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Effects of anion competitive adsorption on arsenic enrichment in groundwater

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Long-term intake of high arsenic groundwater has caused serious endemic disease on people in Datong Basin, northern China. The high arsenic groundwater has medium to high alkalinity with a mean pH value of 8.1; the water generally belongs to HCO_3-Na type water and contains HPO_4^{2-} in most samples. In this study, batch experiments and geochemical modeling were conducted to reveal the geochemical processes responsible for arsenic enrichment in the groundwater due to desorption, and to examine the effect of pH, phosphate, bicarbonate and silicate on this desorption in the studied groundwater system. The experimental pH ranging from 7.35 to 8.72 as observed in the high arsenic groundwater, was favorable for arsenic desorption from the aquifer sediments. Arsenic concentration in the aqueous phase significantly increased with the increase of added PO_4^{3-} concentration. An elevated arsenic content of 13.6 μg/L was observed with the highest phosphate loading of 30 mg/L. Although bicarbonate addition caused less desorption of arsenic than phosphate on the mole basis, an elevated arsenic concentration of 56 μg/L in the batch solutions was observed when the added bicarbonate contents was up to 1500 mg/L. The contribution of silicate to arsenic desorption is lower than that of phosphate and bicarbonate.

Keywords: pH, anion, competitive adsorption, arsenic enrichment, groundwater.

Introduction

Long-term intake of groundwater with high concentration of arsenic will cause serious diseases, including arsenical dermatosis, hyperkeratosis and arsenicosis.[1,2] In Shanyin County, Yinxian County and Shuocheng District in the Datong Basin of northern China, for instance, endemic poisoning cases were quite serious, where the victims totalled at 5,087 in 63 villages.[3] High concentrations of arsenic have been detected in groundwater from Quaternary aquifers at Datong, a semi-arid area of Shanxi Province in northern China, where groundwater is the major source of drinking water. Endemic arsenic poisoning was first confirmed in the Datong Basin early 1990s. According to Wang et al.,[4] 54.4% of the total tested 3083 quaternary wells in the study area contained arsenic concentration exceeding 50 μg/L, the arsenic maximum contaminant level (MCL) for drinking water in China before 2007. Groundwater in Quaternary aquifers typically contained arsenic concentrations between 2.0 and 1300 μg/L, with pH from 7.09 to 8.71 and high HPO_4^{2-} contents up to 4.91 mg/L.[5]

Various geochemical processes have been proposed to explain the occurrence of high arsenic content in groundwater.[6–8] It was reported that arsenic enrichment in groundwater was closely linked to the pH conditions as well as the presence of competing anions and cations which affect arsenic adsorption/desorption.[9–12] Several types of ions in groundwater may compete with arsenic for the available adsorption sites and even alter the electrostatic charge of the adsorbent surfaces.[13–15] Among them, bicarbonate, silicate, sulfate, phosphate and calcium ion have received more attention, since their competition has the potential to elevate the total arsenic concentration in groundwater.[16–18]

Geochemical modeling helps to better understand the major geochemical processes in groundwater systems.[19–23] Speciation and adsorption modeling of As in groundwater were performed as early as 1994 by Davis and co-workers.[24] Forward modeling combined with surface complexation modeling of adsorption was also used to determine the influence of different surface areas available for adsorption and competition for adsorption sites with

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anionic species.[25] Competitive adsorption of arsenate and phosphate on goethite in high ionic strength solution was studied by Gao and Mucci.[26] Arsenic sources in the As-enrichment groundwater was studied using surface complexation modeling to calculate the desorption of arsenic from ferric hydroxide (HFO).[27]

However, there has been no systematic work on the effects of pH and competitive adsorption of phosphate, bicarbonate and silicate on arsenic mobilization from high arsenic sediment. In this study, batch experiments and geochemical modeling on arsenic desorption were carried out using sediment samples from Datong Basin. This will help to find new evidences about the geochemical processes responsible for arsenic mobilization.

Material and methods

Field sampling

Groundwater samples were collected in November 2006 and in September 2008. The water samples were filtered through 0.45 μm membrane on site and then collected in four 550 mL polyethylene bottles, which had been rinsed twice with both deionized and sample waters. For metallic element analysis, reagent-quality HNO_3 was added to two of these polyethylene bottles until pH of samples reached 1.0. Unstable hydrochemical parameters including water temperature, pH, and electrical conductivity (EC) were measured in-situ using portable Hanna EC and pH meter that had been calibrated before use. Alkalinity was measured on the sampling day using the Gran titration method. Anion concentrations of the sample were determined using IC (Ion Chromatography, Dionex 120). The contents of major cations were analyzed using ICP-AES (Inductive Coupled Plasma-Atomic Emission Spectrometer, Thermo Fisher Scientific), while As, Fe, Mn and other trace elements were analyzed using ICP-MS (Inductively Coupled Plasma-Mass Spectrometer, Poems III, Thermo Jarrell Ash).

