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Chemical Fate of Arsenic and Other Metals in Groundwater of Bangladesh: Experimental Measurement and Chemical Equilibrium Model

A. Hussam,^{1,*} M. Habibuddowla,² M. Alauddin,³ Z. A. Hossain,³
A. K. M. Munir,⁴ and A. H. Khan⁵

¹Chemistry Department, George Mason University, Fairfax, Virginia, USA

²Frankfort, Kentucky, USA

³Department of Chemistry and Chemical Technology,
Islamic University, Kushtia, Bangladesh

⁴Department of Environment Initiative, Sono Diagnostic Center,
Courtpara, Kushtia, Bangladesh

⁵Department of Chemistry, University of Dhaka, Dhaka, Bangladesh

ABSTRACT

The presence of toxic level of inorganic arsenic in groundwater used for drinking in Bangladesh and neighboring India is unfolding as one of the worst natural disaster in the region. The purpose of this work is to ascertain the chemical fate of arsenic and other metals in groundwater of Bangladesh. A combination of techniques was used to measure 24 metals, 6 anions, E_h , pH, dissolved oxygen, conductivity, and temperature to understand the distribution of components which were then used in computational chemical equilibrium model, MINEQL+, for detailed speciation. It was found that the fate of arsenic and its speciation were inextricably linked to the formation of hydrous ferric oxide (HFO) and its kinetic. The HFO induced natural attenuation removes 50–75% of total arsenic in first 24 h through a first order kinetics. Adsorption on HFO is the predominant mode of removal of arsenic,

*Correspondence: A. Hussam, Chemistry Department, George Mason University, Fairfax, VA 22030, USA. E-mail: ahussam@gmu.edu.



iron, manganese, and most trace metals. The equilibrium model points to the presence of excess active sites for the removal of arsenic. MINEQL+ shows that significantly higher concentration of HFO forming iron is required to remove arsenic below maximum contamination level (MCL) of 50 µg/L than predicted by stoichiometry. The practical implication of this work is the prediction of water quality based on models.

Key Words: Arsenic; Speciation; Groundwater; MINEQL+; Water quality; Bangladesh.

INTRODUCTION

Arsenic contamination of groundwater in the Bengal basin is unfolding as one of the worst natural geo-environmental disaster to date.^[1-4] The source of arsenic is the special underground geochemical condition by which arsenic is mobilized as soluble species in the groundwater, primarily, mobilization by dissolution within the sediment by virtual quantitative reduction of As(V) to As(III).^[5-8] Groundwater is the primary source of drinking water for millions of people in Bangladesh and neighboring India. It is mostly pumped out by hand-operated tubewells (with a metal casing) from 30–200 feet underground. World Health Organization (WHO, 1999) reports that there are about 2.5 million tubewells in Bangladesh (unofficial estimates are 10 million tubewells) and more than 95% of the Bangladesh population of 120 million drinks well water.^[9] It is estimated that at least 40% of the wells are contaminated with more than the maximum contamination level (MCL) of arsenic in drinking water is 50 µg/L (0.05 mg/L 50 ppb; ppb: part-per-billion). Total arsenic measurement shows that more than 60% of water from shallow and deep tubewells has above 10 µg/L guideline value.^[10] Long-term exposure to low concentrations of arsenic has been reported to cause cancer of bladder, skin, and other internal organs.^[11-13] In Bangladesh, disease related to drinking arsenic contaminated water has been reported.^[14] Arsenic in its various ionic forms is also known to be very toxic to many microorganisms.^[15] The present crisis may have affected more than 50 million people in Bangladesh and the neighboring India and the long-term consequence of this exposure is still unknown.

Significant work has been done to survey the extent of this crisis both in number of tubewells contaminated and understanding the disease caused by arsenic ingestion. However, very little attention has been paid to understand the fate of arsenic and chemical speciation of metals present in groundwater. In particular, there is almost no report to understand the present situation on the basis of groundwater chemistry. Without such understanding it is not possible to identify the source and transformation of arsenic or devise mitigation procedures. This work also complements our ongoing efforts to develop inexpensive methods for the purification of water from arsenic.^[16,17]

In Bangladesh, it is commonly known that groundwater high in iron when left in the open forms a brownish precipitate and removes some inorganic species. The water, locally known as 'bashi pani,' is then collected by decanting. The process by which this occurs is the natural attenuation of groundwater (NAGW). Experimental measurement of inorganic species in fresh groundwater (FGW), NAGW and computational



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chemical equilibrium models were used to understand the chemical fate of arsenic and other cations and anions in groundwater. Because an initial removal of precipitates in NAGW can substantially improve the efficiency of various filters, this work could be useful in designing better water purification strategy. The most pressing need for this work is to unravel the nature of chemical attenuation process by which the fate of arsenic and other toxic metals is determined.

