation period are reported in column six. One slope (Minn-10) was significantly different from zero, but for the other samples, the slopes were very near zero, and the final changes in As(III) concentration were less than ±5%, i.e., well within the ±10% criterion for successful preservation. The reason why Minn-10 did not maintain a zero slope was likely due to the presence of sulfide in that sample. In an upcoming publication, the effect of sulfide on the preservation will be discussed.

In addition to the 16 triplicate samples discussed above, 30 day stability tests were run on 35 other single samples from the same three states. Again, the slopes were very close to zero and produced a maximum change in As(III) concentration of less than ±3% during 30 day storage.

On the basis of the experimental results, it was concluded that EDTA−HAc could preserve the inorganic As(III/V) species efficiently for more than 30 days.

Supporting Information Available

Composition of the synthetic groundwater and the effects of Eh and pH. This material is available free of charge via the Internet at http://pubs.acs.org.

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