Based on previous hydrogeochemical studies and field investigation, a site for the sediment sampling was chosen where the groundwater arsenic content was high up to 1,060 μg/L.[4] The sediment sample was collected in May 2006 from one of the boreholes (named as DY in Fig.1) at depth of 46.0 m and was capped immediately with a PVC pipe and wax-sealed, thereby minimizing the exposure to the atmosphere. After collection, the samples were stored at 4°C in the dark. The collected sample was air-dried in the dark at room temperature (23°C), grinded and screened through 150-mesh sieve. Analysis of the major elements (SiO_2, Fe_2O_3, TiO_2, Al_2O_3, CaO, P_2O_5, MgO and MnO) in the sample was carried out using an XRF spectrometer (Rigaku model RIX2100).
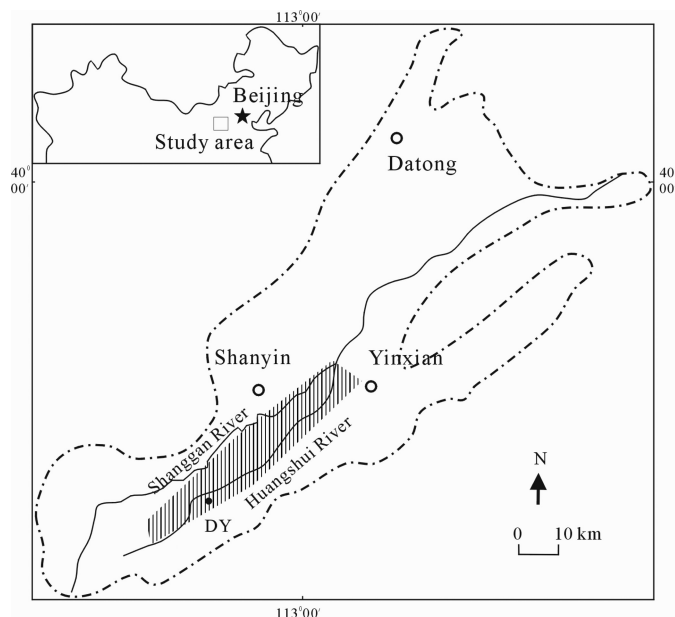

Fig. 1. Location of the study area and the drilling site (DY) for sediment sampling. The shadow area indicates where high arsenic groundwater occurs.

Batch experiments

Batch experiments were performed to investigate the effect of pH and ion concentrations on arsenic desorption from the sediment samples. A solid to solution ratio of 1: 4 was employed with 1 mM $Ca(NO_3)_2$ as the electrolyte. All solutions were prepared using purified DI water (Milli-Q Ultrapure Water Purification System, Millipore). The Eh value of prepared solution ranges between 220–240 mV. The batch tubes were equilibrated for 72 h on a shaker table (cell production roller drum, Bellco) at a speed of 39 rpm. To avoid the possible interference from reductive dissolution of soil iron oxides such as ferrihydrite or goethite which could lead to the release of adsorbed arsenic, all the experiments were performed under open atmospheric conditions and no precautions were taken to exclude O_2 and CO_2 from the tube atmosphere.

In reference to local groundwater composition as well as those found in the literature, the ions selected in this study included PO_4^{3-}, HCO_3^- and SiO_3^{2-}. The stock solutions of competitive ions were prepared in the laboratory by dissolving pre-weighted amount of reagents of Na_2SiO_3, $NaH_2PO_4 2H_2O$ and $NaHCO_3$, into DI water. All the chemicals were of reagent grade and were used without further purification. All glassware was acid-washed and rinsed with DI water.

For the competitive anion experiments, six to seven concentration levels for each anion were selected. These values cover the range from the highest to the lowest concentrations of each anion found in the groundwater of the study area. The initial pH of batch test solution was adjusted with 0.1 N HCl and/or NaOH to 8.0. After equilibration, the

Table 1. Statistical summary of the hydrochemistry of high arsenic groundwater samples from the shadow area in Figure 1 (in mg/L except for T, pH, EC, Eh and As).

Parameter	Min	Max	Mean	STD	Parameter	Min	Max	Mean	STD
T (°C)	6.0	10.5	7.82	1.19	K^+	0.25	56.4	3.85	9.56
pH	7.35	8.72	8.10	0.31	Na^+	23.5	1251	397	319
EC (μS/cm)	430	10,640	2,296	2179	Ca^{2+}	4.03	76.0	25.0	16.3
Eh (mV)	−83.1	−11.8	−56.0	15.77	Mg^{2+}	9.60	65.0	27.1	46.4
TDS	268	4351	1367	1122	Ba	0.009	0.129	0.057	0.031
Alkalinity (as $CaCO_3$)	81.3	1,241	504	268	B	0.133	2.91	0.946	0.781
HCO_3^-	99.1	1,513	615	326	Fe	0.005	5.43	0.662	1.07
Cl^-	1.82	1700	292	377	Mn	0.005	0.083	0.025	0.142
SO_4^{2-}	0.32	1,155	206	273	P	0.0235	2.12	0.548	0.498
F^-	0.18	39.0	5.11	6.92	S	0.0197	104	19.3	26.7
NO_3^-	1.64	270	53.4	78.7	Si	2.15	5.88	3.48	1.16
HPO_4^{2-}	1.02	29.2	7.91	7.19	Sr	0.14	5.35	0.96	1.21
Br^-	bd	45.1	4.77	8.40	As (μg/l)	4.25	1,547	270	366

*T is groundwater temperature; bd, below detection limit; STD, standard deviation; EC, electrical conductivity.

mixture was centrifuged at 6000 rpm for 30 min and then filtered through 0.22 μm membranes, analyzed using the Inductively Coupled Plasma Mass Spectrometer (ICP-MS, PerkinElmer SCIEX ELAN®DRC II).