EXPERIMENTAL SECTION

The FGW and the same spiked with excess arsenic (sodium arsenate, As(V)) were left in 500 mL high-density clear polyethylene (HDP) bottles without a headspace for 24 h to 6 weeks under normal room light condition. The same water was acidified with 1 M HCl to pH 2 and kept in similar bottles without a headspace as controls. The water from both samples was analyzed for As(III), As(total), 24 other metals, anions and other water quality parameters as described later. FGW and NAGW samples were not filtered in order to retain the natural usage condition of common household of Bangladesh.

Measurements of As(III) and As(total) were accomplished by a Model HQ-2040 (Advanced Analytics, Virginia, USA) personal computer controlled electrochemical analyzer. For arsenic analysis the instrument uses a staircase anodic stripping voltammetry (SASV). The preparation of electrodes, analytical protocols, and method validation were based on published results,^[18–23] and that of a modified EPA method 7063: Arsenic in Aqueous Samples and Extracts by Anodic Stripping Voltammetry (ASV).^[24] The method of standard addition was employed to eliminate matrix effect of solution. The electrochemical method can be used to measure As(III) in presence of As(V) at all concentrations and the total arsenic after reduction of As(V) to As(III) by Na₂SO₃. The same instrument was used to obtain transient and equilibrium redox potential, E_h , by measuring the open-circuit potential of a polished glassy carbon electrodes against the Ag/AgCl(s), satd. KCl reference electrode and corrected for standard hydrogen electrode. Dissolved oxygen was also measured during the E_h measurement.

A Perkin–Elmer model 5100 Zeeman-effect atomic absorption spectrometer with a graphite furnace (AASGF-Z) and model A-60 autosampler were used for low level arsenic measurement. A 24-trace metal profile of water samples was measured by a direct reading Echelle inductively coupled plasma atomic emission spectrometer (ICPAES) with radial and axial view (Leeman Labs, NH, USA). The ICPAES method detection limits are shown with less than (<) symbol preceding the value. Both AASGF-Z and ICPAES were used to validate electrochemical SASV measurement of arsenic. Total soluble iron (Fe(II) and Fe(III)) was measured by visible spectrophotometric procedure based on Fe(II)-phenanthroline colored complex. Total ionic conductivity, pH, and temperature were measured by standard digital meters. Dissolved oxygen was measured by polarographic type oxygen sensor (LT-Lutron Model DO-5510, Taiwan). Anion profile of naturally attenuated groundwater (NAGW) samples was measured by ion chromatography (Lachat QuickChem-8000, Lachat Instruments Division, Milwaukee, WI, USA). Cl⁻ was



also measured with an ion selective electrode on a serum electrolyte analyzer (Model-EasyLite Plus, M.I.T Services Inc., USA). Concentrations of CO_3^{2-} and HCO_3^- were obtained from micro-titration of groundwater with standard HCl.^[25]

Chemical equilibria modeling and species distribution calculations are based on MINEQL+ program (Version 4, Environmental Research Software, Hallowell, ME, USA). The computational model involves defining a system through selection of basic chemical components, creation of chemical species from components by using thermodynamic data base, fixing total concentration of individual components, and solving the chemical mass and charge balance equations by Newton–Raphson method. Details of the original program and explanation of parameters are obtained elsewhere.^[26]

RESULTS AND DISCUSSION

Nature of Groundwater

Experiments reported in this paper were performed with groundwater obtained from a tubewell in Kushtia Sadar, which has been continuously monitored for As(III) and As(total). About 40% of groundwater in Kushtia was contaminated with more than 50 $\mu\text{g/L}$ As(total).^[19] The water quality of the tubewell is representative of the groundwater used by about 400 thousand people of Kushtia Sadar (area 316 sq. km). People in this area may have been drinking this water for many years. Patients with confirmed cases of arsenical keratosis are identified here and many other parts of Bangladesh.^[27] The groundwater used in this study is somewhat representative of that available throughout Bangladesh except for the concentrations of iron and arsenic as the critical variable components pertinent to this study.

Table 1 shows the elemental composition of major, minor, and trace elements in fresh groundwater (FGW), naturally attenuated groundwater (NAGW or locally known as ‘bashi pani’), and the composition used in the chemical equilibrium models. Table 1 also shows parameters such as pH, ionic strength, temperature, total alkalinity, E_h , and dissolved $\text{O}_2(\text{aq})$. Except for E_h , and dissolved $\text{O}_2(\text{aq})$, they were also used as model inputs. The concentration range shown in Table 1 is for four samples from the same tubewell except for arsenic, which was increased by spiking the natural groundwater value $134 \pm 20 \mu\text{g/L}$. Visually the fresh groundwater is clear but turns brownish after leaving for few hours in the open. Spectrophotometric and ICPAES measurements show 6–7 mg/L of total soluble iron in groundwater, which plays a significant role in the attenuation process. The concentration change in naturally attenuated groundwater and the choice of input concentrations in model are discussed later in connection with steady-state measurement.

