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Preservation strategies for inorganic arsenic species in high iron, low-*Eh* groundwater from West Bengal, India

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Abstract Despite the importance of accurately determining inorganic arsenic speciation in natural waters to predicting bioavailability and environmental and health impacts, there remains considerable debate about the most appropriate species preservation strategies to adopt. In particular, the high-iron, low-*Eh* (redox potential) shallow groundwaters in West Bengal, Bangladesh and SE Asia, the use of which for drinking and irrigation purposes has led to massive international concerns for human health, are particularly prone to changes in arsenic speciation after sampling. The effectiveness of HCl and EDTA preservation strategies has been compared and used on variably arsenic-rich West Bengali groundwater samples, analysed by ion chromatography–inductively coupled plasma–mass spectrometry (IC–ICP–MS). Immediate filtration and acidification with HCl followed by refrigerated storage was found to be the most effective strategy for minimizing the oxidation of inorganic As(III) during storage. The use of a PRP-X100 (Hamilton) column with a 20 mmol L^{-1} $NH_4H_2PO_4$ as mobile phase enabled the separation of Cl^- from As(III), monomethylarsonic acid, dimethylarsinic acid and As(V), thereby eliminating any isobaric interference between $^{40}Ar^{35}Cl^+$ and $^{75}As^+$. The use of EDTA as a preservative, whose action is impaired by the high calcium concentrations typical of these types of groundwater, resulted in marked oxidation during storage. The use of HCl is therefore indicated for analytical methods in which chloride-rich matrices are not problematical. The groundwaters analysed by IC–ICP–MS were found to contain between 5 and 770 ng As mL^{-1} exclusively as inorganic arsenic species. As(III)/total-As varied between 0 and 0.94.

Keywords IC–ICP–MS · Arsenic · Speciation · Preservation · Groundwater

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Introduction

There is widespread interest [1–7] in the analysis of arsenic and arsenic speciation in natural waters, in particular groundwaters in West Bengal [8–11], Bangladesh [12–16], SE Asia [17, 18] and other countries [1, 7] where the extensive use of such groundwaters with arsenic concentrations in excess of the WHO guideline for drinking water of 10 ng mL^{-1} [19] has led to massive concerns for their impact on human health. Arsenic typically occurs in groundwaters at concentrations less than 10 ng mL^{-1} [1], however, concentrations up to 5000 ng mL^{-1} are not uncommon in some environments [1, 20], notably acid rock drainage (ARD), aquifers contaminated with arsenic-bearing wastes such as pesticides [21], geothermal systems [5, 7, 22], oilfield brines [23] and marine [24] or terrestrial [1, 12–18] sedimentary porewaters. Arsenic occurs in natural waters predominately as inorganic As(III) or As(V) species [1]. The pentavalent forms, H_3AsO_4 (aq), $H_2AsO_4^-$ (aq), $HAsO_4^{2-}$ and AsO_4^{3-} (aq) are typically predominant in oxidizing environments whereas the trivalent H_3AsO_3 (aq), $H_2AsO_3^-$ (aq), $HAsO_3^{2-}$ (aq) and AsO_3^{3-} (aq) are mostly found in reducing environments [1, 25]. The degree of protonation of the As(III) and As(V) species is largely determined by pH. The higher p K_a for the first deprotonation of H_3AsO_3 (aq) compared with that for H_3AsO_4 (aq) means that over a wide range of slightly acidic to near-neutral pH typical of groundwaters, inorganic As(III) occurs predominantly as a neutrally charged species whereas inorganic As(V) occurs mostly as singly- or doubly-

charged oxyanionic species. Arsenic has also been found in reducing groundwaters as the methylated species monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA), but it unusual for the concentrations of such species to exceed 5 ng mL^{-1} [11, 26].

