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Mobility of arsenic in aquifer sediments at Datong Basin, northern China: Effect of bicarbonate and phosphate

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ABSTRACT

Effects of phosphate and bicarbonate concentration on mobilization of arsenic in aquifer sediments have not been extensively studied in flow-through experiments, where the dynamic-release behavior of elements can be monitored. In this work, these effects were investigated both through batch and column experiments, using a high-arsenic sediment sample from the Datong Basin, northern China. A solution of 1.0 mM $\text{Ca}(\text{NO}_3)_2$ was first applied to a water-saturated column packed with the sediment; this was followed by leaching with either 0.10 mM Na_2HPO_4 or 8.2 mM NaHCO_3 solutions. When the sediment was initially leached with 1.0 mM $\text{Ca}(\text{NO}_3)_2$ solution, a rapid spike of As, Fe, Mn, and major cations was observed in the first 20 column pore volumes, reflecting the initial equilibration of the sediment to the influent $\text{Ca}(\text{NO}_3)_2$ in response to cation exchange (for cations) and sorption equilibrium (for Mn, Fe, As). After the $\text{Ca}(\text{NO}_3)_2$ solution was replaced with either the Na_2HPO_4 or NaHCO_3 solution, a rapid increase in As concentration in the effluent was observed, consistent with the batch test results. Induced desorption of As from oxyhydroxide sorbents by Na_2HPO_4 suggests that phosphate competition was the major factor responsible for the observed increase of As, as indicated by a coinciding increase of K^+ replaced in the exchange process. In the column leached with 8.2 mM NaHCO_3 , high concentrations of sodium result in greater clay dispersion, and the transport of Fe/Mn oxyhydroxides with adsorbed arsenic may account for the enhanced arsenic concentration in the effluent, as suggested by the concurrently observed increase in Fe and Mn concentrations in the effluent.

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1. Introduction

The consumption of high-arsenic (As) groundwater has become a major threat to human health in many parts of the world (e.g., Dhar et al., 1997; Fendorf et al., 2010). Elevated concentrations of arsenic have been detected in groundwater from Quaternary aquifers in the Datong Basin, a semi-arid area of Shanxi Province in northern China. In this basin, groundwater is the major source of drinking water and endemic arsenic poisoning was recorded in the early 1990s; melanosis, leucomelanosis, keratosis, gangrene, carcinoma, and skin cancer were noted among the possible effects. Wang et al. (2004) tested a total of 3083 wells tapping the Quaternary aquifers of the study area, and 54.4% were found to contain arsenic concentrations exceeding 0.67 μM (50 $\mu\text{g/L}$).

It has been noted that the sediments of aquifer systems containing high-As groundwater typically hold large amounts of labile arsenic. This is true in such areas of endemic arsenic poisoning as the Bengal Delta (e.g., Sengupta et al., 2004) and the Datong Basin (e.g., Wang

et al., 2009). Release of arsenic from the sediment may contribute to the elevated arsenic content in groundwater (Anawar et al., 2004; Islam et al., 2004). Biogeochemical mechanisms responsible for the release of arsenic into groundwater in alluvial aquifers have been a research focus in the past two decades. Oxidation of arsenic-rich ferrous sulfide in aquifer sediments has been proposed as one possible mechanism (Chakraborti et al., 2001); however, this is considered unlikely in the Datong Basin where there is little evidence of sulfide minerals in the sediments. Other studies have indicated the importance of arsenic desorption by phosphate and bicarbonate and by changes in the sorptive capacity of ferric oxyhydroxides (e.g., Appelo et al., 2002; Gao et al., 2010). An additional factor that causes arsenic release from sediments is the microbiologically-mediated reductive dissolution of arsenic-rich Fe(III) oxyhydroxides in the aquifers. This may actually be the primary mechanism for elevated arsenic concentration in groundwater (Fendorf et al., 2010; McArthur et al., 2004; Nickson et al., 2000); the production of other competing sorbate ligands (bicarbonate, phosphate, and dissolved organic carbon) may further exacerbate arsenic release.

Although the processes described above may have all played a role in arsenic mobilization, there are indications that competitive anions may also play a critical role in promoting the mobility of arsenic under both oxic and anoxic conditions. For instance, significant

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desorption of arsenic in groundwater and adsorption of carbonate on ferrihydrite in soil was reported by Appelo et al. (2002); the work of Gao and Mucci (2001) also showed the competitive adsorption of arsenate and phosphate on goethite in high ionic-strength solution. Furthermore, arsenic was positively correlated with bicarbonate and phosphate concentrations in the groundwater of Datong Basin, suggesting that bicarbonate and/or phosphate may be competing anions that favor arsenic mobilization (Wang et al., 2009).

There are only a limited number of published investigations in which flow-through experiments have been used to study the effects of possible competing anions on arsenic release. This is true even for studies involving natural sediments. In column experiments with synthetic iron oxide-coated sands, Radu et al. (2005) observed no major effect of carbonate concentrations on As mobility. Using sands coated with synthetic ferrihydrite, Saalfeld and Bostick (2010) reported major effects of bicarbonate on As sorption only in the presence of Ca^{2+} or Mg^{2+} as adsorbing cations. In this study, a sediment from the high-As aquifer system in the Datong Basin was used in laboratory column and batch experiments to investigate the role of phosphate and bicarbonate in mobilizing sorbed arsenic into groundwater.

2. Materials and methods

2.1. Groundwater sampling

The Datong Basin is a Cenozoic basin of the Shanxi rift system (Fig. 1). The evolution of the Datong Basin began in the early Pleistocene; the sediments were mainly alluvial and lacustrine sands and silts. Rivers have developed during the Holocene, and the uppermost

aquifers occur in Holocene alluvial sands, silts, and clays. The thickness of Cenozoic sediments in the basin ranges from 50 to 2500 m. Shallow groundwater occurs in the Quaternary alluvial, alluvial-pluvial and alluvial-lacustrine aquifers. The shallow aquifer (<60 m) sediments are usually made up of lacustrine and alluvial-lacustrine medium-fine sand, silty clay and clay; the color is gray to blackish. The depth of the water table is generally less than 2 to 5 m in the study area, and decreases from the mountain front to the center of the basin. Groundwater moves from areas near the mountain front to more central discharge areas (Wang et al., 2009).

Groundwater sampling in the Datong Basin was carried out in September 2005 and in June 2009, with a total of 64 groundwater samples collected (Fig. 1). Groundwater samples were collected from drinking-water wells having diameters between 0.1 and 0.2 m, and depths between 15 and 60 m. Before each sampling, the well was pumped for over 1 h at a rate of 0.5–1.0 L/min. During sampling, all water samples were filtered through 0.45 μm membranes on site. Samples were collected in two 500 mL polyethylene bottles, which had been rinsed twice with deionized water. Samples for metallic element analysis were acidified by adding 2–3 mL of Aristar-grade nitric acid to prevent adsorption on the interior walls of the storage bottle, and to minimize post-sampling microbial activities. Unstable hydrochemical parameters including water temperature, pH, Eh, and electrical conductivity (EC) were measured in-situ using calibrated portable Hanna meters. Alkalinity was measured on the sampling day using the Gran titration method. Concentration of major anions of the samples was determined using ion chromatography (Dionex 120). The concentrations of major cations were determined using an inductive coupled plasma-atomic emission spectrometer (ICP-AES,