Geochemical modeling

Geochemical modeling on the adsorption/desorption of arsenic on ferric hydroxide was also employed to validate and interpret the results of batch experiments. Ferric hydroxides play an important role in controlling the migration of As in aquifer systems in the study area.[28] Both As(III) and As(V) can be adsorbed by hydrated ferric oxides under either oxidizing or reducing conditions. Generally, there is an initial rapid adsorption period (less than five minutes) of uptake, followed by continued slow uptake (normally longer than eight days) for As diffusion to adsorption sites on Fe oxyhydroxides surfaces.[29] In our simulation, the concentrations of total arsenic and different species of As were calculated using PHREEQC with thermodynamic database from WATEQ4F.[30] Selected sorption reactions and corresponding thermodynamic equilibrium constants are based on the diffuse double-layer Surface Complexation Model (SCM).[31] Equilibrium constants for adsorption of all species were derived from the results of experimental adsorption on ferrihydrite.[31] The number of reactive sorption sites on Fe oxyhydroxides was calculated on the basis of the site density for strong and weak binding sites and the specific surface area recommended by Dzombak and Morel for hydrous Fe oxide (600 m^2/g).[31] The amount of Fe oxyhydroxides in contact with water (0.01 g/L) was obtained from sequential extraction using the method described in detail by Dzombak and Morel[31]. The amount of adsorbed As on Fe oxyhydroxides surface can also be estimated from the results of sequential extraction. The species distribution of As in aqueous solution is dependent mainly on pH and

the electron activity (Eh or pe values). The pH was then programmed to shift from a starting pH value 8.0, except for the modeling of arsenic desorption depending on pH. The pe value was set to pe = + 4 at the model's starting point in order to be consistent with the monitored Eh = 220 – 240 mV (Eh = 0.059 pe (Volt)) in the prepared solution. Major minerals in the sediment such as albite and calcite were added into the model calculation as equilibrium phases.

Results and discussion

Arsenic in groundwater

The arsenic content in groundwater samples from the study area ranged between 0.5 μg/L and 1547 μg/L, showing a trend of increase from the piedmont plain to the alluvial plain and further to the low-land basin center around the banks of Huangshui River and Shanggan River.[3,5] Gradual decrease of Eh values were observed along this groundwater flow path which indicates a change from oxidation condition to reductive condition. The highest Eh value was found in piedmont plain about 280 mV while the lowest one was −83.1 mV from the low-land center area.[3,5] The corresponding As(V) percent in groundwater ranged from 7.65 % in reductive condition to 98.5 % in oxidation condition.[3] High arsenic groundwater samples were collected from upper semi-confined aquifer along the banks of Huangshui River and Shanggan River in an area of 6 km wide and 90 km long (Fig. 1). The groundwater samples typically contained low concentrations of sulfate and nitrate (less than 10 mg/L), low Eh values (mean value of −56 mV), moderate to high alkalinity (an average value of 504 mg/L) with a mean pH value of 8.1 (Table 1). Elevated contents of HPO_4^{2-}, K, Na, Ca, Mg, Cl and silicate were detected in most of the high arsenic groundwater samples. Most of the high arsenic groundwater belongs to HCO_3-Na type

Table 2. SI values for major iron-bearing mineral phases for selected groundwater and batch test solution.

Minerals	G1	G2	G3	DYa	DYb	DYc
Fe(OH)$_3$(a)	−0.07	0.47	0.55	2.27	2.25	2.29
Fe$_3$(OH)$_8$	−3.73	−2.11	−1.88	3.29	3.24	3.34
Goethite	5.82	6.37	6.44	8.16	8.15	8.19
Hematite	13.65	14.75	14.89	18.34	18.3	18.4
Maghemite	3.26	4.35	4.5	7.95	7.91	7.98
Magnetite	12.75	14.39	14.61	19.78	19.73	19.83
Melanterite	−10.19	−6.58	−8.19	−5.45	−5.46	−5.44
Scorodite	−6.85	−3.95	−4.68	−3.5	−3.51	−3.48
Siderite	−1.86	0.33	0.35	1.54	1.55	1.53
Jarosite(ss)	−12.2	−2.96	−6.44	1.67	1.64	1.73

* DYa, DYb and DYc are respectively the three batch test solution with solid (sediment sample): liquid (1mM Ca(NO$_3$)$_2$ solution as electrolyte) ratio of 1 g: 4 mL; the location of selected groundwater samples G1, G2 and G3 are N39°22′06″ E112°52′30″, N39°21′03″ E112°50′48″, and N39°22′58″ E112°50′47″, respectively; (a), amorphous phase.

