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Voltammetric determination of arsenic in high iron and manganese groundwaters

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ABSTRACT

Determination of the speciation of arsenic in groundwaters, using cathodic stripping voltammetry (CSV), is severely hampered by high levels of iron and manganese. Experiments showed that the interference is eliminated by addition of EDTA, making it possible to determine the arsenic speciation on-site by CSV. This work presents the CSV method to determine As(III) in high-iron or -manganese groundwaters in the field with only minor sample treatment. The method was field-tested in West-Bengal (India) on a series of groundwater samples. Total arsenic was subsequently determined after acidification to pH 1 by anodic stripping voltammetry (ASV). Comparative measurements by ICP-MS as reference method for total As, and by HPLC for its speciation, were used to corroborate the field data in stored samples. Most of the arsenic ($78 \pm 0.02\%$) was found to occur as inorganic As(III) in the freshly collected waters, in accordance with previous studies. The data shows that the modified on-site CSV method for As(III) is a good measure of water contamination with As. The EDTA was also found to be effective in stabilising the arsenic speciation for longterm sample storage at room temperature. Without sample preservation, in water exposed to air and sunlight, the As(III) was found to become oxidised to As(V), and Fe(II) oxidised to Fe(III), removing the As(V) by adsorption on precipitating Fe(III)-hydroxides within a few hours.

1. Introduction

Inorganic arsenic (As) pollution of drinking water is a global hazard [1] with new areas of contamination regularly reported [2]. West Bengal (India) and Bangladesh where millions of people consume water from shallow tube wells is the most reported on account of the population affected [3]. This contamination has been described by the World Health Organisation (WHO) as 'the largest poisoning of a population in history' [4]. Long term exposure to arsenic in drinking water has been identified as a cause of skin lesions [5] as well as large numbers of bladder, lung, kidney and skin cancers [6]. Increased awareness of chronic exposure has meant the national Indian drinking water limit of 50 $\mu g\,L^{-1}$ (0.7 μM) of As, has now been deemed unsafe by WHO, with a provisional guideline value of 10 $\mu g\,L^{-1}$ (0.13 μM) As. The As problem has recently been reviewed [7].

In groundwaters inorganic forms of arsenic, arsenite (As(III)) and arsenate (As(V)), dominate, whilst organic arsenic compounds, methylarsonic acid (MMA) and dimethyl arsinic acid (DMA), form a negligible percentage of the total arsenic [8]. It is essential to determine the speciation of arsenic in groundwater for its effects on geochemical mobility in groundwater and the uptake of arsenic by plants.

Stable arsenic species are commonly determined in the laboratory by hyphenated techniques coupling liquid chromatography (LC) to inductively coupled plasma mass spectrometry (ICP-MS) or atomic absorption/fluorescence spectroscopy (AAS/AFS) [9]. Sampling, storage and transport are required prior to the analysis in the laboratory, and each step may affect the original arsenic speciation [10]. For this reason field measurement of As species has major advantages related to immediate assessment of water toxicity, the possibility of direct mitigation action and prevention of changes in speciation during sample storage.

Instrumentation for voltammetric analysis is portable and therefore suitable for on-site speciation, which makes it possible to evaluate water quality without sample transport. Voltammetric procedures to determine As(III) in water have existed for a long time [11] and use either a mercury drop or a gold electrode, and are based on cathodic (CSV) [12,13], or anodic stripping voltammetry (ASV) [14–16]. ASV using a mercury drop electrode has been used before for on-site As(III) determination [17]. However, these methods require a chemical reduction step involving sample heating

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to determine total dissolved As, which is inconvenient in the field and has concomitant instability of the generated As(III). A recently developed method using a gold, microwire, electrode is very sensitive and can be used to determine As(III) at natural pH in CSV mode [18], and combined (As(III) + As(V)) by ASV after mild acidification to pH 1 [19]. The CSV method has advantages for As(III) measurement in the field as it is insensitive to interference by dissolved oxygen or copper [18], and should not require any reagents.

In regions of West Bengal there are near neutral-pH, reducing groundwaters, where As is released via reductive dissolution from oxides, especially iron oxyhydroxides (FeOOH) [20]. These waters have a specific chemical signature, with high levels of reduced species such as As(III), ferrous iron (Fe(II)) and dissolved organic carbon (DOC) as well as high bicarbonate in solution [21]. Low As (<130 nM) waters in this region are associated with high levels of Mn [22]. The As in these waters appears to be predominantly As(III) [14], with only a very minor proportion of organic As (<5%) [23]. These waters were selected to validate the new CSV method [18] in a study of arsenic speciation.

Preliminary attempts at measuring the concentration of As(III) in samples of these waters revealed a major interference making it impossible to obtain a signal for arsenic. Experiments in this work reveal that the interference was directly related to high micromolar levels of Fe and Mn, which were found to lower the response for As(III), and finally block it altogether. This work shows that the interference is eliminated by addition of ethylenediaminetetraacetic acid (EDTA) resulting in an improved CSV procedure suitable for arsenic in any waters. The experiments demonstrating the cause of the interference and its subsequent elimination using EDTA are described here. The new method is applied in the field to groundwaters in West Bengal (India), and the results compared to reference analyses using conventional laboratory techniques.

EDTA and sample acidification with HCl have been used before to preserve the As speciation for extended sample storage with conflicting results [24,25]. In the course of this work, the effectiveness of these two preservation methods is tested by comparison of analyses of samples in the field to those of preserved samples.