Dynamics of Arsenic Precipitation in Fresh Groundwater

The general observation that groundwater, after exposure to air, turns brown with visible floc formation is indicative of a natural attenuation process. The attenuation

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Table 1. Composition of major, minor, and trace metals for fresh groundwater (FGW), naturally attenuated groundwater (NAGW or 'bashi-pani'), and concentrations used in computational models.

Elements	Fresh Groundwater (FGW) mg/L	NAGW (Bashi Pani) mg/L	Conc. Used in Models mg/L (M)
Aluminum, Al	<0.015–0.022	<0.015–0.022	0.022 (8.15×10^{-7})
Antimony, Sb	<0.013–0.017	<0.013	
Arsenic, As	0.114–1.160	0.064–0.400	1.160 (1.55×10^{-5})
Barium, Ba	0.161–0.170	0.003–0.082	0.161 (1.17×10^{-6})
Beryllium, Be	<0.001	<0.001	
Cadmium, Cd	<0.001	<0.001	
Calcium, Ca	111–117	17.7–87.4	111 (2.77×10^{-3})
Chromium, Cr	<0.002	<0.002	
Cobalt, Co	<0.002	<0.002	
Copper, Cu	0.004–0.009	0.002	0.007 (1.10×10^{-7})
Iron, Fe	6.77–7.19	<0.005	6.77 (1.21×10^{-4})
Lead, Pb	<0.004–0.005	<0.004	
Magnesium, Mg	21.4–23.1	19.31–20.9	21.4 (8.88×10^{-4})
Manganese, Mn	0.69–0.74	<0.001–0.01	0.705 (1.28×10^{-5})
Molybdenum, Mo	0.001–0.003	0.002	
Nickel, Ni	<0.002	<0.002	
Potassium, K	1.88–2.45	1.76–2.09	2.45 (6.27×10^{-5})
Selenium, Se	<0.012	<0.012	
Silver, Ag	<0.002	<0.002	
Sodium, Na	18.2–20.4	17.8–19.3	20.4 (8.87×10^{-4})
Strontium, Sr	0.280–0.297	0.190–0.272	0.281 (3.21×10^{-6})
Thallium, Tl	<0.067	<0.067	
Tin, Sn	<0.002–0.01	0.007–0.01	
Vanadium, V	<0.001	<0.001	
Zinc, Zn	0.012–0.021	<0.007	0.021 (3.21×10^{-6})
Other Measured Parameters as Model Inputs			
pH	6.9	7.7	
Ionic strength (M)	9.66×10^{-3}	9.66×10^{-3}	
Temperature (°C)	27	29	
Total alkalinity (M)	0.0101	0.0101	
E_h (mV) vs. NHE ^a	127–250	340–440	
O ₂ (aq), mg/L ^a	0.8–1.0	1.0–2.4	

^aNot used as model inputs. Parameters show observed minimum and maximum values in FGW measured immediately and that of NAGW measured after 4 h.

process is accompanied by precipitation of hydrous ferric oxide (HFO–Fe₂O₃, 2–3 H₂O) and coprecipitation of trace cations and anions from groundwater.^[28] To understand the dynamics of arsenic coadsorption and coprecipitation, a set of experiments was performed by measuring arsenic concentration as a function of time.

**Table 2.** First order fitting parameters for the decay of arsenic in groundwater samples by natural attenuation on HFO (first order precipitation data).

Sample	As _{t=0} (µg/L)	k (h ⁻¹)	t _{1/2} (h)	r ²
bpec1	187	0.0338	20.50	0.9780
bpec2	832	0.0274	25.30	0.9931
bpec3	1401	0.0426	16.27	0.9480
Average		0.0346	20.68	0.9730
%RSD		22.0	21.8	2.36

The total arsenic was measured by SASV as discussed earlier. Data for first order decay of arsenic concentration from three initial values are summarized in Table 2.

Table 2 shows that the first order decay of arsenic is a process with average rate constant of 0.0346 h⁻¹ and a half-life of 21 h. The first order process is further evidenced by the independence of rate constant on initial concentration and good precision (2.4% RSD) in data fitting. The calculated and experimental As_{t=0} also agreed within 10%. A 21 h half-life along with the observation of brownish precipitation indicates the formation of HFO as the rate limiting step. In natural groundwater (pH > 6), however, the formation of HFO must precede oxidation of Fe²⁺ to Fe³⁺. At pH > 6, we calculate the half-life for the oxidation process is about 4 min.^[29] Overall, there are four steps for the formation of HFO where the slow step is the formation of large polymeric ferric hydroxo complexes from monomer, dimer, and small polymers.^[30] The final fast step is the precipitation of solid HFO. The resulting HFO, if pure, is amorphous with a very large surface area (600 m²/g) and adsorbs large quantities of arsenite, arsenate, and other ions. In a closed system such as these, with fast oxidation of Fe²⁺ which could be catalyzed by metal ions such as Mn²⁺, dissolved oxygen and the surface of the container (plastic or clay) the rate of formation of HFO controls the sorption rate of trace contaminants. Therefore, the natural attenuation and consequent removal of many ions particularly those of heavy metals are controlled by the rate of formation HFO.^[28]