Fig. 2. Contents of As, Fe, Mn and Si in solution after 72 h of equilibrating with sediment sample at pH 7.0, 8.0, 9.0 and 10.0. The solid: liquid ratio was 1 g: 4 mL and the temperature was 23°C. Concentrations are shown as the mean value of the triplicates; As$_C$ (dash line) is the calculated dissolved arsenic in solution.

water.[32] Some of the high arsenic groundwater samples belong to HCO$_3$-Cl-Na-Mg and Cl-SO$_4$-Na-Mg type water, with a moderate to high Cl and SO$_4^{2-}$ content and Na and Mg as the dominant cations. Samples with high arsenic contents commonly have high Fe contents. Results of saturation index (SI) calculations using PHREEQC for major iron-bearing minerals in selected groundwater samples and batch test solutions are listed in Table 2. They show that the groundwater samples are commonly oversaturated with respect to ferric oxides and hydroxides such as goethite, implying that As adsorption processes may be to some extent controlled by these mineral phases. This is consistent with the result of our previous work of sequential extraction of high arsenic sediments from the same area, which revealed the existence of Fe mineral phases in oxalate extractable fraction.[28]

Geochemical properties of sediment samples

The sediment sample used in this study consisted of 16% gravel, 24% sand, 31% silt, and the remaining 29% clay and other colloidal particles; it is grouped as gravelly clay according to the USDA soil classification system. The sediment belongs to alkaline soil with pH values of about 7.98 for a solid: water ratio of 1:4, and about 8.02 for a solid: water ratio of 1:20. The EC value of the sediment was about 890 μS/cm. The main chemical constituents of the sediment include Al$_2$O$_3$, SiO$_2$, Fe$_2$O$_3$, K$_2$O, CaO, P$_2$O$_5$, MgO, Na$_2$O and MnO with an average value (n = 3) of 10.7%, 52.6%, 4.43%, 4.09%, 5.92%, 0.16%, 3.78%, 1.64% and 0.09%, respectively. The total organic carbon in the sediment ranged between 0.21% − 0.23%. A significant fraction of oxalate extractable As and Fe, representing As in oxyhydroxide fraction, was noted in the sediment samples.[28] The content of Mn in the sediment was 34.5 mg/k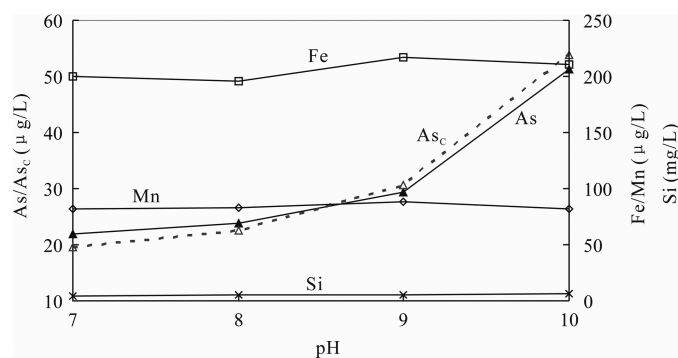g (mean value, n = 3). The CEC value measured by ammonium acetate method was 26.8 cmol/kg. All the parameters of the sediments fall within the range reported by Su et al. (2006) and Xie et al. (2008) for sediments from the study area.[5,28]

Effects of adsorption/desorption processes on arsenic enrichment in groundwater

Batch experiments and geochemical modeling were performed to understand the effects of major factors controlling arsenic adsorption/desorption processes in the high arsenic groundwater system at Datong Basin. According to the results of previous work of us and other authors on different high arsenic groundwater systems, pH and HPO$_4^{2-}$, HCO$_3^-$ and SiO$_3^{2-}$ were selected respectively as the major factor and as the competitive anions for our experiments and modeling.[3,4,23,28,32−38]

Effect of pH on As adsorption/desorption

Many studies suggested that the effect of pH on arsenic mobility is linked to the adsorption/desorption equilibrium during water-sediment interaction.[39] In our experiments, the solution was adjusted to obtain a relatively constant pH of 7, 8, 9 and 10. It covers the range of pH expected under natural conditions in the study area. Figure 2 shows the arsenic content in the solution after equilibrium with sediment samples at these pH values. Significant elevation of arsenic content was found with the increase of pH, indicating the release of arsenic from sediment samples into the solution. An increase of arsenic concentration from 21.9 μg/L to 29.3 μg/L was observed in batch solutions with the initial pH from 7.0 to 9.0 (Fig. 2). There was little change of Fe/Mn content in the batch test solution when pH increased from 7.0 to 10.0, indicating that the amount of sorbents, such as iron/manganese oxides, was stable. A slight increase of silica content (from 4.37 to 6.42 mg/L) was found in the batch test solution (Fig. 2). This
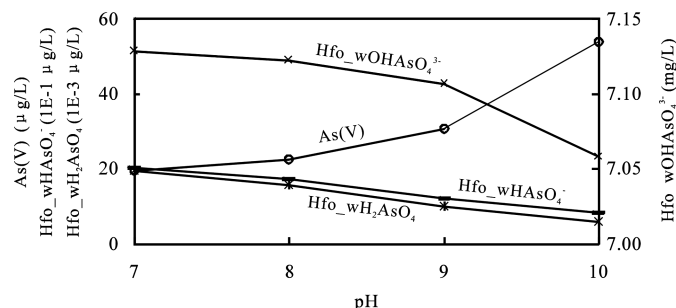
Fig. 3. The distribution of dissolved and adsorbed As(V) species in modeling system at different pH values.

may partly contribute to the elevation of arsenic content in batch solution.