2. Experimental

2.1. Study area

Groundwaters were collected from the contiguous villages of Ardevok and Moyna in southern West Bengal at 22°44.43N, 88°29.450E (Indian/Bangladesh datum) in 24-Parganas (North) district, on the northern peri-urban fringe of the town of Barasat. The geology and groundwater composition, speciation apart, is described in [22]. This area was selected because of the level of detail on local geology, hydrogeology, and groundwater composition afforded by these prior studies. In the region, two connected aquifers exist. To the northeast is a palaeo-interfluvial aquifer of brown sand capped by a regional palaeo-sol: its groundwater is low in arsenic (<10 nM As) and high in manganese (>25 μM Mn), as the aquifer is poised at the stage of Mn-reduction. In the remainder of the study area is a palaeo-channel aquifer of grey sand that hosts water that is high in iron (20–140 μM Fe) and high in arsenic (>0.5–7 μM As): this part of the aquifer has experienced a considerable amount of Fe-reduction. In both water types, concentrations of bicarbonate are typically 8–16 mM as a result of microbial metabolism of organic matter.

2.2. Reagents

Solutions were made using 18 MΩ cm Milli-Q water (MQ). A 10^{-2} M As(III) stock solution was prepared from As_2O_3 (purity 99.5%, AnalaR, BDH Chemicals Ltd., England), acidified with HCl to pH 2 and wrapped in aluminium foil to prevent photochemical oxidation. Standard solutions with concentrations 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} M As(III) were prepared freshly every month at pH 2. H_2SO_4 (0.5 M) used for conditioning of the electrode was from BDH (AnalaR grade). Solutions of Fe(II) and Mn(II) (1 mM each) were prepared daily in deoxygenated MQ from $Fe(II)Cl_2{\cdot}4H_2O$ and $Mn(II)Cl_2{\cdot}4H_2O$ (BDH chemicals Ltd., England) acidified to 0.01 M HCl. The HCl was purified by sub-boiling distillation of commercially available AR grade HCl (Fisher Scientific) on a silica condenser. A 0.5 M stock solution of EDTA was prepared from the EDTA, disodium salt (purity 99.5%, AnalaR, BDH Chemicals Ltd., England) and adjusted to pH 9 using NaOH.

A multielement standard for ICP-MS calibration was made up from single element ICP-MS standards (High Purity Standards, Charleston, SC) and diluted using water (18 MΩ cm) from an ELGA (Marlow, UK) system, and acidified using nitric acid (65%, Fluka, Suprapure). Dimethylarsinate (DMA(V), $(CH_3)_2AsO_2Na$), 98%, Strem Chemicals UK) was used for the quantification of all arsenic species due to the species-independent arsenic response of the ICP-MS.

2.3. Sample collection and pre-treatment

Ground water samples were collected in acid washed, Nalgene, low-density, polyethylene bottles from 23 hand-pumped domestic wells, or from clusters of wells forming two piezometers nests across the As gradient, covering an area of 750 m × 450 m, shown in a map [22]. Sampling from piezometer nests allowed the distribution of As and its speciation to be determined as a function of depth.

All samples were taken back to the laboratory for later analysis to check for stability and for comparison against other analytical methods. The following elements were determined in all samples: As(III), arsenate (As(V)), total As, Mn, Fe, and copper (Cu). Samples from artesian wells were left unfiltered and were acidified to pH 1 with HCl to a final concentration of 0.1 M for later determination of total As, Fe and Mn. Piezometer samples (0.5 L) were extracted using a surface-mounted vacuum pump that sampled from 1 m above the top of the well screen in each of the boreholes in the piezometer nests. In each case the water was pumped until clear and was then filtered through 0.45 μm acetate membrane filters; 10 mM EDTA was added (final pH 9) to these samples and they were stored at room temperature. To investigate changes in speciation upon storage 23 samples were stored with HCl and 12 with EDTA.

2.4. Instrumentation

Voltammetric measurements in the field utilised a battery-powered (dry, 10 Ah, 6 V) Palmsens potentiostat (Palmsens, Netherlands) controlled by Ivium software (Palmsens). The software had been modified to enable automation of the measurements. The working electrode (WE) was a 25 μm diameter, gold microwire (2 mm long, 99.99%, hard, Goodfellow), and the counter electrode (CE) was a 200 μm iridium wire (3 mm long, Goodfellow) [19,26]. The Ag/AgCl reference electrode (RE) was a solid state pseudo-reference electrode, and was made from a 1.5 mm diameter, 2.5 cm, Ag wire (99.99%, Rasmussen AS, Norway) [27]. To enable on-site detection, a vibrator was attached to the combined electrode [18,28], which had a cable length of 6 m. In the laboratory the vibrating electrode was fitted in a Metrohm VA696 stand, controlled by a μAutolabIII potentiostat (Ecochemie, Netherlands) and GPES software. In this case the reference electrode was double-junction, Ag/AgCl(s), 3 M KCl.

2.4.1. Total As (As_T)

Inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500c, Agilent Technologies, Tokyo, Japan) was used in normal mode for elemental determinations. The elements Mn (m/z 55), Fe (m/z 56 and 57), Cu (m/z 63), As (m/z 75), Sb (m/z 121), and as internal standard In (m/z 115), were recorded. All standards and samples were acidified with HNO_3 to 1% HNO_3. Calibration was with an external multi element calibration standard. The internal standard showed a decrease in signal intensity, so correction was necessary. Correction was made by dividing all counts per seconds (cps) of each standard and sample by the cps of the internal standard. The limit of detection (LOD) for each element was: Mn 20 nM, Fe 35 nM, Cu 8 nM, As 5 nM and Sb 0.5 nM (3σ of blank). The determined As was defined as the total As (As_T) concentration.