The aqueous speciation of arsenic is a major factor controlling its biogeochemical cycling and bioavailability. The solubility of As(III) is controlled in reducing sulfur-bearing groundwaters by co-precipitation with iron sulfides, such as pyrite, or by precipitation as arsenic sulfides, such as arsenopyrite or loellingite. In reducing sulfur-poor environments, however, these controls do not exist and high concentrations of As(III) can potentially build up. In contrast, As(V) is easily adsorbed on various surfaces and its concentration in groundwaters is limited by sorption on to iron oxyhydroxides, aluminium hydroxides, manganese oxides, clay minerals and organic matter where such phases exist [7, 27, 28]. As(III) may also sorb on to these phases, with the partitioning of As(III)/As(V) between groundwater and these mineral surfaces being governed by the pH, the As:Fe ratio, and total dissolved arsenic concentration [28]. Arsenic exhibits a complex biogeochemistry in groundwaters [29, 30]. Pentavalent arsenic oxyanions can be used by some bacteria in anaerobic respiration as terminal electron acceptors [31]. Microbially induced reduction of hydrated ferric oxides to which arsenic is sorbed can result in the release of sediment bound arsenic to groundwaters [30]. Indeed, this has been postulated to be an important mechanism of arsenic release to shallow groundwaters of Bengal [32].

Meaningful analysis of arsenic speciation in groundwaters requires the design and implementation of strategies that effectively preserve the in-situ speciation during sampling and storage. A variety of preservation strategies have been published [2, 6, 7, 33–39], but not all of these are wholly applicable to, or have been tested for, high iron, low-*Eh* (redox potential) groundwaters such as those found in hazardous arsenic-rich aquifers in Bengal and which are particularly prone to changes in arsenic speciation during storage. Although, methylation and demethylation of aqueous arsenic species and reduction of inorganic As(V) have been observed elsewhere [2, 7, 33, 34], arguably the most problematic preservation issue for high iron, low-*Eh* groundwaters is oxidation of inorganic As(III). It is generally agreed that the major processes by which changes in arsenic speciation occur in stored groundwater samples are due to either microbial activity or inorganic reactions involving a variety of redox-sensitive species, most notably those of iron. In most reducing groundwaters concentrations of aqueous Fe(III) species are negligible, but the formation of Fe(III)-bearing colloids or precipitation of Fe(III) oxyhydroxides can great accelerate rates of arsenic oxidation. Thus, effective preservation strategies are likely to be those that act to reduce microbial activity and prevent the formation of Fe(III) colloids or solids during storage. The importance of filtration, storage in the dark and refrigeration to around 4°C to removing much colloidal and microbial mass and minimising microbial activity is widely recognized [2, 6, 7, 34–40]. Nevertheless, there remains considerable debate about the most effective chemical preservative to add to groundwater samples high in dissolved iron; HCl and EDTA have been suggested by various workers.

In this paper, we test the effectiveness of HCl and EDTA at preserving arsenic speciation in high iron, low-*Eh* groundwaters from a well-characterized [11, 41–43] arsenic "hot-spot" in West Bengal, India. The processes resulting in the observed differences in preservation method are discussed and recommendations for sampling and preservation procedures made.

Experimental

Sampling and major element analysis

Groundwaters from depths of 8–84 m were sampled from tubewells in Lalpur, Nadia district, West Bengal, an area well documented to contain high arsenic groundwaters [11, 41–43]. Tubewells were purged for a minimum of 5 min prior to sampling. In-situ measurements of temperature, pH and *Eh* were made using portable probes. The groundwater was immediately filtered (0.45 μm) into acid-cleaned opaque PE bottles. Samples for major element (Na, K, Ca, Mg, Fe, Mn, Si,) analysis were acidified to 24 mmol L^{-1} HCl (Aristar, BDH, UK) and refrigerated until analysis by ICP–AES (Horizon, VG Elemental, UK). Total arsenic concentrations were also determined in these samples by ICP–MS (PlasmaQuad II, VG Elemental, UK) after mathematical correction for $^{40}Ar^{35}Cl^{+}$ interference using the Plasmalab ICP–MS software as follows:

$$I(^{75}\mathrm{As}) = I(75) - R(^{35}\mathrm{Cl}/^{37}\mathrm{Cl}) \times \{I(77) - R(^{77}\mathrm{Se}/^{82}\mathrm{Se}) \times [I(82) - R(^{82}\mathrm{Kr}/^{83}\mathrm{Kr})]\}$$