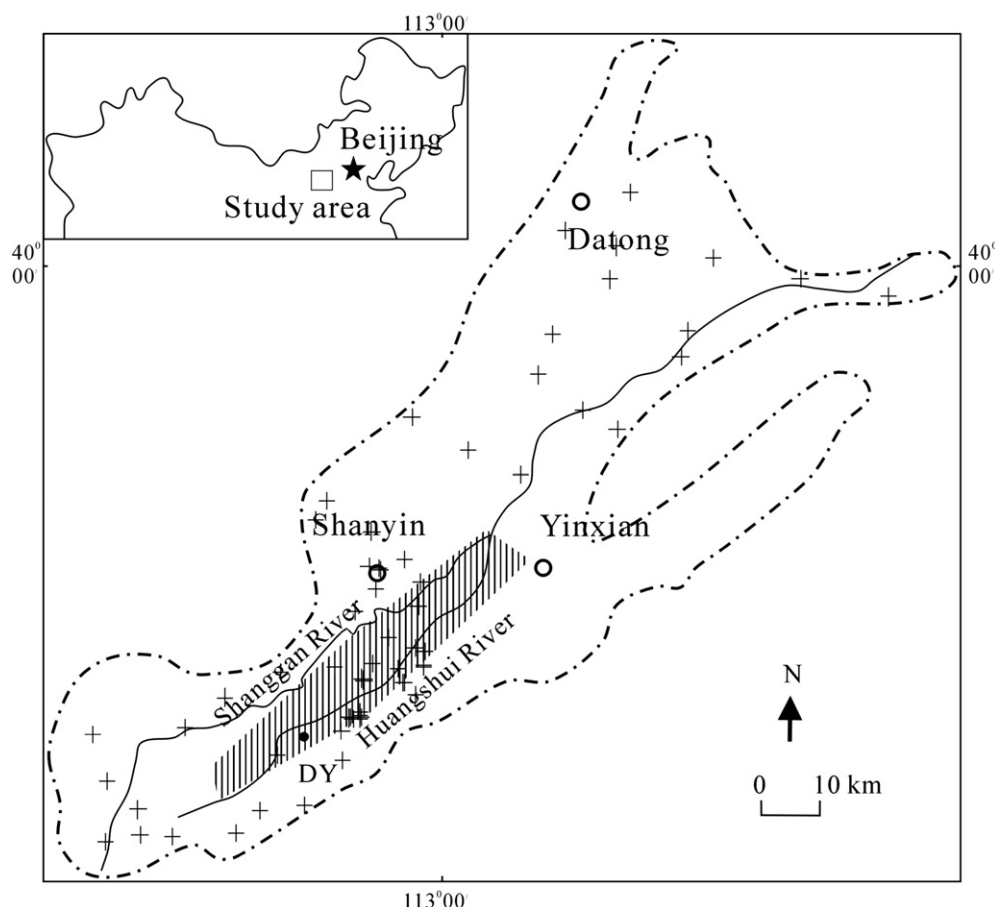


Fig. 1. Location of the groundwater (+) and sediment sampling sites (the sediment sample used in this study was collected from borehole named as DY at depth of 46.0 m). The dash-and-point line represents the basin limit, and the shadow area indicates where high arsenic groundwater occurs.

Thermo Fisher Scientific), while As, Fe, Mn and other trace elements were analyzed using ICP-mass spectrometer (ICP-MS, Poems III, Thermo Jarrell Ash).

2.2. Sediments sampling

A total of 76 sediment samples were collected between August 2005 and May 2006 from the Datong Basin. Sediment samples were retrieved from depths between 0 and 50 m at intervals of 1.5 to 3 m. The sediment sample used in this work was collected from one of the boreholes (labeled DY in Fig. 1) in the study area with groundwater arsenic contents up to 14.2 μM . The samples were immediately capped in a well-sealed PVC pipe to minimize exposure to the atmosphere.

After collection, all drill-core samples were wrapped with a preservative film and stored, in the field, at 4 °C and in the dark. When using the samples, the drill core was placed in a container connected to a vacuum pump and dried at 4 °C. After drying, the sediment was stored in desiccators. The major elements and trace elements of the sediment were measured within two weeks of sampling. Analysis of the major-element oxides (SiO_2 , Fe_2O_3 , TiO_2 , Al_2O_3 , CaO , P_2O_5 , MgO and MnO) in the solid samples was carried out using an XRF spectrometer (Rigaku model RIX2100) in the State Key Laboratory of Geological Processes and Mineral Resources, according to the standard EPA method. Trace elements were measured by ICP-MS after digestion, which was accomplished by adding 9 mL concentrated HNO_3 , 2 mL HClO_4 , and 3 mL HF to a 0.5 g dry sample, then heating at 180 °C for 24 h, evaporating to dryness, and adding 50 mL of 2% (V/V) HNO_3 . Mineral phase identification was performed by using X-ray powder diffraction (X'Pert Pro DY2198) with $\text{Cu-K}\alpha$ radiation at 40 kV and 40 mA. The content of organic carbon in sediments was measured using liquiTOC II. The sediment sample used in batch and column tests of this study was chosen from a borehole where the groundwater arsenic content was measured at concentrations of up to 14.15 Mm .

The sediment samples were screened through a 2 mm sieve and stored in desiccators. Note that the original reducing state of the sediments was not preserved, and the experimental study was performed in an atmospheric (oxic) setting, as the focus of this study was not on redox processes, but on the effect of possible competing anions and fluid composition on arsenic release from natural sediments.

2.3. Batch experiments

Batch experiments were performed to evaluate the ability of chloride, nitrate, bicarbonate, phosphate, sodium, and calcium to enhance the release of arsenic from the sediment sample. Results of the batch experiments were used to select the leaching solutions for the column experiments. A solid to solution ratio of 1:4 was employed, with the solution being DI water, NaHCO_3 (8.20 mM), Na_2HPO_4 (0.10 mM), $\text{Ca}(\text{NO}_3)_2$ (0.1, 0.5, 1.0 mM), NaNO_3 (0.24, 0.81, 1.94 mM), or NaCl (0.2, 4.1, 8.20 mM). The ionic strength ranged between 0.1 mM and 8.2 mM. The concentrations of 8.2 mM HCO_3^- and 0.10 mM HPO_4^{2-} were selected to approximate their measured levels in the groundwater of the Datong Basin. Three concentration levels were used for $\text{Ca}(\text{NO}_3)_2$, NaNO_3 and NaCl to evaluate the potential impacts of NO_3^- and Cl^- on arsenic release. The initial pH value of the leaching solutions was adjusted to about 8.0 with diluted HCl and/or NaOH.

All chemicals were of reagent grade and used without further purification. The chemical solutions were prepared in the laboratory by dissolving pre-weighed amount of reagent into purified DI water (Milli-Q Ultrapure Water Purification System). All glassware was acid-washed and rinsed with DI water.

The batch tests were conducted in triplicate and equilibrated for 72 h on a shaker table (cell production roller drum, Bellco), at a speed of 39 rpm, inside an incubator with a temperature of 23 °C. After equilibration, the sediment-solution slurry was centrifuged at

6000 rpm for 30 min and further filtered through a 0.2 μm membrane. The aqueous samples were then diluted with 1% high-purity nitric acid and analyzed using the ICP-MS. A PerkinElmer SCIEX model Elan® DRC II ICP-MS was used for the measurements of major and trace elements; a solution contained 5 $\mu\text{g/L}$ of In-115, Sc-45, Li-6 and Bi-209 as internal standards. The accuracy of the analyses was confirmed using the certified reference material TMDA-54.4.