Steady-State Measurement of Arsenic in Preserved Groundwater

To observe the fate of arsenic and other metals, groundwater samples containing normal and elevated level of arsenate were left in HDP containers without headspace for 6 weeks. Duplicate samples of the same were also preserved in acid (1 M HCl) to retain the original composition of groundwater. Samples preserved without acid showed brownish precipitate adhering strongly to the HDP surface. Arsenic concentrations from these samples were measured after carefully decanting the water. The same samples were also used to measure concentrations of 24 other metals by ICPAES as discussed later. Table 3 shows the results of arsenic concentrations before and after the samples were preserved.

Table 3 shows 50–75% of initial arsenic is removed by the precipitate formed during the preservation of groundwater at indicated level of iron, pH and

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Table 3. Removal of arsenic by adsorption on HFO formed from soluble iron in groundwater (pH = 7.7, temperature = 29°C).

Expt #	Total Fe (μg/L)	As (μg/L) Before	As (μg/L) After	μM As Adsorbed	μM Fe Precipitated	μM As Adsorbed Site Dens Type 1	μM As Adsorbed Site Dens Type 2	% As Removed
1	6440	158	39	1.59	115.4	0.58	23.1	75
2	5886	552	191	4.82	105.5	0.53	21.1	65
3	5849	776	358	5.58	104.8	0.52	21.0	53
4	6770	1160	376	10.47	121.3	0.61	24.3	67

temperature. The equilibrium concentration of arsenic (as arsenate) in water, except for the first sample, did not go below the MCL. We found that nearly 100% iron was precipitated in the process (ICPAES data as discussed later). Assuming that the precipitate-HFO has two active adsorption sites with site densities 0.005 and 0.2 mols/mol of Fe (Ref. [28], p. 92–94), micromoles of arsenic adsorbed at these sites can be estimated as shown in Table 3. It shows that the actual concentration of arsenic adsorbed has saturated site 1 and then part of site 2, but less than the estimated saturation limit of 24 μmols. The incomplete adsorption of arsenate indicates the presence of lower concentration of active sites in HFO than that of the literature values and competition from other inorganic and, possibly, organic species present in groundwater at much higher concentrations. Chemical equilibrium models as discussed later further examine these findings.

Distribution of Total Ions in Groundwater

To understand the equilibrium concentrations of total ionic species in groundwater, ICPAES measurements of 25 metals were taken with FGW samples preserved in acid and that without acid i.e., NAGW. The concentrations are shown in Table 1. It shows concentrations of all metals have decreased. In particular, the concentrations of Fe and Mn are reduced below the detection limits and, therefore, completely precipitated as their hydroxides. It also shows that total arsenic concentration decreased from 114 to 64 μg/L in the low range and 1160–400 μg/L in the high range. The equilibrium AsO_4^{3-} concentrations in the preserved water measured after 3 months were higher than predicted by the first order kinetic. This could be due to the aging of the HFO to more crystalline iron oxide (usually goethite) and exclusion of arsenate during transformation of HFO from amorphous to crystalline phase.^[31] The concentrations of Pb, Cu, and Zn have also decreased significantly. While the concentrations of Ca and Ba have decreased by more than 40%, the concentrations of other alkali and alkaline earth metals did not diminish significantly.

We have also measured anion concentrations in NAGW as shown in Table 4. The first six entries in Table 4 were obtained by ion chromatography. Arsenate and

**Table 4.** Composition of anions for fresh groundwater and naturally attenuated groundwater.

Species	Conc., mg/L (M)	Comments ^a
As(V) as AsO_4^{3-}	0.973 (7.0×10^{-6})	FGW, MI, ANOXIC
As(III) as AsO_3^{3-}	0.712 (5.65×10^{-6})	FGW, MI, ANOXIC
Fluoride, F^-	0.268 (1.51×10^{-5})	NAGW, IC, MI
Chloride, Cl^-	3.27 (9.22×10^{-5})	NAGW, IC, MI
Nitrite, NO_2^-	0.47 (1.02×10^{-5})	NAGW, IC, MI
Nitrate, NO_3^-	0.98 (1.58×10^{-5})	NAGW, IC, MI
Phosphate, PO_4^{3-}	0.023 (2.42×10^{-7})	NAGW, IC, MI
Sulfate, SO_4^{2-}	0.424 (4.42×10^{-6})	NAGW, IC, MI

^aNAGW—naturally attenuated groundwater, FGW—fresh groundwater, IC—ion chromatography, MI—model input.