2.4.2. Arsenic speciation by HPLC–ICP-MS

An Agilent 1100 HPLC system coupled to an Agilent 7500c ICP-MS was used to determine inorganic As(III) ($As(III)_{HPLC}$) and inorganic As(V) ($As(V)_{HPLC}$). The HPLC flow was set to 1 mL/min with an isocratic buffer (10 mM phosphate at pH 6.2). 50 μL of standard and sample were injected onto a PRP-X 100 anion exchange column (250 × 4.1 mm I.D., 10 μm, Hamilton, Reno, NV) tempered at 20 °C. Chloride interference and selenium were measured at m/z 77 and 82, and indium was used as an internal standard and measured at m/z 115. Internal standard showed no decrease in signal intensity, therefore no correction was necessary. The LOD for arsenic was 25 nM (3σ of blank).

2.5. Voltammetric procedures for arsenic speciation: electrode conditioning

The microwire WE was cleaned in 0.5 M H_2SO_4 by hydrogen generation at −1.7 V (15 s), when the electrode was new, or when fouling was suspected. Subsequently optimum behaviour of the electrode was tested in the same solution by cyclic voltammetry (3 scans) from 0 to 1.5 V (100 mV s^{-1}). In these scans the height and symmetry of the Au/Au_2O_3 reduction peak gives an indication of how the electrode is working, for example a shoulder on the negative side of the reduction peak can correspond to poor signal and a loss in peak height a loss of part of the electrode surface.

2.6. Reactive arsenite determination by CSV

Reactive As(III) was determined immediately upon sampling by CSV [18]. The reactive As(III) ($As(III)_R$) is defined by the species $As(OH)_3{}^0$, which is detected by the CSV method and which is the predominant species in freshwaters of neutral pH. The $As(OH)_3{}^0$ represents all inorganic As(III) as the inorganic speciation converses freely, whilst any organic As(III) species would behave electrochemically inert towards CSV and are not detected. The water samples were analysed on-site immediately after sampling without deaeration and without addition of buffer or electrolyte, unless indicated. EDTA (10 mM) was added to prevent interference by high levels of iron and manganese present in most samples. Voltammetric conditions were: E_{cond} = 0.55 V (10 s), E_{dep} = 0 V (60 s), t_{eq} = 3 s, stripping from 0 to −1.5 V at 1 V s^{-1}, step height 10 mV. The sensitivity was calibrated by addition of As(III) to the sample aliquot (50 mL) in the cell (a polyethylene beaker).

Comparative measurements of arsenite ($As(III)_{ASV}$) were made by ASV [19] in the laboratory in samples which had been stored ~1 month with 0.1 M HCl, or with 10 mM EDTA (in this case 0.1 M HCl was added prior to analysis): E_{cond} = 0.55 V (5 s), E_{dep} = −0.4 V (60 s), t_{eq} = 3 s, scan from −0.5 to 0.5 V, using the square-wave modulation (50 Hz, step size 8 mV, pulse height 50 mV). Calibration was by addition of As(III) standard to the sample in the voltammetric cell sufficient to at least double the initial peak current. The thus detected As(III) would include organic complexes (if they occur) if they dissociate upon acidification. Organic As-compounds (MMA and DMA) are not included in this fraction.

2.7. Combined inorganic arsenic

The combined concentration of inorganic arsenic, As_{inorg} (As(V) + As(III)), was determined by ASV of acidified samples (0.1 M HCl) in the laboratory and in the field using the same measuring conditions as for As(III) except with a more negative deposition potential of −1.2 V (60 s). Samples with high levels of arsenic (>1 μM) were diluted with 0.1 M HCl. Any MMA and DMA would be included in this fraction at a reduced sensitivity (50% lower for MMA and 70% lower for DMA) [19], but not stable, covalent, organic species.

2.8. Use of EDTA to eliminate interference of Fe and Mn with As speciation by CSV

The effect of EDTA on interference by Fe and Mn on CSV of As(III) was tested in model solutions containing 10 mM borate pH buffer (pH 8.9), 2 mM KCl and 20 nM As(III). Fe was added as Fe(II) from 1 μM to 2 mM at varying concentrations of EDTA whilst measuring the CSV response for As(III) using a deposition time of 30 s. The solution was nitrogen-purged to ensure that the added Fe(II) remained in the reduced state. Similar experiments were carried out with Mn(II).

2.9. Species stability experiment in the field

The concentration of $As(III)_R$ and As_{inorg} were monitored as a function of time after collection of a large unfiltered water sample (20 L) from a deep well (station 5) which was left exposed to the sun from 8 AM. The original concentration of As_{inorg} was 320 nM (25 μg L^{-1}) which was 99% $As(III)_R$. Sub-samples were taken at ~hourly intervals, and subjected to immediate analysis of $As(III)_R$ (CSV, pH 8.8, with 10 mM EDTA) and As_{inorg} (ASV, 0.1 M HCl).

3. Results and discussion

Preliminary measurements of reactive arsenic ($As(III)_R$) in groundwaters, some of which very high (>500 μM) in Fe and Mn, were found to be impossible due to interference with the CSV signal. Good sensitivity was obtained in model groundwaters with only low levels of Fe or Mn, but additions of Fe and Mn caused the CSV response for As to diminish to zero. Fig. 1 shows that the response for As is fully depressed at Fe and Mn >30 μM.