where $I(x)$ is the intensity or count rate of the indicated m/z or isotope and R is the ratio of natural abundances of the indicated isotopes. Arsenic speciation was performed by IC–ICP–MS on the HCl-preserved samples and on an additional subset of groundwater samples preserved with 10 mmol L^{-1} EDTA (tetrasodium salt; SigmaUltra, Sigma–Aldrich, UK). Filtered, unacidified samples were collected for major anion analysis using a Dionex 4000I ion chromatography system that utilized a gradient-elution mode ramping from 0 to 30 mmol L^{-1} NaOH (Analar, BDH, UK). Certified reference materials were also included in each analytical run. The measured concentrations were within the uncertainty limits of the certified values for all the constituents analysed. All measurements were performed at Manchester within 3 weeks of collection with the exception of alkalinity, which was determined by acidimetric titration using the Gran method within 24 h of collection.

IC–ICP–MS

Single-species standard stock solutions of 1000 μg As mL^{-1} were prepared in deionised water (18.2 MΩ; Milli-Q, UK) from sodium arsenite, disodium arsenate heptahydrate, dimethylarsinic acid sodium salt trihydrate (all BDH, UK) and monomethylarsonic acid disodium salt (Argus Chemicals, Italy). The arsenic concentration of each stock solution was verified by ICP–AES analysis against an arsenic plasma standard (Johnson Matthey, Germany). The stock solutions were stored at 4°C in the dark. Multi-species calibration standards were prepared on the day of analysis by dilution of the stock solutions using deionised water. HCl- and EDTA-preserved samples were analysed using standards prepared in a matrix of 24 mmol L^{-1} HCl and 10 mmol L^{-1} EDTA respectively.

The method described by Goessler et al. [44] was adapted for use in this work. A strong anion-exchange column (PRP-X100, Hamilton, Switzerland) was used to separate both inorganic [As(III) and As(V)] and methylated (MMAA and DMAA) arsenic species. This was housed in a Personal IC 790 chromatograph (Metrohm, Switzerland) fitted with a 100 μL sample loop. The 20 mmol L^{-1} $NH_4H_2PO_4$ (Analar, BDH, UK) mobile phase was adjusted to pH 8.1 using NH_4OH (BDH, UK) and spiked with 50 ng mL^{-1}Rb internal standard. The eluent was degassed with He for a minimum of 30 min prior to use and filtered online through a 2-μm membrane in the chromatograph. Arsenic species peak integration and external drift correction were calculated using in-house Turbo Pascal programs [45, 46]. The operating conditions are summarised in Table 1.

A typical chromatogram of As(III), MMAA, DMAA and As(V) in an HCl matrix is displayed in Fig. 1. HCl has traditionally not been used to acidify samples for arsenic analysis by ICP–MS due to the $^{40}Ar^{35}Cl^+$ (and, in high calcium matrices, $^{40}Ca^{35}Cl^+$) polyatomic interference with monoisotopic $^{75}As^+$. Although such interferences can be spectrally or chemically resolved by use of magnetic sector or reaction/collision cell-equipped ICP–MS instruments, respectively (e.g. [7, 47]), Fig. 1 demonstrates that chloride may also be chromatographically resolved from the arsenic species of interest, allowing interference-free arsenic speciation measurements to be made.

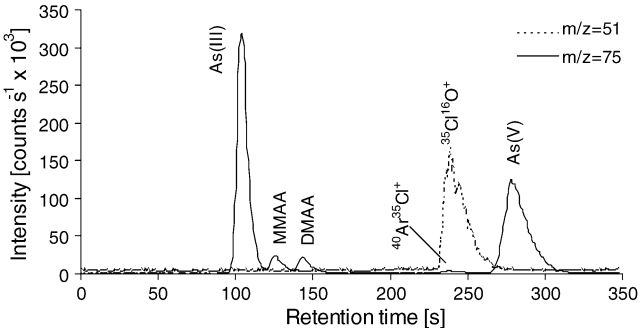

Fig. 1 IC–ICP–MS chromatogram of inorganic [As(III) and As(V), both 50 ng As mL^{-1}] and methylated (MMAA and DMAA, both 5 ng As mL^{-1}) forms of arsenic in 24 mmol L^{-1} HCl demonstrating resolution of chloride (measured as the $^{35}Cl^{16}O^+$ polyatomic) from arsenic species of interest