According to the modeling calculation results, As(V) is the dominant species of arsenic in the solution (Figs. 3 and 4), accounting for over 99% of the dissolved and adsorbed arsenic. The highest content of adsorbed arsenic species is $Hfo\_wOHAsO_4^{3-}$, followed by, $Hfo\_wHAsO_4^-$, $Hfo\_wH_2AsO_4$ and $Hfo\_wH_2AsO_3$. As pH increases, the concentration of solution protons decreases, driving more protons from the adsorbent surface and making the adsorbent surface more negatively charged. Consequently, more anionic species of arsenic such as $H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-}, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} could be repelled and desorbed as the surface negativity increases.

However, not all of the anionic species of arsenic followed the same pattern of desorption, as shown by our modeling results (Figs. 3 and 4). Dramatic decrease of adsorbed $Hfo\_wHAsO_4^-$ and $Hfo\_wH_2AsO_4$ occurred, in contrast with a moderate decrease of $Hfo\_wOHAsO_4^{3-}$ and $Hfo\_wH_2AsO_3$. The elevation of arsenic in solution could be mostly attributed to desorption of $Hfo\_wOHAsO_4^{3-}$ (Figs. 2 and 3). Such a difference in sorption behavior among different species indicates that it is necessary to study arsenic speciation in order to better characterize arsenic mobility in the groundwater-sediment system. The pH value of groundwater in Datong Basin ranged from 7.35 to 8.72, with a mean value of 8.1. Based on the results
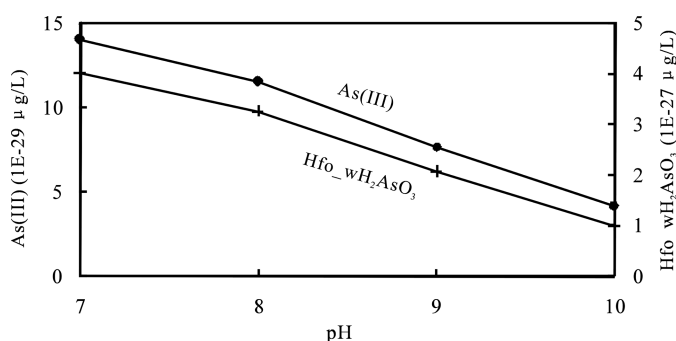

Fig. 4. The distribution of dissolved and adsorbed As(III) species in modeling system at different pH values.

of batch experiments and geochemical modeling, such a weakly alkaline condition favors the desorption of arsenic from sediments. Therefore, pH is not self-governed in the high As aquifer system and its effect on arsenic desorption is evident, although it is difficult to quantify the effect under field conditions.

Competitive adsorption of phosphate

To quantify the effect of phosphate on arsenic desorption, batch experiments were performed using NaH_2PO_4 as the source of phosphate in solution equilibrated with sediment sample at pH 8.0 with initial HPO_4^{2-} concentrations of 0, 1, 2, 5, 10, 20 and 30 mg/L. The highest HPO_4^{2-} concentration, 30 mg/L, was the same as the highest phosphate content in high arsenic groundwater samples from Datong Basin (Table 1). Geochemical modeling using PHREEQC was performed to evaluate the effect of competing anions on arsenic release in the sediment sample. All calculations were carried out with solution at initial pH of 8.0 which is close to the average pH value of 8.1 in the study area.

In the presence of PO_4^{3-}, there was a significant elevation in arsenic concentration with the increase in PO_4^{3-} concentrations, as shown in Figure 5. A HPO_4^{2-} loading of 10 mg/L produced almost 28% increase of arsenic concentration in the solution. Similar phenomenon was observed in our geochemical modeling results (Fig. 5). The desorption rate of arsenic was high at low PO_4^{3-} concentration (10 mg/L) and then gradually reduced with increase in PO_4^{3-} concentration. This indicates that the competition is relatively more effective at lower loading of phosphate. The arsenic content in batch solution is a little higher than the calculated one at phosphate loading lower than about 15 mg/L. This may be related to the dissolution of phosphate and silicate in the sediment. Increase in silicate content from 3.85 to 4.50 mg/L in the batch test solution may promote arsenic release, though its contribution is much smaller to the total increase of arsenic content of 13.6 μg/L.

A PO_4^{3-} concentration of 0.7 to 1.2 mg/L was monitored in the batch solution as a background value. The additional dissolution of phosphate in sediment may also cause some desorption of arsenic from sediment. Little change in Fe and Mn contents in solution indicates that the effect of PO_4^{3-} on the surface of available Fe/Mn-oxides was not significant which were considered as the most important sorbents in the study area.[4,28] According to the results of our batch experiments, the contribution of phosphate to arsenic desorption was 0.45 μg/L per mg/L phosphate at the highest phosphate loading of 30 mg/L.