2.4. Column experiments

One-dimensional saturated miscible displacement column tests were conducted to study the As leaching with 1 mM $\text{Ca}(\text{NO}_3)_2$ and phosphate-leaching (P-column) or bicarbonate-leaching (C-column) solutions. Two glass columns (Omnifit) with an inner diameter of 1.5 cm and length of 7.0 cm were uniformly packed with the same sediment used in the batch test experiments. The sediment, with a moisture content of 0.7% (measured at 105 °C), was poured into the columns in 2 g increments and hand-tamped with a plastic dowel. The total mass of sediment in the columns was 17.50 and 17.52 g for P- and C-columns, respectively. Filters (0.25 cm thick and 10 μm pore diameter) were used at the top and bottom of each column to prevent solid particle movement.

A constant upward flow rate of 0.3 mL/min, corresponding to a pore-water velocity of 10.19 cm/h based on porosity calculated below, was maintained using a peristaltic pump to inject the leaching solution. The columns were initially leached with 1.0 mM $\text{Ca}(\text{NO}_3)_2$ solution to establish the background level of released As from the sediments. When the released As content was constant, the influent solution was switched to either Na_2HPO_4 (P-column) or NaHCO_3 (C-column); both solutions contained 4.0 μM ReO_4^- as the nonreactive tracer to evaluate the hydrodynamic process of the column (Harvey et al., 1992; Hu et al., 2008). Column effluent was collected in an automatic fraction collector (Spectra/Chrom CF-1, Spectrum Chromatography) every 10 min, which represented the time required for about 0.66 column pore volume (PV) to discharge from the column. The column pore volume was measured to be 1.67 and 1.72 mL, with the corresponding porosity of 0.135 and 0.139, from the weight difference of sediment and column, before and following full saturation with the leaching solution. The effluent passed 10 μm membrane at the end of column, without further filtration. Frequent pH measurements were made by immersing a combined pH microelectrode in column effluent. Eluent samples were also acidified to 1% HNO_3 prior to ICP-MS analysis for the determination of total aqueous concentrations of As, Al, Si, K, Mg, Ca, Na, Mn, Fe, Re, and Ba.

3. Results

3.1. Groundwater geochemistry in the Datong Basin

Groundwater in the aquifers of the Datong Basin typically contains arsenic concentrations between 0.067 μM and 24.23 μM , with pH from 7.09 to 8.71 (Table 1). The high-arsenic groundwater samples were collected primarily from the upper semi-confined aquifer along the banks of Huangshui River and Shanggan River (Fig. 1). The groundwater samples with high arsenic concentrations typically contained low levels of sulfate and nitrate (up to 0.16 mM), moderate to high alkalinity (an average value of 8.26 mM as HCO_3^-), and a mean pH value of 8.1. Elevated levels of HPO_4^{2-} , Fe and Mn were detected in most of the high-As groundwater samples. The high-As groundwater was generally found to be HCO_3^- -Na type water, with HCO_3^- and Na as the dominant anion and cation. However, some of the high-As groundwater samples were found to be HCO_3^- -Cl-Na-Mg or Cl-SO₄-Na-Mg type waters, with moderately high contents of chloride (3.71–25.1 mM) and sulfate (0.86–9.24 mM), along with Na^+ and Mg^{2+} as the dominant cations.

Table 1
Parameters of high-arsenic groundwater and sediments (mg/kg) from Datong Basin.

Groundwater		Sediments			
Parameters	Mean (N = 64)	Parameters	Max	Min	Mean (N = 76)
T (°C)	8.5	Al ₂ O ₃ (%)	13.1	5.3	8.7
pH	8.72	SiO ₂ (%)	59.8	22.1	37.8
EC (μS/cm)	1355	Fe ₂ O ₃ (%)	5.6	2.3	3.6
Eh (mV)	-83.1	K ₂ O (%)	2.4	1.4	2
TDS (mg/L)	672	CaO (%)	10.5	3.3	6
K (mM)	0.013	MgO (%)	4.4	1.3	2.2
Na (mM)	2.71	Na ₂ O (%)	3.3	0.7	1.4
Ca (mM)	0.193	As	118.2	4.9	18.6
Mg (mM)	0.825	P	772	465	590
Si (mM)	0.156	Nb	114.5	55.1	76.5
HCO ₃ ⁻ (mM)	7.90	Pb	14.5	4.1	11.6
F ⁻ (mM)	0.187	Rb	24.6	10.5	18.1
Cl ⁻ (mM)	6.04	Zn	98.4	42	63.8
NO ₃ ⁻ (mM)	0.31	Th	14.2	7.9	11.3
HPO ₄ ²⁻ (mM)	0.23	Ba	571	395	476
SO ₄ ²⁻ (mM)	0.25	Cu	49.5	20.5	33.7
Sr	3.01	Mn	1,006	376	560
Mn	1.75	Sr	595	176	282
Fe	1.27	Co	21.5	6.8	13
Ba	0.21	Ni	49.5	20.5	33.3
B	12.74	La	43.8	13.2	30.3
P	16.24	Ce	89.6	29	64.6
Br ⁻	1.00	Pr	10.7	3.6	7.8
As	1.41	Nd	38.7	13.4	28.5
		Sm	8.1	2.7	5.9
		Eu	1.6	0.8	1.2
		Gd	6.9	2.3	4.9
		Tb	1.1	0.3	0.8
		Dy	6.1	2	4.4
		Ho	1.2	0.4	0.9
		Er	3.5	1.1	2.4
		Tm	0.5	0.2	0.4
		Yb	3.3	0.9	2.4
		Lu	0.5	0.1	0.4
		Y	30.8	9.2	20.9

3.2. Geochemistry of sediments in Datong Basin

The sediments of both high- and low-arsenic aquifers in the Datong Basin are mainly silty clay, with no significant difference in mineralogy (Su, 2006). The major (about 70–80%) minerals in Datong sediments were quartz, feldspar, and calcite with minor contents of chlorite, dolomite, illite and other clay minerals. The measured contents of major and trace elements in these sediment samples are summarized in Table 1. The content of arsenic varied from 4.9 to 118.2 mg/kg, with a mean value of 18.6 mg/kg; this is comparable to levels reported for modern unconsolidated sediments throughout the world (typically 5–170 mg/kg) (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002). The contents of iron (Fe₂O₃) and magnesium in the Datong sediments ranged between 2.3–5.6 wt.% and 376–1006 mg/kg, respectively. According to Xie et al. (2008), a moderate correlation of arsenic with iron was observed in sediment samples from Datong, while the correlation with other geochemical parameters was commonly low. Contents of organic carbon and inorganic carbon are 0.01–0.613 wt.% and 0.430–2.71 wt.%, respectively.