Even higher levels of either Fe or Mn are typical for these groundwaters and were the cause of the lack of a CSV signal for As. The high Fe in the groundwaters occurred as Fe(II) as it originated from reductive dissolution from As bearing Fe-hydroxides, in response to ingress of organic matter [22]. We hypothesise that, during the voltammetric measurement, the Fe(II) becomes oxidised to Fe(III)-hydroxide at the surface of the electrode, thus blocking the surface. For instance, the conditioning potential of 0.55 V is amply sufficient to oxidise Fe(II) and Mn(II) to their more oxidised, insoluble, state, causing them to precipitate on the electrode surface. If this mechanism is true, then addition of a strong chelating agent should be sufficient to eliminate this problem. Preliminary experiments using EDTA were successful and optimisation of this method is reported here.

Addition of EDTA, whilst repeating the gradual additions of Fe, caused the decrease in the CSV response to move to higher Fe concentrations as any oxidised Fe became complexed and remained dissolved (Fig. 1A). At 10 mM EDTA the CSV response was unaffected until 500 μM Fe, whilst for 20 mM EDTA the response was

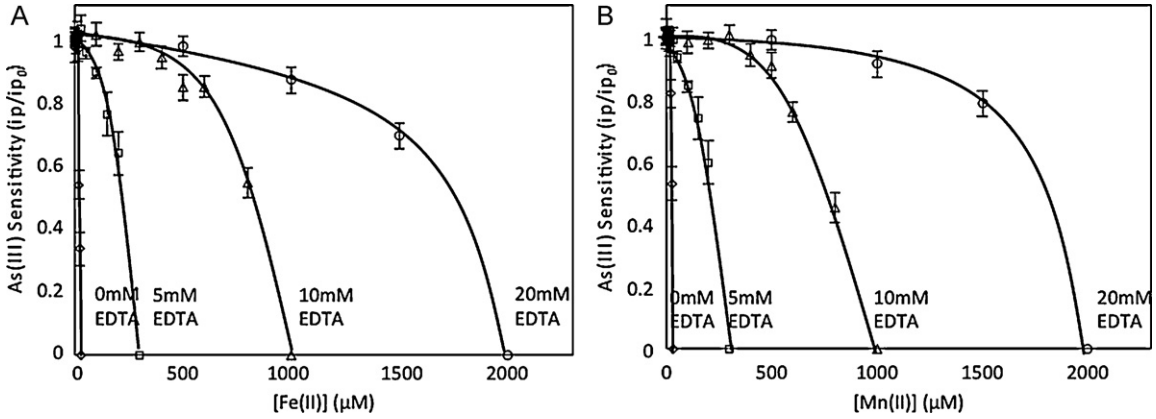

Fig. 1. Effect of varying the concentration of EDTA on interference of Fe and Mn with the determination of As(III) in freshwaters. (A) CSV sensitivity for As(III) as a function of the Fe concentration. (B) CSV sensitivity for As(III) as a function of the Mn concentration. The interference of very high Fe and Mn in groundwaters is eliminated at 10–20 mM EDTA.

unaffected until 1.5 mM Fe (Fig. 1A). The effect of adding EDTA on the interference by Mn was similar to that of Fe (Fig. 1B). Up to 0.6 mM Mn was tolerated for 10 mM EDTA and up to 1.5 mM for 20 mM EDTA. The concentrations of Fe and Mn where the interference occurs are high, but these high concentrations are typical for ground waters affected by organic matter causing anoxia [22]. Addition of 10 mM EDTA was selected for CSV of As(III) in the high-iron groundwaters from West Bengal, as this was found to be sufficient to eliminate the iron interference and to stabilise the CSV response for most samples.

The stable CSV response suggested that, in addition to resolving the interference, the effect of EDTA on retaining oxidised Fe and Mn species in solution could stabilise the As speciation of the water samples for extended sample storage. Further measurements in the field were used to confirm the predominant species of As in freshly collected groundwaters, and samples were stored in the presence of either EDTA or acid to verify successful stabilisation of the As speciation.

The quantitative elimination of the CSV signal for As with increasing levels of Fe and Mn, and its amelioration by addition of EDTA, are evidence that Fe and Mn are the cause for the interference in these groundwaters. It is likely that their oxides precipitate on the surface of the electrode during the conditioning step at 0.5 V. Apparently, in the absence of EDTA, the oxides remained on the electrode, physically blocking access of arsenite ions during the deposition step. The CSV response was stabilised by EDTA because this kept the oxidation products in solution. The stable CSV response for $As(OH)_3{}^0$ at 10 mM EDTA suggests that the dissolved arsenite speciation was also stabilised, because the oxidised Fe did not form a solid, adsorptive, hydroxide. The arsenite stabilisation was verified with measurements in samples after prolonged storage, which is shown below.

3.1. Arsenic distribution in groundwaters of the field site in West Bengal

The speciation of As was determined before and after sample storage to verify whether (1) the speciation, and (2) the total concentration of arsenic, can be preserved for long-term storage, and to determine the rate of change in the speciation in unpreserved samples. The water composition with respect to metals (Fe, Mn and Cu) was determined by ICP-MS in acidified aliquots and is shown along the As speciation in Table 1. Levels of Fe were found to range from 4 to 141 μM (0.2–8 mg L^{-1}), of Mn from 0.8 to 45 μM (0.03–2.4 mg L^{-1}), and of Cu from 4 nM to 1.3 μM (0.2–80 μg L^{-1}). The concentration and distribution of Mn, Fe and total As are similar to those found previously on the same site [22]. The previous work showed that high As was associated with high Fe and low As with high Mn.