Table 1 IC–ICP–MS operating conditions

IC	
Chromatograph	Metrohm Personal IC 720
Anion-exchange column	Hamilton PRP-X100 250 × 4.1 mm
Mobile phase	20 mmol L^{-1} $NH_4H_2PO_4$; pH 8.1
Flow rate	1.5 mL min^{-1}
Sample loop	100 μL
Elution mode	Isocratic
ICP–MS	
Instrument	VG PlasmaQuad II
Instrument power	1,350 W
Reflected power	≤ 2 W
Coolant gas flow rate	13.5 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Nebulizer gas flow rate	0.95 L min^{-1}
Nebulizer	Concentric glass
Spray chamber	Water cooled impact bead (3°C)
TRA / *m*/*z*	51, 53, 75, 77, 78, 82, 83, 85
Detection mode	Pulse counting

Results

Major element and arsenic chemistry of Bengali groundwaters

A summary of the groundwater chemistry is displayed in Table 2. The groundwaters sampled were circumneutral, reducing and calcium-bicarbonate dominated. Elevated concentrations of dissolved iron and manganese were

Table 2 Summary of the chemical composition of groundwaters sampled in Lalpur, Nadia district, West Bengal ($n = 26$, each sample analysed in triplicate)

	Mean ± standard error	Median	Min–max
pH	7.3 ± 0.7	7.3	7.0–8.5
Eh (SHE) (mV)	+91 ± 13	+66	−11–+233
Ca (μg mL^{-1})	100 ± 10	100	35–160
Mg (μg mL^{-1})	29 ± 2	29	9.3–51
Na (μg mL^{-1})	33 ± 5	26	15–96
K (μg mL^{-1})	4.2 ± 0.5	3.6	1.8–13
Fe (μg mL^{-1})	4.8 ± 0.9	2.8	0–14
Mn (μg mL^{-1})	0.73 ± 0.08	0.59	0.03–1.3
HCO_3 (μg mL^{-1})	530 ± 30	530	200–770
Cl (μg mL^{-1})	41 ± 9	29	4.3–160
SO_4 (μg mL^{-1})	7.7 ± 1.8	4.3	0–136
NO_3 (μg mL^{-1})	0.52 ± 0.30	0	0–6.8
NH_4 (μg mL^{-1})	3.6 ± 0.8	2.2	0.10–12.1
PO_4 (μg mL^{-1})	0.02 ± 0.01	0	0–0.35
As(III) (ng As mL^{-1})	160 ± 40	120	3.5–710
As(V) (ng As mL^{-1})	14 ± 3	8.6	1.0–53
Total As (ng As mL^{-1})	170 ± 40	130	5.2–770

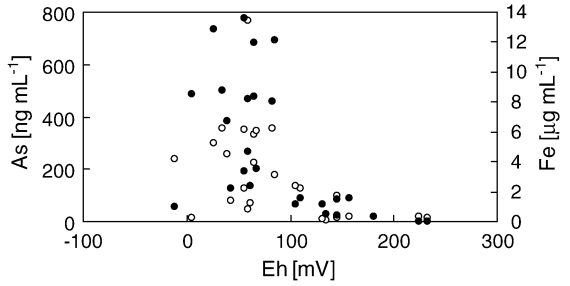

Fig. 2 Variation of dissolved arsenic (*open circles*) and iron (*closed circles*) with redox potential