arsenite concentrations were obtained from measurement of As(III) and As(total) by ASV and As(total) by ICPAES. We have also assumed that As(total) measured is of inorganic origin. Total alkalinity and thus the CO_3^{2-} and HCO_3^- were obtained from acid–base micro-titration of fresh groundwater purged with nitrogen as mentioned in the experimental section. Ionic strength was calculated from the ionic conductivity of fresh groundwater.^[32] We were able to measure anions only in attenuated groundwater because they were not preserved with acid. One of the major problems in working with groundwater is its unstable nature in contact with air and a continuous change in speciation unless preserved in strong mineral acid. The preservation procedure generally retains total cation concentrations but not the anions. However, in a dilute solution such as groundwater majority of the univalent anions is non complexing and therefore does not contribute to speciation. The multivalent anions, on the other hand, may affect speciation at concentrations similar to those of many trace metals. This can be studied either by using measured concentrations or by using realistic concentrations in the model. Chemical components in Tables 1 and 4 are used for speciation modeling as discussed later.

Chemical Equilibrium Model and Speciation

To understand chemical speciation of inorganic species in groundwater, a computational chemical equilibrium modeling system—MINEQL+ was used. The inputs for the program are listed in Tables 1 and 4. Here, MINEQL+ is used to find the equilibrium concentrations of components and species in solution under natural conditions. Table 5 shows the distribution of components and species with concentrations greater than 10^{-7} M for FGW, which is nearly anoxic and closed to atmospheric $\text{CO}_2(\text{g})$. In Table 5 the percent removed is based on the molar concentrations and the mg/L unit is based on the atomic weight of metal in the complex. To simulate the groundwater condition we have assumed the presence of reduced state, Fe(II)



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Table 5. Concentration distribution of components and species present in groundwater of composition shown in Table 1.

Components	FGW, ANOXIC		NAGW, OXIC		% Removed
	[M]	mg/L	[M]	mg/L	
Ca(2+)	1.55×10^{-3}	62.000	2.90×10^{-6}	11.600	81.3
Cl(-)	9.22×10^{-5}	3.273	9.22×10^{-5}	3.273	0.0
CO ₃ (2-)	4.80×10^{-6}		2.46×10^{-5}		-412.5
Fe(2+)	1.26×10^{-5}	0.706	0	0	100.0
F(-)	1.35×10^{-5}	0.257	1.38×10^{-5}	0.262	-2.2
K(+)	6.27×10^{-5}	2.458	6.27×10^{-5}	2.458	0.0
Mg(2+)	8.25×10^{-4}	20.048	2.44×10^{-4}	5.929	70.4
Mn(2+)	1.13×10^{-5}	0.620	0	0	100.0
Na(+)	4.32×10^{-3}	99.32	6.13×10^{-3}	140.93	-41.9
NO ₂ (-)	1.02×10^{-5}	0.469	1.02×10^{-5}	0.469	0.0
NO ₃ (-)	1.58×10^{-5}	0.980	1.58×10^{-5}	0.980	0.0
SO ₄ (2-)	3.66×10^{-6}	0.351	4.14×10^{-6}	0.397	-13.1
Sr(2+)	3.21×10^{-6}	0.281	3.20×10^{-6}	0.280	0.3
Zn(2+)	1.45×10^{-6}	0.095	2.11×10^{-7}	0.014	85.4
Species					
H ₃ AsO ₃ (aq)	6.16×10^{-6}	0.462	0	0	100.0
HAsO ₄ (2-)	5.57×10^{-6}	0.417	9.23×10^{-6}	0.692	-65.7
H ₂ AsO ₄ (-)	2.94×10^{-6}	0.220	7.59×10^{-7}	0.057	74.2
CaHCO ₃ (+)	9.98×10^{-5}	4.000	1.55×10^{-5}	0.621	84.5
CaF(+)	1.25×10^{-7}	0.005	2.54×10^{-8}	0.001	79.7
CaSO ₄ (aq)	5.13×10^{-7}	0.021	1.12×10^{-7}	0.004	78.2
H ₂ CO ₃ (aq)	2.39×10^{-3}	0.000	2.95×10^{-4}	0	87.7
HCO ₃ (-)	9.18×10^{-3}	0.000	7.09×10^{-3}	0	22.8
MgHCO ₃ (+)	5.97×10^{-5}	1.451	1.38×10^{-5}	0.335	76.9
MnHCO ₃ (+)	1.33×10^{-6}	0.073	0	0	100.0
NaHCO ₃ (aq)	0	0	2.16×10^{-5}	0.497	—
ZnHCO ₃ (+)	1.06×10^{-6}	0.069	1.26×10^{-7}	0.008	88.1
CaCO ₃ (aq)	4.81×10^{-6}	0.193	4.89×10^{-6}	0.196	-1.7
Mg(SO ₄)(aq)	2.39×10^{-6}	0.006	8.10×10^{-8}	0.002	66.1
MgCO ₃ (aq)	1.70×10^{-6}	0.041	0	0	100.0