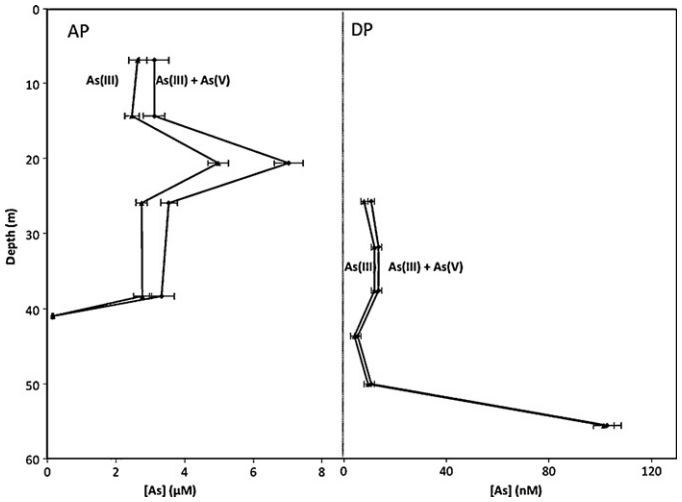

Fig. 2. Speciation of As as a function of depth in adjacent piezometric wells drilled to different depths. Site AP: high-As, high-Fe waters; site DP: low-As, high-Mn waters.

Two depth profiles were constituted from piezometric wells drilled to different depths closely together, at a low As- and a high As-site (DP and AP, for locations see map [22]). The total As in the depth profiles was found to vary between 10 and 98 nM (0.8 and 7 μg L^{-1}) at station DP (a low-As site) and between 0.15 and 7 μM (11 and 512 μg L^{-1}) at station AP (a high-As site). Total As was highest (98 nM) at greatest depth in the deepest sample of DP (56 m), whilst it was highest (7 μM) at intermediate depth (21 m) of site AP (Fig. 2).

3.2. Rapid changes in the speciation and concentration of As upon well-water exposure to air–oxygen and sunlight

The concentration of As(III) and inorganic As (As_{inorg}) were monitored as a function of time after collection of a large unfiltered water sample (20 L) from deep well 5 which was left exposed to the sun from 8 AM. The original concentration of inorganic As was 320 nM (25 μg L^{-1}) which was 99% As(III). Sub-samples were taken at ∼hourly intervals, and subjected to immediate analysis. The As(III) concentration was found to rapidly decrease, its concentration dropping by ca 70% within an hour (Fig. 3), and dropping to zero after 5 h. Inorganic As was found to decrease more slowly with

Table 1
Speciation of arsenic and general composition of the groundwater; <values were below the indicated limit of detection; – indicates a % for both values below the limit of detection.

Date collected	Site	Depth (m)	pH	Voltammetry					HPLC				ICP-MS			
				$As(III)_{CSV}$ (nM)	$As(III)_{ASV}$ (nM)	$As(III)+(V)_{ASV}$ (nM)	% As(III) on-site	% As(III) lab	As(III) (nM)	As(V) (nM)	As(III)+(V) (nM)	% As(III)	As (nM)	Fe (μM)	Cu (nM)	Mn (μM)
07/03/2009	4	45.7	7.0	1491 ± 80	1350±95	1480 ± 75	100	92	1267	210	1476	86	1534	82	456	8
	41	32.3	7.0	13 ± 3	12±1	19 ± 2	71	64	<10	<10	<10	–	16	7	6	45
	13	44.5	6.9	1710 ± 16	860±60	2390 ± 170	71	36	234	2208	2440	10	2043	6	5	19
	17	43.9	7.3	12 ± 3	<1	16 ± 2	75	<2	<10	<10	<10	–	12	6	10	34
	39	49.4	7.2	40 ± 5	40±3	40 ± 3	100	100	44	<10	44	100	16	11	13	14
08/03/2009	15	48.8	6.9	15 ± 1	<1	15 ± 2	100	<7	<10	<10	<10	–	17	7	13	45
	16	33.5	6.9	1998 ± 26	1260±90	2290 ± 160	88	55	785	1511	2295	34	2288	35	11	45
	18	44.2	7.0	11 ± 1	<1	12 ± 2	91	<9	<10	<10	<10	–	11.2	4	8	28
	43	43.3	7.1	11 ± 1	8±2	13 ± 1	84	60	<10	<10	<10	–	12.3	4.4	16	34
	3	18.3	7.1	12,700 ± 680	9310±625	13,400 ± 940	95	70	3265	11,253	14,503	23	17,035	96	1272	0.7
09/03/2009	10	42.7	7.0	12 ± 1	7±1	12 ± 1	100	56	<10	<10	<10	–	14	22	11	28
	32	29.3	7.0	1880 ± 190	1660±116	1880 ± 132	100	89	1508	233	1739	87	2072	116	171	0.9
	38	41.1	7.1	5540 ± 300	5530±390	6110 ± 430	91	91	5500	640	6133	90	7182	141	523	1.5
	30	39.6	7.1	817 ± 42	650±45	930 ± 65	88	70	432	553	984	44	881	5	6	12
	27	41.1	7.0	500 ± 14	490±35	610 ± 43	82	81	522	76	597	87	544	10	4	10
11/03/2009	21	33.5	7.0	4350 ± 65	4170±290	5530 ± 388	79	75	4042	1531	5568	73	6851	112	261	0.6
	7	45.7	7.0	6840 ± 35	6680±470	7690 ± 539	89	87	6707	1074	7773	86	8073	53	303	0.3
	24	39.6	7.0	5780 ± 150	5160±360	6040 ± 423	96	86	5501	636	6131	90	6966	107	442	0.7
	20	33.5	7.0	5700 ± 130	5320±370	6080 ± 425	94	87	5321	750	6065	88	6288	56	358	0.5
	1a	137.2	6.90	110 ± 5	98±7	160 ± 11	69	62	138	104	242	42	138	20	27	2
	5	115.8	7.15	350 ± 31	390±30	395 ± 28	89	100	415	5	421	100	415	33	11	3
	23	125	7.28	20 ± 3	13±2	24 ± 2	83	56	22	<10	22	100	22	15	32	2
	300		7.30	43 ± 5	34±3	37 ± 3	100	92	38	<10	38	100	38	8	53	1.5