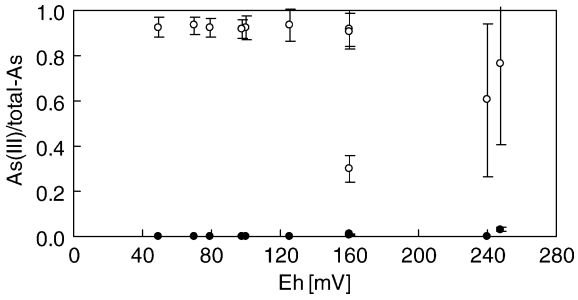

Fig. 4 Comparison of the proportion of arsenic as As(III) present in HCl- (24 mmol L^{-1}; *open circles*) and EDTA- (10 mmol L^{-1}, *closed circles*) preserved Bengali groundwater samples as a function of redox potential

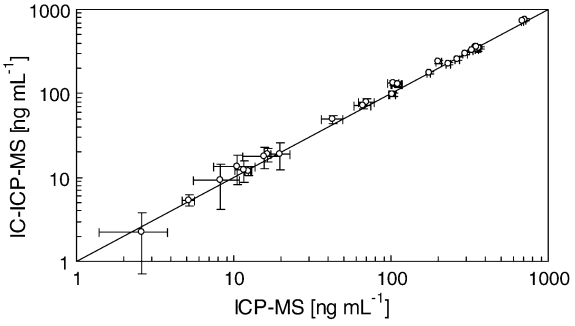

Fig. 3 Comparison of the total arsenic concentration determined in Bengali groundwater samples preserved in 24 mmol L^{-1} HCl by IC–ICP–MS and ICP–MS. The *straight line* indicates the line of equal relation

observed while the concentrations of nitrate and sulfate were generally low, which may indicate that nitrate and sulfate reduction are active processes in the groundwaters. The former is supported by the presence of ammonium in the majority of waters sampled. High arsenic and iron concentrations occur exclusively at low *Eh* (Fig. 2), most probably because of the reductive dissolution of arsenic-bearing ferric oxides; the mechanisms leading to the genesis of such high arsenic waters will not be discussed further here, however.

Total arsenic

Total dissolved arsenic concentrations were between 5 and 770 ng mL^{-1}; the Indian drinking water limit (50 ng mL^{-1}) and the WHO recommended threshold (10 ng mL^{-1}) were exceeded in 18 and 24 tubewell water samples, respectively. The total arsenic concentrations determined by IC–ICP–MS and ICP–MS analysis of the HCl-preserved samples were in excellent agreement with each other (Fig. 3) and with total arsenic determined by IC–ICP–MS analysis of EDTA-preserved samples (data not shown).

Arsenic speciation

IC–ICP–MS analysis of both the 24 mmol L^{-1} HCl- and 10 mmol L^{-1} EDTA-preserved samples indicated the presence of only inorganic As(III) and As(V) species. No methylated species were detected, in contrast with previous studies of arsenic speciation in West Bengali groundwaters [11, 26]. That the sum of the arsenic species in Bengali groundwater acidified to 24 mmol L^{-1} HCl determined by IC–ICP–MS agree well with those determined by ICP–MS (Fig. 3) suggests no other significant arsenic species were present in the samples analysed. In particular, there is no evidence of significant concentrations of thioarsenite species, which can be an important form of dissolved arsenic in groundwaters that contain moderate sulfide concentrations [48]. Smieja and Wilkins [49] have stated that loss of arsenic will occur from near-neutral waters containing as little as 0.4 µg mL^{-1} sulfide should they be acidified to pH 2 with HCl. Given that the total arsenic concentration of the EDTA- and HCl-preserved samples is in good agreement it is unlikely that thioarsenite species formed

Table 3 Results of IC–ICP–MS analysis of natural water certified reference materials (CRM)

CRM	As(III) (ng As mL^{-1})	As(V) (ng As mL^{-1})	Summed species (ng As mL^{-1})	Certified concentration (ng As mL^{-1})
TM-26.2	7.3 ± 0.7[a]	0.7 ± 0.4	8.0 ± 0.8	7.7 ± 1.4
TMDA-54.3	–[b]	44.5 ± 5.5	44.5 ± 5.5	45.3 ± 7.2