The laboratory sediment samples used in the batch and column tests were all derived from a single field sample, which was taken at a depth of 46.0 m, and was chosen based on its measured high arsenic content. The field sample consisted of 39% sand, 32% silt, and 29% clay. The major mineralogical phases in the sediment were quartz (40%), feldspar (20%), calcite (10%), chlorite (10%), and illite (10%); minor contents of dolomite and amphibole were noted. The sediment is alkaline, having a pH of about 8.7 and an EC value of 890 μS/cm at a solid:water ratio of 1:2.5. The averaged ($n = 3$) contents of Al₂O₃, SiO₂, Fe₂O₃, K₂O, CaO, MgO, and Na₂O were determined as 10.7, 52.6, 4.43, 2.09, 5.92, 3.78, and 1.64 wt.%, respectively. The contents

of trace elements As, P and Mn were measured as 18.0, 683 and 605 mg/kg, respectively. A significant presence of Fe in the sediment is attributed to the Fe oxyhydroxides (Xie et al., 2008), as determined by the oxalate extraction method (Dzombak and Morel, 1990). According to Xie et al. (2008), the content of oxalate-extracted Fe in Datong Basin sediments ranged between 0.15 and 3.16 mM, when 1.0 g sediment samples were extracted using 20 mL extractant. The total organic carbon in the sediment ranged between 0.21% and 0.23%.

3.3. Batch experiments

Compared to DI water, no apparent increase of As content was observed in the batch solutions of Ca(NO₃)₂, NaNO₃ and NaCl (Table 2). Different concentrations of Na⁺ in batch solutions of NaNO₃ and NaCl caused little change in arsenic content. Therefore, the impact of Na⁺ on arsenic release is insignificant up to the Na⁺ concentration of 1.94 mM used in the tests. The highest measured arsenic content was observed in the Na₂HPO₄ and NaHCO₃ test solutions (Table 2). Among various solutions tested, no major changes for the elements K, Na, Ca, Mg, Fe, and Mn were observed, except for a slight release of Mn and Fe in the Na₂HPO₄ batch (Table 2).

3.4. Column experiments

3.4.1. Arsenic mobility and pH/Eh changes

The solution of Ca(NO₃)₂ was used as the initial leaching solution in the column tests to detect more readily the arsenic response when the influent solution was switched to NaHCO₃ or Na₂HPO₄. For the P-column, the changes of As concentration in the effluent, with leaching solutions of Ca(NO₃)₂ and Na₂HPO₄, are presented in Fig. 2a. It can be seen that there was a rapid increase of As concentration, to 0.28 μM, in the first collected effluent solution (about 3 PV) following the introduction of the 1.0 mM Ca(NO₃)₂ influent. The effluent As concentration then decreased gradually and remained constant at 0.12 μM for about 150 PV. A new increase in the effluent arsenic concentration was observed after the 1.0 mM Ca(NO₃)₂ solution was switched to 0.10 mM Na₂HPO₄. The increase of As concentration in the effluent solution occurred at about 50 PV after the switch, and reached a peak value of 0.56 μM after about 155 PV. The

Table 2
Measured elemental concentrations in different solutions of batch experiment.

Elements\solution	DI water	NaHCO ₃ (8.2 mM)	Na ₂ HPO ₄ (0.1 mM)	Ca(NO ₃) ₂		
				0.1 mM	0.5 mM	1.0 mM
As (μM)	0.374	0.742	0.490	0.376	0.378	0.382
Fe (μM)	1.817	1.853	2.127	1.814	1.846	1.846
Mn (μM)	1.926	1.955	2.191	1.960	2.004	2.028
Si (mM)	0.127	0.155	0.154	0.129	0.132	0.135
K (mM)	0.306	0.289	0.338	0.322	0.353	0.376
Na (mM)	0.892	–	–	0.953	1.066	1.157
Ca (mM)	0.841	0.252	0.314	–	–	–
Mg (mM)	1.279	1.164	1.337	1.300	1.366	1.378
pH	8.06	8.10	8.16	8.07	8.08	8.10
Elements\solution	NaNO ₃			NaCl		
	0.24 mM	0.81 mM	1.94 mM	0.2 mM	4.1 mM	8.2 mM
As (μM)	0.379	0.379	0.380	0.379	0.382	0.383
Fe (μM)	1.828	1.833	1.859	1.817	1.850	1.896
Mn (μM)	1.889	1.897	1.851	1.915	1.979	2.019
Si (mM)	0.131	0.133	0.135	0.128	0.135	0.135
K (mM)	0.306	0.327	0.346	0.306	0.326	0.357
Na (mM)	–	–	–	–	–	–
Ca (mM)	0.838	0.836	0.843	0.836	0.843	0.851
Mg (mM)	1.362	1.423	1.427	1.423	1.432	1.440
pH	8.10	8.10	8.12	8.07	8.06	8.08

DI water: deionized water.

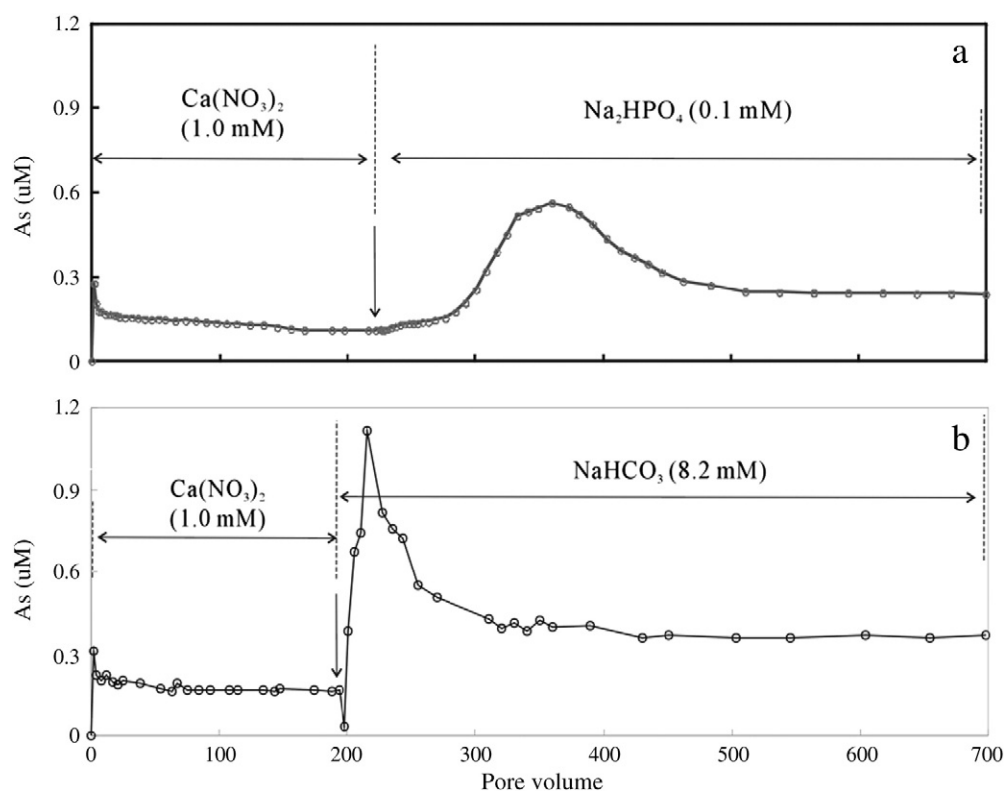


Fig. 2. Column effluent As concentration during leaching of 1.0 mM Ca(NO₃)₂ followed by 0.10 mM Na₂HPO₄ (a) and 8.2 mM NaHCO₃ (b). Arrows indicate pore volumes when influent solution was changed.

release curve of effluent As concentration then showed a tailing effect, and became stable at around 0.25 μM after 300 PV (Fig. 2a).