The effect of phosphate on different arsenic species (As(V), As(III), $Hfo\_wH_2AsO_3$, $Hfo\_wHAsO_4^-$, $Hfo\_wH_2AsO_4$, and $Hfo\_wOHAsO_4^{3-}$) was modeled using PHREEQC (Figs. 6 and 7). Both As(V) and As(III) increased with increase in phosphate content. It is interesting that not all of the above 4 arsenic species showed
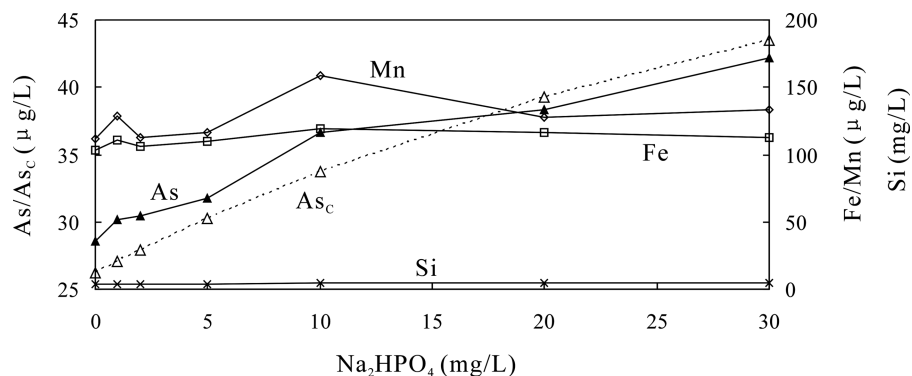
Fig. 5. Contents of As, Fe, Mn and Si in solution after 72 h of equilibrating with sediment sample at pH 8.0 with initial NaH_2PO_4 concentration of 0, 1, 2, 5, 10, 20 and 30 mg/L. The solid: liquid ratio was 1 g: 4 mL and the temperature was 23°C. Concentrations are shown as the mean value of the triplicates; As_C (dash line) is the calculated dissolved arsenic in solution.

significant desorption in the simulating solution, at the presence of competitive phosphate. Desorption of $Hfo\_wOHAsO_4{}^{3-}$ was more intensive than that of $Hfo\_wHAsO_4{}^-$ and $Hfo\_wH_2AsO_4$, while desorption of $Hfo\_wH_2AsO_3$ was negligible (Figs. 6 and 7). This implies that desorption of arsenic and adsorption of phosphate are complicated. More energy is needed to break the bond between the sorbent surface and $Hfo\_wOHAsO_4{}^{3-}$ with a desorption ratio of 0.5%. As a result, it is easier for $Hfo\_wH_2AsO_3$ (the desorption ratio about 32%) to be replaced by phosphate from the sorbent surface. Phosphate is an inner-sphere complex-forming anion that is strongly sorbed to mineral surfaces. In the solution with low phosphate concentrations (normally lower than 10 mg/L), phosphate may tend to replace As(V) and As(III) first before its competitive desorption of other arsenic species.

Competitive adsorption of bicarbonate

Since the high arsenic groundwater at Datong Basin commonly has bicarbonate as the major anion, the role of competitive adsorption of bicarbonate should not be neglected. According to the results of batch experiments of Kim et al. (2000), leaching solution of $NaHCO_3$ and $KHCO_3$

released the greatest quantity of arsenic (1.2–1.6 mg/kg) from the aquifer materials (with a total arsenic concentration of 26.4 mg/kg), as compared to $CaSO_4$, $MgSO_4$, KCl and deionized water (less than 0.2 mg/kg).[13] The high pH condition of soda water (water with $HCO_3{}^-$ as the dominant anion) favors arsenic desorption from oxyhydroxide surfaces, thereby increasing the concentration of arsenic in the aqueous phase.[4]

However, Fuller et al.[40] also reported that carbonate species had no effect on arsenic adsorption by ferric hydroxide. Meng et al.[41] found that the binding affinity for arsenate on iron hydroxides is stronger than arsenite. Therefore, a more detailed evaluation of $HCO_3{}^-$ is still needed to better understand the effect of $HCO_3{}^-$ on arsenic desorption in Datong Basin sediment.

In our batch experiments, initial concentration of bicarbonate was $100 - 1500$ mg/L as $NaHCO_3$ with an initial pH of 8.0. The concentration range was chosen according to the $HCO_3{}^-$ contents measured in Datong groundwater. It can be seen from Figure 8 that bicarbonate addition caused desorption of arsenic, although the intensity was less than
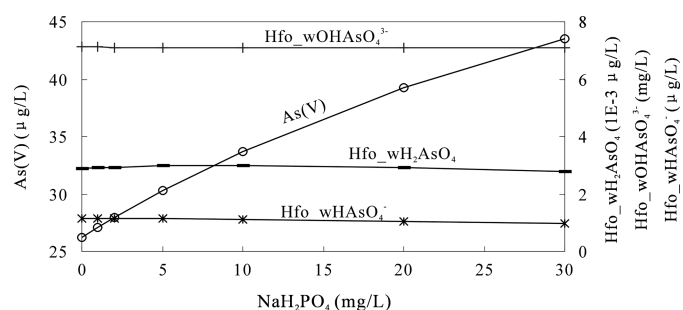

Fig. 6. The distribution of dissolved and adsorbed As(V) species in modeling system when different amount of NaH_2PO_4 was added into the initial solution.
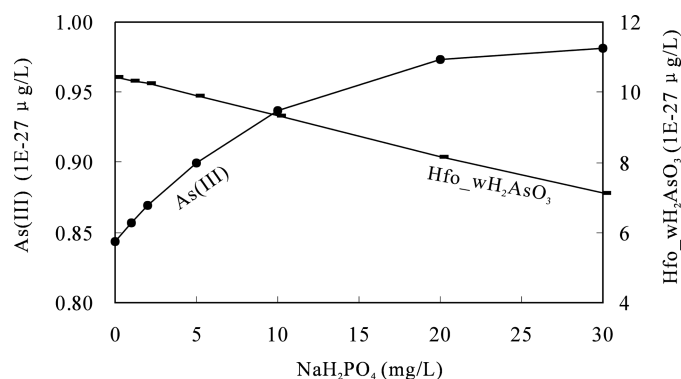