[a]Stated errors represent 95% confidence limits calculated by an in-house Turbo-Pascal program [46] based on the method of Miller and Miller [50]
[b]Species not detected

a significant portion of the dissolved arsenic speciation. Excellent agreement is also observed between the sum of the arsenic species determined by IC–ICP–MS in two natural water certified reference materials and the certified total arsenic concentration (Table 3). Although only certified for total arsenic, the dissolved arsenic burden of TM-26.2 and TMDA-54.3 (both NWRI, Canada) is composed almost entirely of As(III) and As(V), respectively. Thus, these solutions can be used for validation of arsenic redox species analysis in the current absence of natural water reference materials specifically certified for As(III) and/or As(V).

The proportion of total arsenic occurring as As(III) in the HCl-preserved samples ranged from 0.30 to 0.94 (median 0.92), with As(III) being the predominant species in most of the samples analysed. In contrast, arsenic was found to occur almost exclusively as inorganic As(V) in the EDTA-preserved samples (Fig. 4).

Discussion

Evaluation of preservation strategies

Previous work by our group has indicated that EDTA-stabilised groundwater samples might be more susceptible to oxidation than their HCl counterparts [18]. The groundwater samples collected by Polya et al. [18] were broadly comparable with those studied here and were filtered (0.45 μm) and preserved with 1.25 mmol L^{-1} EDTA according to the procedure of Bednar et al. [37]. As in this study, these EDTA-preserved samples exhibited lower As(III)/total-As ratios than HCl-preserved samples and furthermore EDTA-preserved samples analysed after 15 weeks exhibited even lower ratios than the same samples analysed just 2.5 weeks after collection. The As(III)/total-As ratios in HCl-preserved samples remained relatively constant over the same period. These data lead us to conclude that the discrepancy between arsenic oxidation state in the EDTA- and HCl-preserved samples in both this study and that of Polya et al. [18] was primarily due to oxidation of As(III) in the EDTA-preserved samples.

Explanation of oxidation in EDTA-preserved samples

Possible explanations of the poor performance of EDTA compared with HCl in preventing oxidation of As(III) include:

- competitive complexing with EDTA by calcium and magnesium;
- pH dependence of oxidation rates of Fe(II) and As(III); and
- failure to inhibit microbial activity.

Any explanation needs to also account for the higher rates of oxidation observed in this study in samples preserved with 10 mmol L^{-1} EDTA compared with those observed by Polya et al. [18] for similar samples preserved with just 1.25 mmol L^{-1} EDTA.

Competitive complexing of EDTA by calcium and magnesium

EDTA is not a particularly selective chelating agent and will form stable complexes with divalent cations other than iron, for example calcium and magnesium. If the concentration of EDTA added as a preservative is not in excess of the calcium and magnesium concentrations of the groundwater samples, then its ability to complex with dissolved iron, thereby reducing the saturation index of Fe(III) oxyhydroxides, may be significantly jeopardized. This is particularly important for the type of groundwaters studied here, because they contain relatively high (up to 7 mmol L^{-1}) concentrations of combined calcium and magnesium. However, modelling using Geochemist's Workbench indicates that FeOOH (goethite) saturation was not greatly exceeded in the samples analysed in either study. Moreover, in neither this study nor that of Polya et al. [18] was any evidence found of precipitation of Fe(III) oxyhydroxides during storage. In both studies, EDTA acted as an effective preservative of total arsenic and total iron. Thus, although in theory competitive complexation by calcium and magnesium might be an issue to consider for some groundwaters, it does not provide a viable explanation for the oxidation of As(III) observed in this study.

pH dependence of rates of oxidation of Fe^{2+} (aq) and As(III) (aq)