For the C-column, the arsenic concentration changes in the effluent, with leaching solutions of 1.0 mM Ca(NO₃)₂ and 8.2 mM NaHCO₃, are presented in Fig. 2b. Again, leaching with Ca(NO₃)₂ solution triggered an increase of As concentration in the effluent; the As concentration then decreased gradually from 0.30 μM to 0.14 μM after 55 PV. When the leaching solution was switched to NaHCO₃, the effluent As concentration significantly increased, to 1.12 μM. A sharp front immediately appeared in the release curves of As, with the peak concentration of As occurring after the introduction of about 16 PV of the NaHCO₃ solution. After leaching for about 120 PV of the NaHCO₃ solution, the effluent As concentration was stable at around 0.36 μM (Fig. 2b).

To better illustrate the effect of the interaction between leaching solutions and sediments, the change of effluent pH and Eh with pore volume is presented in Table 3. It can be seen that the pH value of the effluent from both the P- and C-columns increased with initial introduction of each of the leaching solutions of Ca(NO₃)₂, Na₂HPO₄, and NaHCO₃. The maximum pH value almost coincides with the onset of maximum As concentration, suggesting that the elevated As concentration is partly related to the high pH value of the effluent. The pH value remains constant after the introduction of about 100 PV of each new solution; it stabilizes at a value about 0.1 to 0.15 higher for the Na₂HPO₄ and NaHCO₃ solutions than for the initial leaching solution of Ca(NO₃)₂.

A slight increase of the Eh value of the effluents from both the P- and C-columns was observed with the introduction of the Ca(NO₃)₂, Na₂HPO₄, and NaHCO₃ solutions. However, the final Eh value of the column effluent remained almost constant in all cases, at a value almost the same as that in the initial solution of Ca(NO₃)₂, Na₂HPO₄, or NaHCO₃. The Eh value for the P-column effluent before and after the introduction of Na₂HPO₄ solution was 220–239 and 227–253 mV, respectively. For the C-column, the Eh value was 220–243 and 226–250 mV, respectively, before and after the introduction of the NaHCO₃ solution. Obviously, there was no appreciable change of Eh value in the effluents,

which would be expected for experiments conducted under atmospheric conditions.

3.4.2. Release of major cations

The highest concentrations of major cations in the P-column effluent were observed immediately after the sediment was leached with 1.0 mM Ca(NO₃)₂: K⁺ 0.36 mM, Na⁺ 9.59 mM, Ca²⁺ 5.20 mM, and Mg²⁺ 4.69 mM (Fig. 3a); these concentrations were all much higher than the corresponding concentrations (all less than 0.01 mM, except for 1.0 mM Ca²⁺) in the leaching solution of Ca(NO₃)₂. The concentrations decreased gradually, and became stable after about 145 PV for K⁺ and Na⁺. Effluent As concentration significantly increased when the leaching solution was switched to Na₂HPO₄. The effluent K⁺ concentration peak appeared after 90 PV leaching of Na₂HPO₄ solution, and then remained at about 0.26 mM. The elution curve of Na⁺ showed a sharp concentration front at 10 PV, and remained stable after 500 PV continuous leaching with Na₂HPO₄ solution. The effluent concentration peak of Ca²⁺ (a slight spike up to 1.29 mM) was only observed at 10 PV. When leaching with Na₂HPO₄ solution, the effluent Ca concentration remained at around 1.04 mM, which was very similar to that in the 1.0 mM Ca(NO₃)₂ leaching solution used in the experiment. The Mg²⁺ concentration in the effluent increased very slightly from 0.096 to 0.15 mM when the leaching solution was switched to Na₂HPO₄. A gradual decrease in Mg²⁺ concentration was observed after leaching with the Na₂HPO₄ solution for 30 PV; the concentration then remained at 0.02 mM through 500 PV.

For the C-column, after a rapid release to the Ca(NO₃)₂ leaching solution, the concentrations of major cations remained stable as follows: K⁺ 0.04 mM, Na⁺ 0.02 mM, Ca²⁺ 1.03 mM and Mg²⁺ 0.19 mM, through almost 150 PV leaching with the Ca(NO₃)₂ solution (Fig. 3b). The highest concentrations in the initial spike for K⁺, Na⁺, Ca²⁺ and Mg²⁺ were 0.35, 8.80, 4.73 and 4.09 mM, respectively. When the leaching solution was switched to the NaHCO₃ solution, small effluent concentration peaks for K⁺, Ca²⁺ and Mg²⁺ appeared

Table 3
Values of pH and Eh monitored in effluents of column experiment.

P-column leaching solution	1.0 mM Ca(NO ₃) ₂						0.1 mM Na ₂ HPO ₄					
Pore volume	0	1	10	50	100	200	210	230	250	300	500	700
pH	7.52	8.11	8.08	7.64	7.52	7.53	7.69	7.84	7.74	7.64	7.62	7.63
Eh (mv)	220	239	232	220	223	225	245	253	243	235	228	227
C-column leaching solution	1.0 mM Ca(NO ₃) ₂						8.2 mM NaHCO ₃					
Pore volume	0	1	10	50	100	190	200	210	250	300	500	700
pH	7.50	8.07	7.91	7.54	7.53	7.52	8.24	8.01	7.76	7.65	7.64	7.64
Eh (mv)	220	243	238	226	224	223	250	248	239	233	226	227

after a few PV of leaching with the new solution; these concentrations then gradually decreased to K⁺ and Mg²⁺ levels lower than those in the effluent of the Ca(NO₃)₂ leaching solution. By contrast, the effluent Na concentration increased first and then remained constant at about 8.25 mM, which was consistent with the concentration of the leaching solution.

3.4.3. Release of iron and manganese

Changes of effluent Fe and Mn concentration are presented in Fig. 4a and b, respectively. Large amounts of Fe were released during the first 15 PV of leaching with the Ca(NO₃)₂ solution, with peaks of 33.8 μM in the P-column and 26.4 μM in the C-column. Replacing the leaching solution with Na₂HPO₄ resulted in a minor increase of Fe concentration in the effluent. In contrast, leaching with the NaHCO₃ solution in the C-column resulted in a Fe concentration peak (21.5 μM) at about 20 PV (Fig. 4b), coinciding with the spike of released As in the effluent (Fig. 2b). Furthermore, the final concentration of Fe in the effluent of the P-column was about 5.0 μM, in contrast to the concentration of 10.5 μM measured in the effluent of the C-column.

Similar to Fe, a significant mobilization of Mn was observed when the sediment was initially leached with Ca(NO₃)₂ solution. During the input pulse of Ca(NO₃)₂, Mn concentration in the effluent was consistently high for both columns (Fig. 4), and then became stable at 0.22 μM in the P-column, and at 1.10 μM in C-column. Switching of leaching solution from Ca(NO₃)₂ to Na₂HPO₄ caused no change in the Mn concentration of the P-column effluent, but was followed by some perturbation (a decrease followed by an increase) in the Mn concentration of the C-column effluent (Fig. 4b).