Fig. 7. The distribution of dissolved and adsorbed As(III) species in modeling system when different amount of NaH_2PO_4 was added into the initial solution.
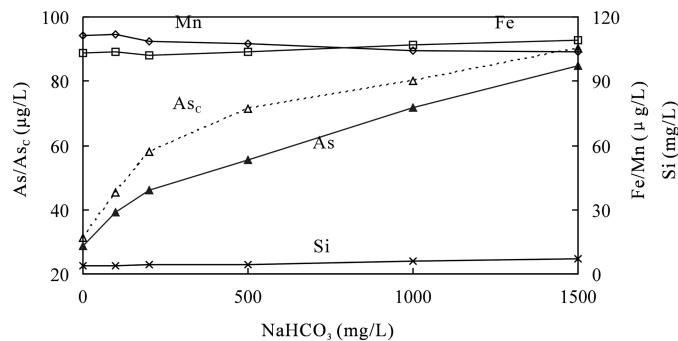
Fig. 8. Contents of As, Fe, Mn and Si in solution after 72 h of equilibrating with sediment sample at pH 8.0 with initial NaHCO$_3$ concentration of 0, 100, 200, 500, 1000, and 1500 mg/L. The solid: liquid ratio was 1 g: 4 mL and the temperature was 23 °C. The ion concentration is the mean value of the triplicates. As$_C$ (dash line) is the calculated dissolved arsenic in solution.

Fig. 9. The distribution of dissolved and adsorbed As(V) species in modeling system when different amount of NaHCO$_3$ (0, 100, 200, 500, 1000, and 1500 mg/L) was added into a solution.

that of phosphate, on a mole released per mole added basis (cp. Fig. 5 and Fig. 8).

However, because the bicarbonate concentration is much higher than phosphate (both in the batch solution and in the groundwater samples), the contribution of bicarbonate to the total arsenic release is still greater. An elevation of about 56 μg/L arsenic concentration in the batch test solutions was observed with the highest bicarbonate content loading of 1500 mg/L (Fig. 8). At bicarbonate concentration lower than about 200 mg/L, the increase of arsenic content in solution was faster. In other words, desorption of arsenic by bicarbonate is significant, even at relatively low concentration levels.

Again, there is little change in Fe and Mn concentration for different bicarbonate concentration levels which indicates a relatively constant amount of Fe/Mn oxides as sorbents. By contrast, a slight increase of silicate content was observed. It may be difficult here to quantify the contribution of increased silicate content (about 3.37 mg/L, Fig. 8) to arsenic desorption. But as discussed in next section, the arsenic content increase caused by silicate competition is much smaller than that by bicarbonate.

Surface complexation models were used to estimate the amount of arsenic desorbed from sediment surface by bicarbonate (Fig. 8). The calculated arsenic concentration change pattern is similar to that in the batch test. The arsenic concentration in our modeling system increased quickly at bicarbonate concentration loading less than 500 mg/L. The difference in the extent between batch test and modeling calculation can be explained by the following reasons: (1) in the batch solution, bicarbonate may form complexes with other cations or anions, and thus reduce the available amount; (2) the solid phase in the sediment is more complicated than that used in modeling calculation, and the total inorganic carbon in modeling calculation may be lower. In spite of the difference, the results of modeling still revealed a similar pattern of arsenic re-
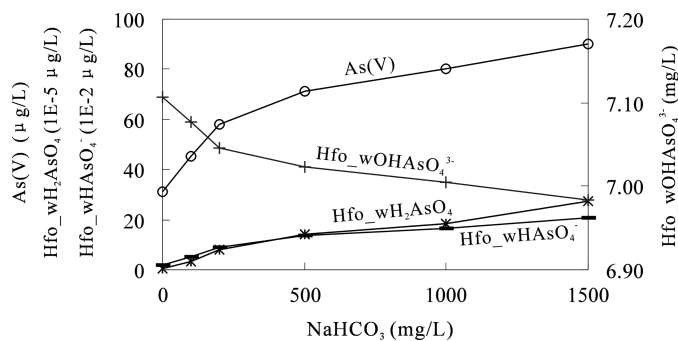
lease. And the desorption of arsenic showed a moderate rate of increase over the bicarbonate concentration range of 500–1500 mg/L in both batch experiments and modeling calculation.

According to the results of modeling calculation, increase of As(V) and As(III) content in solution all result from desorption of Hfo_wOHAsO$_4$$^{3-}$, rather than from the other three species of sorbed arsenic (Figs. 9 and 10). The contribution of bicarbonate to arsenic desorption in the batch experiments was about 3.69 μg/L per 100 mg/L bicarbonate (after subtracting the possible contribution of silicate) at up to 1500 mg/L of bicarbonate.