The pH reduction caused by the addition of HCl substantially reduces the rate of oxidation of Fe^{2+} (aq) to Fe^{3+} (aq), because this rate is strongly positively dependent on the concentration of OH^- (aq) [51, 52]:

$$R_{ox}/\text{mol L}^{-1}\,\text{s}^{-1} = 3.33 \times 10^{11}[Fe^{2+}(aq)]PO_2[OH^-(aq)]^2$$

where R_{ox} is the rate of oxidation of Fe^{2+} (aq) and use of square brackets denotes concentration (mol L^{-1}) of the enclosed species. In contrast, the addition of EDTA and the formation of protonated metal–EDTA complexes will tend to increase the pH and these conditions will not only accelerate the rate of oxidation of Fe^{2+} (aq) but are also likely to accelerate the oxidation of dissolved As(III) species. Because higher concentrations of added EDTA will give rise to larger increases in pH, the observed higher rates of oxidation in this study compared with those noted by Polya et al. [18] are consistent with this explanation. In addition, Fe(III) forms more stable complexes with EDTA, such as Fe(III)$EDTA^-$ (aq), than Fe(II). This will also serve to accelerate rates of oxidation of dissolved Fe(II), resulting in a higher concentration of dissolved Fe(III) potentially capable of oxidizing As(III).

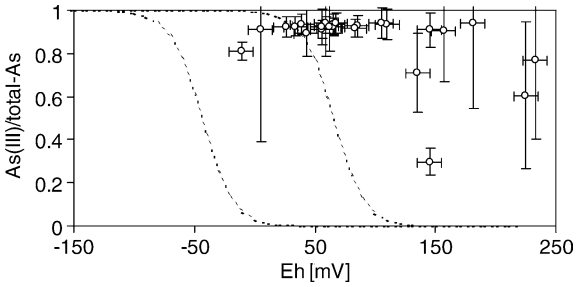

Fig. 5 Proportion of arsenic as As(III) as a function of redox potential for Bengali groundwater samples preserved in 24 mmol L^{-1} HCl. The *dashed lines* envelope the loci of equilibrium values expected for pH between 6.5 (*left line*) and 7.5 (*right line*) calculated using the data of Appelo and Postma [55]

Failure to suppress microbial activity

Microbial activity is implicated in a number of redox reactions taking place in the groundwater systems studied here. Although inorganic processes can satisfactorily explain the tendency for oxidation of As(III) in EDTA-preserved samples, we cannot eliminate the possibility that addition of EDTA fails to act as an effective biocide of sub-0.45 μm diameter bacteria as HCl may do.

Arsenic redox disequilibria

The As(III)/total-As ratio appears to be shifted from equilibrium for these groundwaters (Fig. 5). Because the kinetics of transformation between inorganic arsenic species are relatively slow [53], the mixing of reducing groundwater with oxygenated shallow/surface waters might explain this shift. Also, discrepancies between *Eh* measurements made in the field using a Pt electrode and those calculated from different aqueous redox couples are often observed. In a large study of groundwater samples, field measurements of *Eh* did not match well with those calculated from a range of redox couples [54], leading the authors to conclude that aqueous groundwater redox reactions are usually not at equilibrium. This result emphasizes the importance of directly analysing the concentration of redox-sensitive species in low-temperature aqueous systems rather than relying exclusively on theoretical equilibrium models.

Conclusions

The efficacy of HCl and EDTA in preserving the dissolved arsenic speciation in Bengali groundwaters has been compared, with the former giving the most promising results. Although EDTA might be effective at stabilising the arsenic oxidation state in many water types, it seems to be a poor choice of preservative for low-*Eh* groundwaters rich in dissolved calcium, magnesium and iron, such as those studied here. The mechanisms responsible for the As(III) oxidation apparent in the EDTA-spiked samples are unclear but might include increased rate of oxidation under the higher pH conditions resulting from EDTA addition, and oxidation of Fe(II) due to Fe(II)EDTA complex formation. Although these effects can be limited by reducing the concentration of EDTA used, this compromises its ability to complex aqueous iron in high calcium/magnesium waters. HCl is the preferred additive for conservation of the redox distribution of dissolved arsenic in low-*Eh*, high-iron subsurface waters. Samples preserved in this fashion can be analysed by IC–ICP–MS without $^{40}Ar^{35}Cl^{+}$ interference, because of chromatographic resolution of chloride from both inorganic and methylated arsenic species.

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