3.4.4. Release of silica and rhenium

Silica in the effluent was monitored as a potential competitive anion with As. A concentration pulse of Si appeared in the effluent of both columns when the Ca(NO₃)₂ solution was introduced. A slight elevation of Si concentration in effluent was observed when the leaching solution was switched from Ca(NO₃)₂ to Na₂HPO₄ in the P-column (Fig. 5a); in contrast, the introduction of NaHCO₃ resulted in a significant increase of Si in the effluent of the C-column (Fig. 5b). After about 250 PV leaching with the Na₂HPO₄ or NaHCO₃ solutions, the effluent Si concentration remained at 13.4 in the P-column and 50.2 μM in the C-column. Perrhenate (ReO₄[−]) was used in this work as the tracer based on its conservative physico-chemical characteristics (Darab and Smith, 1996; Einat et al., 2010). Though it was not added into the leaching solutions of Ca(NO₃)₂, a concentration peak of it was found at the beginning of Ca(NO₃)₂ leaching (Fig. 5a and b), indicating that there existed a trace amount of Re-bearing soluble minerals in the sediment. When the leaching solution was switched to either the Na₂HPO₄ or NaHCO₃ solutions, the presence of introduced Re tracer in the column effluent was immediately detected, and quickly reached the input concentration level.

4. Discussion

Measured As contents in the Datong sediments were within the reported range for modern unconsolidated sediment (Smedley and Kinniburgh, 2002). It follows that the high arsenic concentration in Datong Basin groundwater is not due to the enrichment of arsenic in the sediments, but rather to the release of sorbed arsenic in response to biogeochemical processes. A moderate correlation of arsenic with iron observed in the Datong sediments suggests that the occurrence of arsenic in these sediments may be closely associated with iron-bearing minerals. Changes of groundwater composition may induce the release of arsenic from iron oxyhydroxides, as indicated from the batch and column experiments in this work.

According to Goldberg and Johnston (2001), a change of ionic strength in solution caused adsorption or desorption of arsenite on amorphous Fe and Al oxyhydroxides. However, the mobility of As in Datong sediment showed little changes in our batch test solutions with different ionic strengths, which is consistent with other results (Antelo et al., 2005; Manning and Goldberg, 1997; Smith et al., 1999). Antelo et al. (2005) reported that arsenic adsorption was insensitive to ionic strength where goethite or amorphous Fe oxyhydroxides were the sorbents. Therefore, the change in ionic strength does not appear to be the key factor directly controlling the adsorption/desorption of arsenic from the Datong sediments.

In the column experiments, the rapid release of As and all cations when the sediment was initially leached with Ca(NO₃)₂ solution indicates a significant influence of cation exchange on the release of major cations, and of sorption equilibrium on the release of Mn, Fe, and As. Continued leaching with Ca(NO₃)₂ solution only resulted in relatively stable effluent concentrations of As in the Datong Basin sediment, similar to those observed by Fallman and Aurell (1996). However, when the leaching solution was switched to either the Na₂HPO₄ or NaHCO₃ solution, the effluent As concentration significantly increased. Some factors discussed below could be responsible for the observed elevation of As concentration as a response to a change in fluid composition.

Competing anions (such as phosphate, bicarbonate and silicate) present in the leaching solutions will compete with arsenic for the available adsorption sites and even alter the electrostatic surface charge of the sorbents (Choi et al., 2009; Dixit and Hering, 2003; Kim et al., 2000; Roberts et al., 2004). Studies have shown the significant capability of silicate on arsenic desorption from several sorbents (Ciardelli et al., 2008). However, according to the results of our previous work using the same sediment as in this study, adding 0.4 mM Na₂SiO₃ in the influent caused a total increase in the effluent As concentration of only 0.23 μM (Gao et al., 2011). The effect of silicate on arsenic mobility in the Datong sediment therefore appears to be negligible.

Arsenic adsorption is decreased at higher bicarbonate concentrations, as suggested by the results of model simulations and laboratory experiments (Appelo et al., 2002; Gao et al., 2011). Phosphate can increase As(V) mobility in soil and sand columns, as reported by

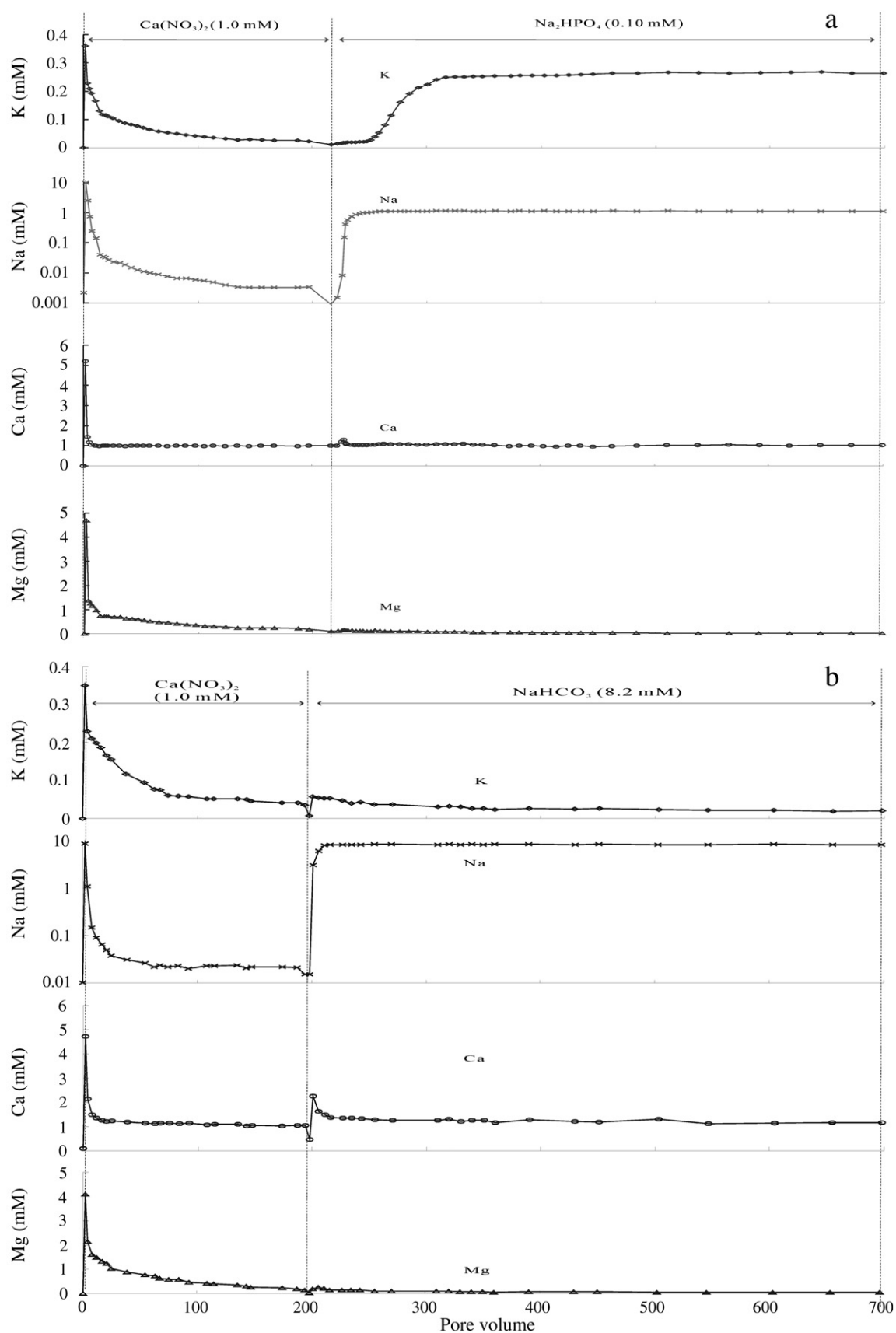


Fig. 3. Concentration changes of major cations in column effluent during leaching of 1.0 mM $\text{Ca}(\text{NO}_3)_2$ followed by 0.10 mM Na_2HPO_4 (a) and 8.2 mM NaHCO_3 (b).