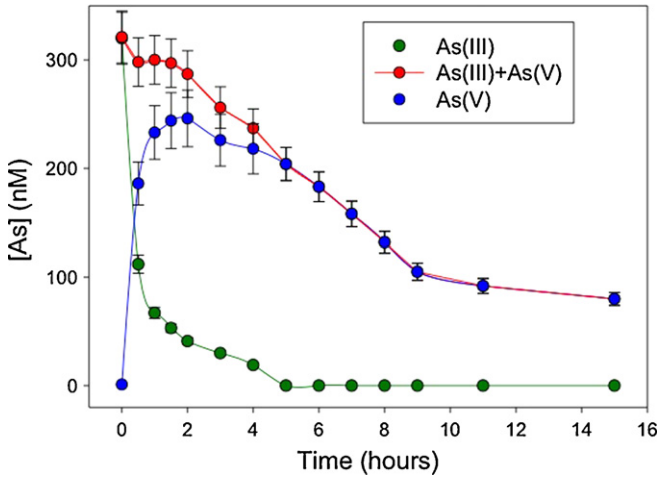

Fig. 3. Changes in the arsenic speciation as a function of exposure time to air and sunlight, of a freshly collected, 10 L, well sample.

time (loss of 75% in 10 h) indicating that As(III) is first rapidly oxidised to As(V) and As(V) is subsequently removed from the solution by adsorption on newly formed Fe and Mn oxides. The concentration of dissolved Fe was not monitored during this experiment, but visual inspection showed that flocs of Fe(III)-hydroxides started to form from about 1 to 2 h, indicating that the process of Fe-oxidation overlapped with that of As-oxidation, suggesting that Fe-oxidation may have catalysed the As-oxidation.

The rapid removal of As from groundwater, and its oxidation to As(V) (Fig. 3), illustrate the importance of either stabilising the sample immediately (EDTA, acid) and/or analysing the sample immediately after collection. The rapid As(III) oxidation can be due to a combination of several parameters. Thermodynamically driven oxidation by atmospheric oxygen can take days [29] so it is likely that this is not the main driver. The oxidation could be stimulated by solar irradiation, previous work showing a 54% oxidation of As(III) within 45 min [30]. The rate of oxidation is known to be increased in the presence of Fe(III) due to charge transfer to radicals from iron oxides [31]. Fe(III) can then adsorb and co-precipitate the As(V), which is in agreement with our experimental field data. Bacterial activity may also be a contributory factor, as it has been reported to oxidise and remove As(III) in the presence of Fe(II) and Mn(II) [32].

Subsequent to the As oxidation, precipitation of Fe-hydroxides removed the arsenate out of solution. A settlement and decantation method has previously been recommended as a simple method to reduce As pollution [33], and our data shows that this should be effective.

The subsequent study of arsenic speciation in the field was carried out immediately after sample collection and using EDTA to eliminate Fe and Mn interference and oxidative As removal.

3.3. Arsenic speciation in these West Bengal groundwaters

The concentration of reactive As(III) ($As(III)_R$) was determined by CSV in all samples, and inorganic As(III) by ASV in some samples, in the field immediately upon sampling. Storage effects on the concentration of inorganic As(III) were evaluated from comparative analyses on samples stored acidified for 1 month. The speciation data shows that inorganic arsenite was predominant in all samples, $As(III)_R$ accounting for for 78% of total As ($n = 33$) (Fig. 4A). The predominance of arsenite is to be expected as the arsenic enters the groundwater as a result of reductive dissolution of deposits high in iron and arsenic [22]. The underlying cause (chemical or biological) for the reduction of As to As(III) is subject to further research, but it is currently thought to be a microbiological phenomenon [32].

Comparison of the $As(III)_R$ (CSV) and combined inorganic As (As(III) + As(V)) data (ASV) shows that on average 14% of the inorganic As was As(V). However in-spite of the systematic difference between $As(III)_R$ and inorganic As, the $As(III)_R$ in several samples amounted to 100% of the combined As (Table 1). The short-term sample exposure experiment (Fig. 3) shows that the speciation in unpreserved samples changes rapidly, suggesting that some of the As(III) may have become oxidised to As(V) between sample collection and stabilisation by addition of acid or EDTA, which may have contributed to the systematic presence of As(V) in the stored samples.

The ASV data showed that As_{inorg} was $91 \pm 1\%$ of total As (Fig. 4B). The high proportion of inorganic As leaves only a small fraction (up to $9 \pm 1\%$) of the As in a non-labile, probably organic, species. Organic arsenic species were not detected by the HPLC–ICP-MS measurements, suggesting that the small difference between total (ICP-MS) and inorganic As was due to a systematic difference between the two different techniques, or to undetected complexation with humic substances in the groundwaters.