Competitive adsorption of silicate

Silicate concentration in groundwater was 2.15 – 9.58 mg/L in the study area. Silicate may either compete with arsenic for adsorption sites or change the surface properties of sorbents.[42] Batch experiments were carried out using balance solution with different initial silicate content (as Na$_2$SiO$_3$, at 0, 2, 5, 10, 20 and 30 mg/L) at pH 8.0. The results were shown in Figure 11. With the addition of Na$_2$SiO$_3$ up to 30 mg/L, a total increase of 1.77 μg/L arsenic concentration was achieved. This result is compa-
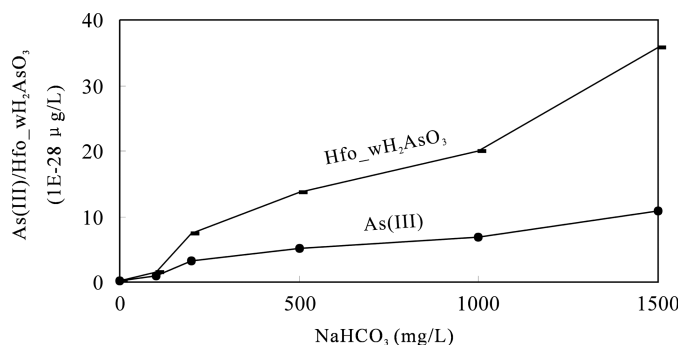

Fig. 10. The distribution of dissolved and adsorbed As(III) species in modeling system when different amount of NaHCO$_3$ (0, 100, 200, 500, 1000, and 1500 mg/L) was added into a solution.
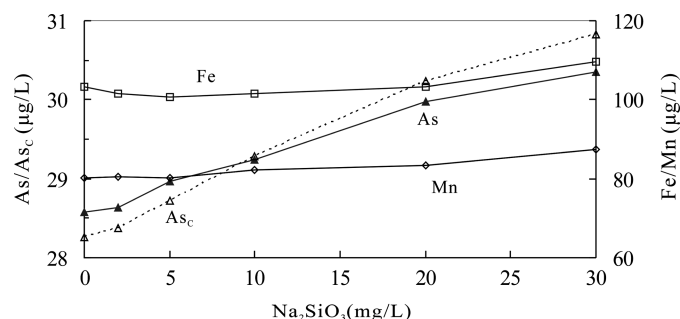
Fig. 11. Contents of As, Fe, and Mn in solution after 72 h of equilibrating with sediment sample at pH 8.0 with initial Na$_2$SiO$_3$ concentration of 0, 2, 5, 10, 20, and 30 mg/L. The solid: liquid ratio was 1 g: 4 mL and the temperature was 23 °C. The ion concentration is the mean value of the triplicates. As$_C$ (dashed line) is the calculated dissolved arsenic in solution.

rable to that of previous study by Davis et al.,[42] who found that silicate decreases arsenate removal by iron hydroxides significantly at pH greater than 7.0 and high silicate concentration (>0.6 mM, 73.2 mg/L Na$_2$SiO$_3$). Obviously the effect of competitive adsorption of silicate on groundwater arsenic content is much smaller than that of both phosphate and bicarbonate (Figs. 5, 8 and 11).

In the batch experiments, an initial silicate content of 3.85 mg/L was taken as the background value (obtained by equilibrating sediment samples with DI water at pH 8.0 for 72 h). An adding of 2 mg/L silicate causes little increase of arsenic in the solution. The addition of higher silicate content causes more obvious increase of arsenic content. By contrast, addition of silicate into batch solution has little effect on Fe and Mn contents. Results of modeling arsenic desorption due to competitive adsorption of silicate showed a similar trend as observed in the batch experiments and they fit well with the experimental results.

Conclusions

To better understand the effect of competitive anions on arsenic enrichment in the high arsenic groundwater in Datong Basin, northern China, batch experiments and geochemical modeling were performed. The parameters: pH, phosphate, bicarbonate and silicate were selected as the main factors controlling desorption of arsenic from aquifer sediments. The following conclusions can be drawn from the present study.

1. In the study area, pH of the high arsenic groundwater samples ranged from 7.35 to 8.72, which favors arsenic desorption in the groundwater - sediment system, as shown by the results of batch experiments and geochemical modeling.
2. There was a significant elevation in arsenic concentration with the increase in HPO$_4^{2-}$ concentration. Loading of 10 mg/L HPO$_4^{2-}$ produced almost 28% increase

of arsenic concentration in the solution. A total increase of 13.6 μg/L arsenic was observed with the highest phosphate loading of 30 mg/L. In the groundwater with lower phosphate concentrations, phosphate may tend to replace more As(V), according to our modeling results.
3. The potential influence of bicarbonate on As adsorption and mobility in groundwater systems is obvious according to the batch experiment results. Bicarbonate addition caused less desorption of arsenic than phosphate, on a mole released per mole added basis. However, the contribution of bicarbonate to the total arsenic release is greater than phosphate because of the much higher content of bicarbonate in the groundwater. An increase of 56 μg/L of arsenic concentration was observed with initial bicarbonate content up to 1500 mg/L.
4. The contribution of silicate to arsenic desorption is lower than that of phosphate and bicarbonate.
5. Although the batch experiment and geochemical modeling results showed similar results, difference in the extent of arsenic desorption between batch experiments and modeling calculation was obvious, which may depend on the geochemical characteristics of minor minerals in the sediment.

Acknowledgments

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