Distributions were calculated by computational chemical equilibrium model, MINEQL+.

and Mn(II). Because FGW has no visible solid present, adsorption was not considered. Naturally attenuated groundwater or 'bashi pani,' on the other hand, is considered to be exposed to atmosphere and Fe(II), Mn(II), and AsO₃³⁻, are oxidized to Fe(III), Mn(III) and AsO₄³⁻, respectively. The formation of HFO in NAGW is used to invoke the two-layer constant capacitance Fe-OH adsorption model. The model includes strong and weak adsorption sites on HFO with densities, 0.005 mols/mol Fe and 0.20 mols/mol Fe, respectively. All model calculations were corrected for zero charge balance under constant ionic strength and observed pH. Table 5 yields the



following important findings:

- (a) Major arsenic species in anoxic groundwater samples are H_3AsO_3 , H_2AsO_4^- , and HAsO_4^{2-} . There is only one primary arsenic species in oxic water: HAsO_4^{2-} with a minor portion of H_2AsO_4^- . In oxic, NAGW water all H_3AsO_3 and 70% of H_2AsO_4^- are converted into HAsO_4^{2-} which is consistent with experimental data. This is primarily due to changes in pH and oxidation state. Table 5 also shows 65% of the arsenic remained in the soluble form and 35% of arsenic was removed by adsorption from an initial input concentration of 1160 $\mu\text{g/L}$. The major iron containing adsorbates are $\text{Fe}(\text{wk})\text{OH}_2^+$ and $\text{Fe}(\text{wk})\text{OH}$. The adsorbed species are identified as $\text{Fe}(\text{wk})\text{HAsO}_4^-$ (16 $\mu\text{g/L}$), $\text{Fe}(\text{wk})\text{H}_2\text{AsO}_4^-$ (1 $\mu\text{g/L}$), and $\text{Fe}(\text{wk})\text{OH}-\text{AsO}_4^{3-}$ (336 $\mu\text{g/L}$). Therefore, adsorption on pure HFO accounts for 35% of total adsorbed arsenic. In NAGW, the HFO precipitate cannot be considered as pure and there must have other adsorbents present, which removed remaining 30% of arsenic. Considering the complexity of natural system the agreement between model and experiment is reasonable. Without invoking the adsorption model, MINEQL+ showed 5% of arsenate as precipitate, mainly as $\text{Ba}(\text{H}_2\text{AsO}_4)_2(\text{s})$ and not as Fe(III) arsenate species as commonly believed.^[33] Therefore, majority of the arsenic species was removed from the system by sorption on HFO and other unknown active sites.
- (b) MINEQL+ has correctly predicted that the concentrations of free Fe and Mn species in NAGW under oxic condition are extremely low in accordance with experimental data. Therefore, Fe and Mn in oxidized form are precipitated as hydroxides. Experimental E_h values show considerable oxidizing condition for the redox species. MINEQL+ database has identified the following precipitated solids: Hematite ($2\text{Fe}(\text{OH})_3, 3\text{H}_2\text{O}$ or $\alpha\text{-Fe}_2\text{O}_3$), bixbyite ($\text{Mn}(\text{OH})_3$), diaspore ($\text{Al}(\text{OH})_3, 2\text{H}_2\text{O}$), $\text{Ba}(\text{H}_2\text{AsO}_4)_2$, calcite, and dolomite. Except for diaspore, calcite, $\text{Ba}(\text{H}_2\text{AsO}_4)_2$, and MnHPO_4 no iron containing species are precipitated out in anoxic, FGW. Therefore, even in the absence of excess iron, formation of solid minerals in anoxic water is possible. Whether, these minerals can adsorb and subsequently remove arsenic from groundwater is not clear from the present model. We note that the speciation and precipitation of minerals did not change significantly even if the model input involves 10-fold increase in sulfate and phosphate concentration in FGW.
- (c) Ba^{2+} removed from the system as $\text{Ba}(\text{H}_2\text{AsO}_4)_2(\text{s})$ is consistent with experimental data. Aluminum is often removed below the detection limit of ICPAES.
- (d) A significant increase in carbonate concentration occurred in NAGW due to equilibration with atmospheric $\text{CO}_2(\text{g})$. Ca and Mg is primarily distributed as carbonate and bicarbonate salts. The removal of Ca and Sr is consistent with the model but not consistent with the decrease of Mg. Zn is removed from the system as adsorbed species, $\text{Fe}(\text{wk})\text{OZn}^+$ and $\text{Fe}(\text{st})\text{OZn}^+$.
- (e) The change in Na concentration is indicative of a requirement by the model to maintain ion balance. There are no changes of alkali metal concentrations in NAGW.