Samples from various depths in adjacent piezometric wells showed a larger spread in the As(III) % than those from the other wells, with a range from 32 to 106%, and an average of 77%. A possible reason for the greater spread is that the piezometric wells are rarely used so the water may be subjected to air for longer.

3.4. Comparison of the speciation determined in the field to that in the laboratory

The inorganic As(III) detected as $As(III)_R$ in the field was essentially the same as that found by the ASV method in the laboratory ($As(III)_R = 101 \pm 2\%$ of $As(III)_{ASV}$) (Fig. 4C). It was also the same as that found using the reference HPLC–ICP-MS method ($As(III)_R = (1.04 \pm 0.03) \times As(III)_{HPLC}$, $n = 22$) (Fig. 4D). These data show that the field measurement of inorganic As(III) by CSV is in excellent agreement with data obtained by reference techniques in the laboratory.

The field data for inorganic As ($As(III)_R$) were produced by CSV using battery powered apparatus. The close co-variation between the $As(III)_R$ with that of total arsenic (slope 0.78 ± 0.02), indicates that the field-measured $As(III)_R$ can be used as predictor of the total As in the samples. This finding much facilitates the monitoring of arsenic in the field. The reason for the good agreement is, that the reduced As is the predominant form of As in these samples, and that the reduced As occurs as $As(OH)_3$, which is the species detected by the CSV method.

An alternative to CSV is ASV [19], which can also be carried out in the field using the same apparatus as used here. The ASV method was used here to monitor total As during the short-term storage experiment. ASV requires addition of HCl: it was not possible to transport the HCl by air to the field and we could acquire this locally only in the course of this study. CSV was selected for the measurement of As(III) because this is measured at near natural pH and it was initially thought this would be the best way to retain the original speciation. It was initially hoped that the CSV method would be reagentless, but it was found to require EDTA to eliminate Fe interference. The use of EDTA in the field presented no problem as the EDTA is readily shipped or carried as hand luggage. In the event, the As(III) found by CSV in the field was the same as that found by ASV in stored samples, because the HCl was found to stabilise the As(III).

The ASV method was found to suffer from interference from Cu and Fe(II): the peak for Cu (at 0 V) overlaps that for As (at −0.2 V) at high Cu concentration (>100 nM Cu) and several samples were found to have a greater concentration of Cu (Table 1). This Cu inter-

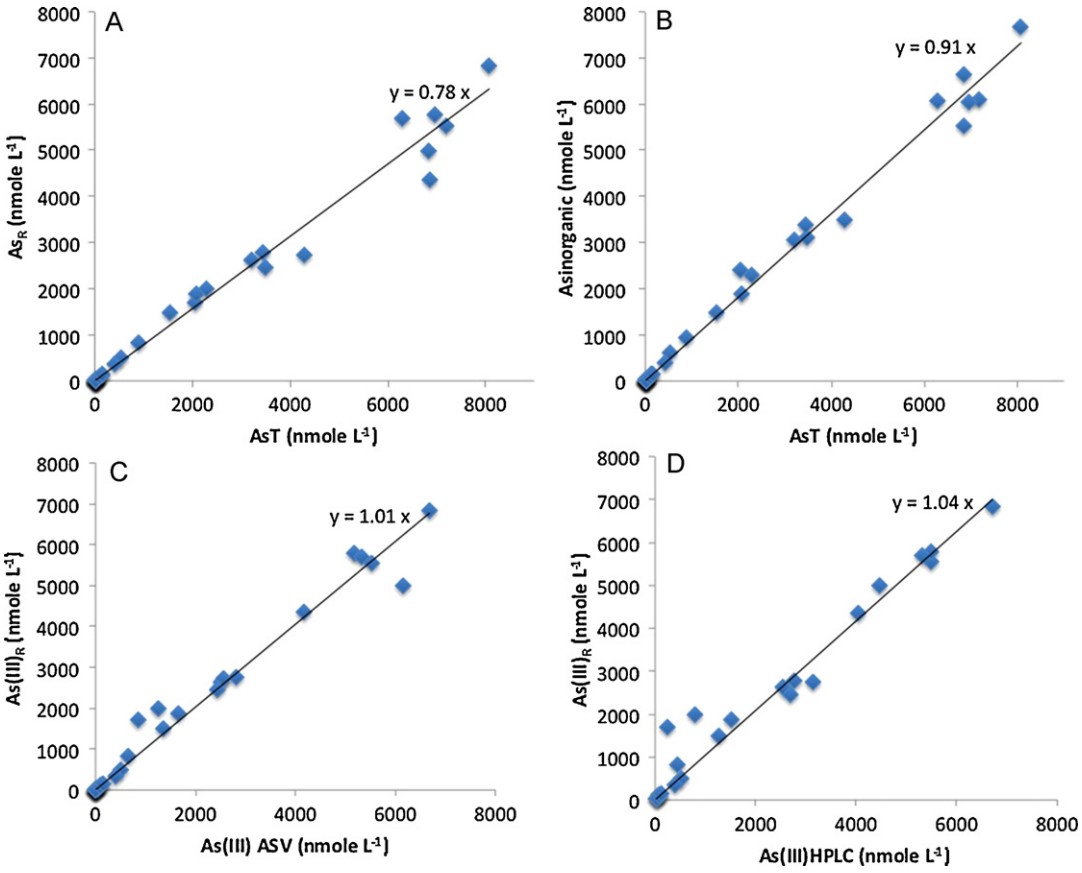

Fig. 4. Effect of sample storage on arsenic concentration and speciation by comparison of measurement in the field to that in the laboratory. (A) Reactive As(III) (CSV in the field) vs. total As (ICP-MS); (B) inorganic As (ASV, lab) vs. total As; (C) Reactive As(III) (field) vs. As(III) (ASV in the laboratory) and (D) reactive As(III) (field) vs. As(III) (HPLC in the laboratory).

ference is a known problem for As(III) detection by ASV using gold electrodes [19,34,35]. High levels of Fe (>50 μM) as Fe(II) were also found to interfere with the ASV method, lowering the ASV sensitivity for As. Both interferences were resolved by sample dilution with 0.1 M HCl.