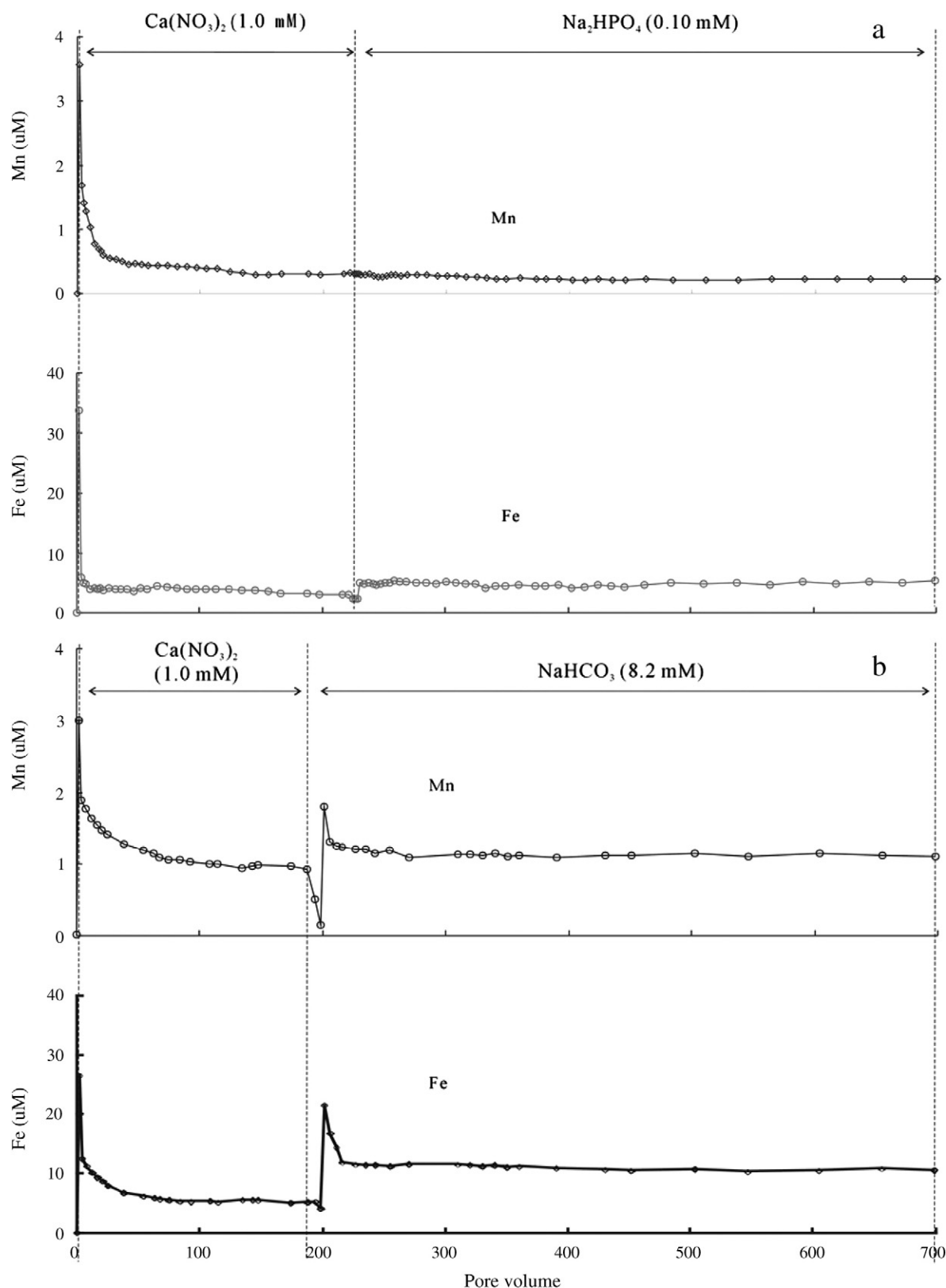


Fig. 4. Concentration of Fe and Mn in column effluent during leaching of 1.0 mM $\text{Ca}(\text{NO}_3)_2$ followed by 0.10 mM Na_2HPO_4 (a) and 8.2 mM NaHCO_3 (b).

Darland and Inskeep (1997) and Melamed et al. (1995). The competitive desorption of As was evaluated by an addition of Na_2HPO_4 or NaHCO_3 in our batch experiments. A significant increase of dissolved As concentration (filtered by 0.2 μm membrane) was observed with the presence of phosphate or bicarbonate (Table 2; Gao et al., 2011).

Therefore, competitive desorption of As from the Datong sediment could be one of the major processes responsible for As concentration increase in groundwater.

Our column experiments indicate that competitive desorption of As from the Datong sediment is more evident with phosphate than