Distribution of Arsenic Species: Effect of Total Arsenate and Total Iron

In localized areas of Bangladesh, the general composition of inorganic components of groundwater varies slightly except those of arsenate and iron critical to the natural attenuation process. Here, the MINEQL+ model is used to understand the distribution of arsenic containing species in the presence of different initial concentrations of iron and arsenic. Figure 1 shows the distribution of adsorbed and free arsenic species as a function of total AsO_4^{3-} in presence of species at concentration indicated in Tables 1 and 4 as inputs.

Figure 1 shows, at very low arsenic concentration arsenic is removed as $\text{Ba}(\text{H}_2\text{AsO}_4)_2(\text{s})$; at $4.0 \times 10^{-6} \text{ M}$ arsenate concentration about 75% of the total arsenic is removed as adsorbed $\text{Fe}(\text{wk})\text{OH}-\text{AsO}_4$ species. At higher concentration of total arsenic, adsorbed $\text{Fe}(\text{wk})\text{OH}-\text{AsO}_4$ decreases with concomitant increase in free HAsO_4^{2-} . At the highest total arsenic ($2.0 \times 10^{-5} \text{ M}$ or $1500 \mu\text{g/L As}$) 68% of the total arsenic remained free as HAsO_4^{2-} and 23% adsorbed as $\text{Fe}(\text{wk})\text{OH}-\text{AsO}_4$. This is consistent with previous model prediction and shows that stoichiometric excess of soluble iron cannot remove soluble arsenic simply by HFO formation and adsorption. This is further studied by varying the total concentration of Fe^{3+} and keeping the total arsenate at the input level. Figure 2 shows the distribution of arsenic species influenced by total Fe^{3+} (0 to $5 \times 10^{-4} \text{ M}$ or 28 mg/L) in groundwater composition shown in Tables 1 and 4.

Figure 2 shows all arsenic species are changing linearly with iron concentration. It predicts total free arsenic species are HAsO_4^{2-} and decreases 10% from initial 70% over the entire concentration range of iron. Most of the arsenic is removed as

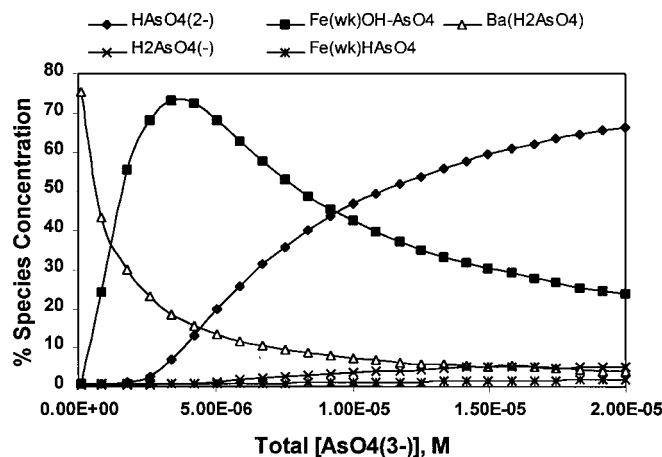


Figure 1. Percent distribution of arsenic species as a function of total AsO_4^{3-} . \blacklozenge — HAsO_4^{2-} ; \blacksquare — $\text{Fe}(\text{wk})\text{OH}-\text{AsO}_4$; \triangle — $\text{Ba}(\text{H}_2\text{AsO}_4)_2(\text{s})$; $*$ — $\text{Fe}(\text{wk})\text{HAsO}_4$; and \times — H_2AsO_4^- . Total soluble $\text{Fe} = 1.21 \times 10^{-4} \text{ M}$ or 6.77 mg/L . Properties of HFO: solid concentration = 0.0108 g/L , surface site density = 2.31 sites/nm^2 , total surface area = $6.48 \text{ m}^2/\text{L}$, surface potential = -36.9 mV .

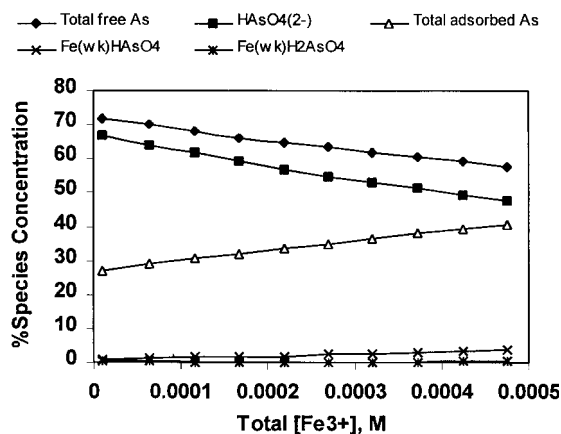


Figure 2. Distribution of arsenic species in naturally attenuated groundwater influenced by total Fe³⁺ in groundwater composition described earlier with constant total arsenic concentration. ◆—Total free arsenic; △—total adsorbed arsenic; ×—Fe(wk)HAsO₄; ■—HAsO₄²⁻; and *—Fe(wk)H₂AsO₄. All other parameters same as in Fig. 1.