The sensitivity of the CSV method for As in groundwaters was less than in model solutions due to competitive adsorption of organic matter on the electrode. As a result the limit of detection was 3 nM $As(III)_R$ (90 s adsorption time, determined in a sample containing 10 nM $As(III)_R$) compared to 0.5 nM $As(III)_R$ in model solutions [18].

Advantages of the CSV method are a longer linear range, no interference by Cu, and elimination of the Fe interference by the EDTA addition up to 1 mM Fe, so dilution was required for only a few samples. So, though both CSV and ASV can be used in the field for detection of As(III) in groundwaters, the CSV has advantages.

3.5. Sample storage of the As speciation

The close agreement between the As(III) found in the field by CSV and that found by ASV in samples stored for a month ($As(III)_R = 101 \pm 1\%$ of $As(III)_{ASV}$) (Fig. 4C) shows that the As(III) was successfully stabilised by either 0.1 M HCl or 10 mM EDTA. This was confirmed by the HPLC–ICP-MS data, which agreed within 4%. This work therefore confirms the previous finding that As(III) is stabilised by addition of EDTA [24,25].

The mechanism of the As(III) stabilisation by EDTA is probably through the complexation and solubilisation of the Fe and Mn species, thus preventing the formation of reactive hydroxide species. The longterm stabilisation without the addition of bactericidal agents, suggests that changes in the Fe redox speciation are the main agent catalysing the As(III) oxidation in these groundwaters, although bacterial activity is thought to play a role in other waters [32]. Photochemical effects (if any) were largely excluded, as the samples were stored in polyethylene bottles.

3.6. Storage effects on total arsenic

Total inorganic arsenic measured within 1 month (either on-site or in the laboratory) (voltammetry at pH 1) can be compared to that (obtained by ICP-MS) after storage (stored acidified for 2 month) in Fig. 4A. The slope of the straight fit to the data is 0.91, indicating that inorganic As amounted to 91% of total As, and was well preserved by acidification. This is expected as co-precipitation of As with Fe or Mn does not occur in this condition. The good agreement between the voltammetric and ICP-MS data suggests that organoarsenic species constitute a negligible fraction of the total arsenic as these would have been detected as part of total As by the ICP-MS method but not by voltammetry unless the samples are UV-digested. It should be noted that here two different techniques are compared, using independent calibrations; agreement within 9% is therefore very good. A significant organic As component in these samples was not detected by the HPLC method, which confirms the previous finding that organoarsenic species are minor in reducing groundwaters of this type [36].

3.7. Storage effects on the speciation of arsenite [As(III)]

The As(III) was found to be stabilised equally well by addition of EDTA (pH 8.5) and by acidification to pH 1 with HCl (Fig. 4B).

The concentration of As(III) found in freshly collected samples by voltammetry in the field was equal to that found by HPLC analysis of samples stored in the presence of 10 mM EDTA or in acidified water (pH 1). This data shows that the original As speciation in the samples was stabilised, allowing storage over several months. Three of the acidified samples showed significantly higher values that the expected 1:1 relationship which could indicate some oxidation of As(III) during storage. The good correlation confirms previous work that the As speciation is preserved by the addition of EDTA [24,25]. A major added advantage of the EDTA addition is the elimination of the interference of high Fe and Mn on the voltammetric detection of As(III) in the field. A further practical advantage of using EDTA over acid is that EDTA is safe to handle in the field and not classified as a dangerous chemical, which is more convenient and cheaper for shipping purposes than HCl.

4. Conclusions

Close agreement with laboratory reference techniques shows here that the speciation of arsenic in groundwaters is readily measured in the field using CSV and battery powered apparatus. Interference by very high (mM) levels of Fe and Mn is successfully eliminated by addition of 10 mM EDTA, thus facilitating the on-site measurements. The addition of EDTA, and separately of 0.1 M HCl, was also effective in stabilising the redox speciation of As for several months, confirming previous work and enabling sample storage for later comparative analysis. This effect of EDTA, without the need for bactericidal compounds, shows that changes in the redox speciation of Fe are the main agent catalysing the oxidation of As(III) to As(V) in well waters, bacteria playing no role, and photochemical effects remaining untested.

The validation of the method in the field shows that most of the As ($78 \pm 0.02\%$) in the study area (West Bengal, India) occurs as inorganic As(III). Without preservation the As(III) becomes rapidly oxidised to As(V); subsequent oxidation of Fe(II) to Fe(III) removes the As(V) within a few hours by adsorption on precipitating Fe(III)-hydroxides. The close co-variation between the $As(III)_R$ with that of total arsenic (slope 0.78 ± 0.02), indicates that the field-measured $As(III)_R$ can be used as predictor of the total As in the samples. The good sensitivity of the field method, with a limit of detection 3 nM ($0.2\ \mu g\ L^{-1}$) As, means that groundwaters can be tested to well below the recommended health limit of $10\ \mu g\ L^{-1}$ As.

The ability to determine As in groundwaters using inexpensive portable apparatus with excellent sensitivity and accuracy much facilitates the testing of suspect well waters in the field.

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