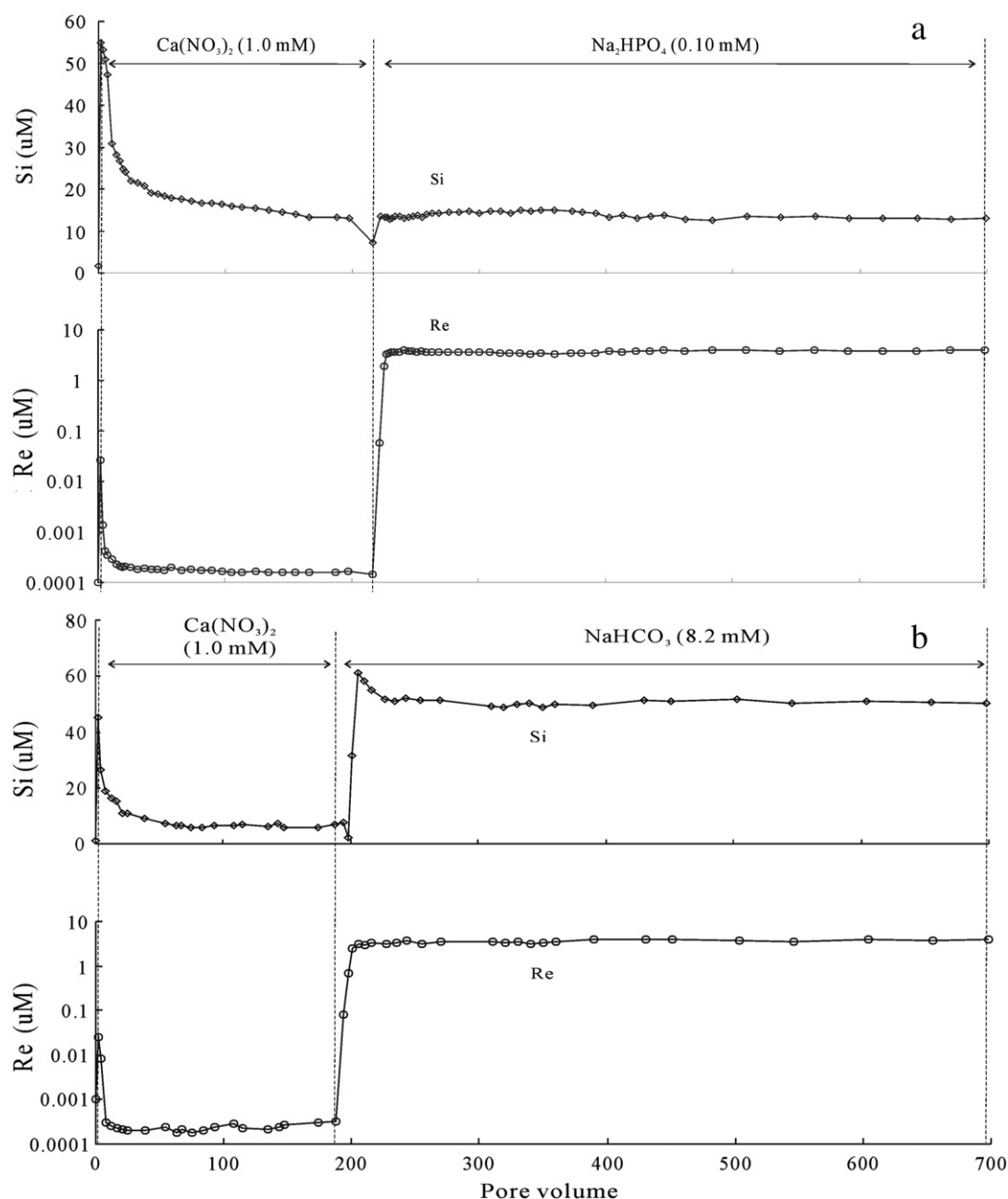


Fig. 5. Concentration of Si and Re in column effluent during leaching of 1.0 mM $\text{Ca}(\text{NO}_3)_2$ followed by 0.10 mM Na_2HPO_4 (a) and 8.2 mM NaHCO_3 (b).

with the bicarbonate anion. Column leaching tests are helpful in monitoring the dynamic release of relevant elements, and thus shed light on the underlying mechanisms. The P-column experiments with phosphate as the competitive anion exhibited a high degree of cation exchange between Na^+ and K^+ , with high K^+ concentration observed to be coincident with As release (Figs. 2a and 3a). Furthermore, extra Na^+ (beyond the input concentration) was desorbed in the P-column tests. In contrast, such effects of replaced Na^+ and K^+ were not evident in the C-column results. The P-column results offer convincing evidence that cation exchange and phosphate adsorption act to displace sorbed As. The rapid attainment of non-sorbing ReO_4^- tracer to the input concentration suggests that advection was the major solute transport process in these homogeneously-packed 1-D columns, and that the impact of dispersion in these experiments was negligible.

For the C-column results, however, competitive desorption cannot well explain the increase of Fe and Mn in the effluent when the column

was leached with NaHCO_3 solution. A strong increase in the sodium mole percentage, in $\text{Na}^+/\text{Ca}^{2+}$ and $\text{Na}^+/\text{Mg}^{2+}$ ratios, and in the sodium adsorption ratio in a solution can increase the dispersion of soil clays (Goldberg and Forster, 1990; Pils et al., 2007). During the injection period of the 8.2 mM NaHCO_3 solution, the observed increases in sodium mole percentage, as well as in the $\text{Na}^+/\text{Ca}^{2+}$ and $\text{Na}^+/\text{Mg}^{2+}$ ratios (Fig. 3b), of the effluent may have helped promote aggregate breakdown, colloid dispersion and mobilization in the column. Consequently, the elevated contents of Fe and Mn in the effluent may be largely associated with the release of Fe and Mn colloidal particles. At the same time, the particulate arsenic complexes with Fe/Mn oxyhydroxides may account for a significant portion of the enhanced arsenic concentration in the effluent. It was also noticed during our experiments that switching of leaching solution from 1 mM $\text{Ca}(\text{NO}_3)_2$ to 8.2 mM NaHCO_3 solution caused an increase of turbidity in the effluent, indicating the increased presence of colloidal particles. This was further

confirmed by the large amount of residual particle materials (with the size range of 0.2–10 μm) collected when the effluent was filtered through a 0.2 μm membrane.

While it's been well established that phosphate has an important competitive effect on As adsorption, the effect of carbonate competition is not conclusive (Radu et al., 2005). In general, the most significant experimental effects have been reported for very high carbonate concentrations (0.05–1 M), typically much higher than those observed in most groundwaters (Radu et al., 2005). Meng et al. (2002) reported that bicarbonate does not have a significant effect on the adsorption of arsenate by Fe oxyhydroxides. The impact of K^+ and Ca^{2+} on arsenic mobility in aquatic environment is deemed to be negligible (Stacowicz et al., 2008), but the work of Saalfeld and Bostick (2010) reported major effects of bicarbonate on As sorption only in the presence of Ca^{2+} or Mg^{2+} as adsorbing cations. Our batch test with 8.2 mM NaHCO_3 also yielded elevated As release from the Datong sediment (Table 2). However, the column experiment results indicate that As release is probably not from the competitive desorption of bicarbonate, but from the effects of high concentration of Na^+ in dispersing As-containing Fe/Mn oxyhydroxides.

The column tests were conducted at a pore-water velocity of 10.2 cm/h, which is comparable to the groundwater flow velocity of 0.83–2.42 cm/h typical of the Datong Basin. Therefore, the process of As release from competitive phosphate exchange and Fe/Mn oxyhydroxides appears to be very relevant to the high As groundwater concentration in the Datong Basin. In addition, the work reported here was performed in an atmospheric setting, as the focus was not on redox processes. The Eh value in the column effluent was used to assess the redox condition in the sediment columns (Table 3); obviously, there was no significant change of Eh value in the effluents, indicating relatively stable oxic conditions in the sediment columns. In the Datong Basin, depending on the redox status, reductive dissolution of metal oxyhydroxides (such as Fe and Mn) sorbents could contribute to the release of As from reducing sediments, and thus to elevated As concentration in groundwater.

5. Conclusions

High-arsenic groundwater samples in the Datong Basin typically contain moderate to high alkalinity (as HCO_3^-) and low concentrations of sulfate and nitrate. Elevated HPO_4^{2-} , Fe and Mn concentrations were also detected in most of the high-As groundwater samples.

In the column experiments, the rapid release of As and other cations when the sediment was initially leached with $\text{Ca}(\text{NO}_3)_2$ solution indicated the contribution of cation exchange (for cations) and sorption equilibrium (for Mn, Fe, As). Increase in the effluent arsenic concentration was observed when the $\text{Ca}(\text{NO}_3)_2$ solution was replaced with Na_2HPO_4 or NaHCO_3 . During all the leaching periods, there was no significant change of Eh value in the effluent, due to relatively stable oxic conditions in the columns and lack of reductive dissolution of Fe and Mn oxyhydroxide.

Desorption of As from oxyhydroxide sorbents by phosphate appears to be the major factor for the elevated As concentration in the effluent. During the leaching period of 8.2 mM NaHCO_3 solution in this study, the observed increases in sodium mole percentage, as well as in the $\text{Na}^+/\text{Ca}^{2+}$ and $\text{Na}^+/\text{Mg}^{2+}$ ratios of the effluent, apparently helped to promote aggregate breakdown, colloid dispersion and mobilization in the columns. Therefore, the elevated contents of Fe and Mn in the effluent of C-column result from the release of Fe and Mn oxyhydroxide particles. At the same time, the particulate arsenic complexes with Fe/Mn oxyhydroxides account for the enhanced arsenic concentration in the effluent. In summary, this work indicates that the elevated As release from the Datong Basin sediment is likely from the competitive desorption for phosphate, and mobilization of As-bearing Fe and Mn oxyhydroxides from Na^+ for 8.2 mM NaHCO_3 leaching experiment.

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