adsorbed species and 28% to 41% of the total arsenic is adsorbed on HFO. Figure 2 indicates that even at 4-fold excess in iron concentration to that of normally present in groundwater there is only 13% increase in adsorption and subsequent removal of total arsenic. It appears that significantly more iron is required to remove arsenic from groundwater with the given composition. If HFO is the only means of arsenic removal then it is consistent with our previous findings that a continuous source of HFO either formed from zero valent iron (as rust) or serial accumulation of HFO in 3-Kolshi filtration setup are required to remove substantial quantities of arsenate. Present experimental data also indicates the possible presence of other adsorbents or active sites for the removal of arsenic. Further work is in progress on the spectroscopic and mineralogical identification of precipitates in NAGW.

Practical Implications

Groundwater containing high concentration of soluble iron, arsenic, and other toxic inorganic impurities are removed partly or completely if left for a while by a natural attenuation process involving HFO formation and adsorption. In a closed container, it takes about 24 h to remove half of the initial arsenic. This means water containing 100 µg/L As can reduce to 50 µg/L MCL in 24 h at the indicated level of soluble iron. It also shows that the natural process completely removes soluble Fe, Mn, and a substantial portion of Ca and Zn. Application of the chemical equilibrium model shows that significantly excess soluble iron is required to remove most of the arsenic. Experimental data indicates the presence of other adsorption sites other than HFO. Clearly, this method of arsenic removal is a choice where groundwater has more than 5 mg/L soluble iron and no other means of arsenic mitigation are available.



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Table 6. Drinking water inorganic quality parameters: comparison of naturally attenuated groundwater (NAGW or 'bashi pani'), 3-Kolshi water with those of USEPA, world health organization (WHO), and Bangladesh standards.^a

Constituent	USEPA (MCL)	WHO Guideline	Bangladesh	3-Kolshi Water	NAGW 'Bashi Pani'
Arsenic (total) (mg/L)	0.05	0.01	0.05	0.003–0.018	0.04–0.38 <i>t</i> _{1/2} = 24 h
Iron (total) (mg/L)	0.3	0.3	0.3 (1.0)	0.08–0.49	< 0.005
pH	6.5–8.5	6.5–8.5	6.5–8.5	7.74 ± 0.1	7.7
Sodium (mg/L)		200		26.7 ± 3.1	19
Calcium (mg/L)			75 (200)	59.1 ± 7.5	87
Copper (mg/L)	1.3	1.0–2.0	1.5	0.005	0.002
Manganese (mg/L)	0.05	0.1–0.5	0.1 (0.5)	< 0.001	0.01
Zinc (mg/L)	5	3.0	5 (15)	0.01	< 0.007
Aluminum (mg/L)	0.05–0.2	0.2	0.1 (0.2)	0.03	0.022
Lead (mg/L)	0.015	0.01	0.10	0.006	< 0.004
Chromium (mg/L)	0.1	0.05	0.05	< 0.002	< 0.002
Cadmium (mg/L)	0.005	0.003	0.01	< 0.001	< 0.001
Barium (mg/L)	2.0	0.7	1.0	0.063 ± 0.01	0.082
Antimony (mg/L)	0.006	0.005		< 0.013	< 0.013
Molybdenum (mg/L)		0.07		0.003	0.002
Nickel (mg/L)	0.1	0.02		< 0.002	< 0.002
Selenium (mg/L)	0.05	0.01		< 0.012	< 0.002
Silver (mg/L)	0.1			< 0.002	< 0.002
Chloride (mg/L)	250	250	200 (600)	110–400	4.0

^aBangladesh standard values are given as maximum desirable concentration with maximum permissible concentration in parentheses. Arsenic concentrations are given as range and half-life (see text for details).

Therefore, the concept of 'bashi pani' or 'drink water after a while' (local sayings 'pani bashi kore khaben') has some merits.

In Table 6, the overall water quality for inorganic components in naturally attenuated groundwater is compared with those of USEPA, World Health Organization (WHO) and Bangladesh Standards and 3-Kolshi filtration system. It shows that arsenic in groundwater can be removed much below the MCL by a simple 3-Kolshi filtration procedure using locally available material and without adding chemicals.^[16,17] The overall water quality obtained from the 3-Kolshi setup meets the guideline values suggested by USEPA, World Health Organization and Bangladesh. Although the NAGW barely meets the water quality for arsenic, one could use the technique to reduce the initial concentration of arsenic and then use other techniques to enhance the efficiency and lifetime of the process. The very low iron content of NAGW can be beneficial to filtration techniques where iron precipitation clogs the filter and, thus, eliminates the need for a prefilter. Further work is underway to learn the dynamics and equilibrium composition of water left in clay pitchers.



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