Arsenic Adsorption and its Fractions on Aquifer Sediment: Effect of pH, Arsenic Species, and Iron/Manganese Minerals

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Abstract Effects of pH, As species, and Fe/Mn minerals on the fractions of adsorbed As in aquifer sediments were evaluated. Kinetic data showed that As adsorption was controlled by diffusion through the external film. Isothermal data of both As(III) and As(V) fitted the Langmuir isotherm well, revealing a monolayer adsorption process. Sequential extraction demonstrated that water-soluble As and non-specifically sorbed As were the major fractions of adsorbed As. Assessing the relationship between the Freundlich K_F and the increases in the amounts of As fractions showed that the pH played a key role in weakly adsorbed As, especially water-soluble As. Although inorganic As species converted each other during the adsorption processes, more non-specifically sorbed As was adsorbed in As(V)-treated sediment than in As(III)-treated sediment, showing that the electrostatic selectivity controlled the non-specific adsorption.

Additionally, specifically sorbed As and As associated with the amorphous phases were predominated by Fe/Mn minerals, especially Fe(III) (hydr)oxides. These results suggested that pH, As species, and Fe/Mn minerals would regulate the As fractions in aquifer sediments, and therefore control As cycling in aquifer systems.

Keywords Arsenic · Adsorption · Fraction · Aquifer sediments · pH · Arsenic species · Fe/Mn minerals

1 Introduction

Hydrogeological occurrence of carcinogenic As is widespread in many regions of the world, posing a serious health impact on an estimated 150 million people (Ravenscroft et al. 2009; Fendorf et al. 2010). Source, migration, and transformation of As in groundwater are controlled by a number of factors (Smedley and Kinniburgh 2002). Sediments in aquifer systems hosting high-As groundwater typically hold large amounts of labile As (Gao et al. 2013). The release of As from these sediments is regarded as a major cause of elevated As concentrations in groundwater (Anawar et al. 2004; Islam et al. 2004; Nath et al. 2008; Gunduz et al. 2010). Looking at this the other way around, adsorption on aquifer sediments is an important mechanism for restricting migration of As.

Iron/Mn (hydr)oxide minerals in aquifers have a strong affinity to As (Goldberg and Johnston 2001; Mohan and Pittman 2007). It has been shown in numerous studies that Fe (hydr)oxide minerals, such as

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ferrihydrite (Jessen et al. 2005; Fritzsche et al. 2011), granular ferric hydroxide (Banerjee et al. 2008), natural/synthetic siderite (Guo et al. 2007, 2010), goethite (Asta et al. 2009), magnetite (Liang and Zhao 2014), and mixed Fe minerals produced during the transformation of siderite into goethite (Guo et al. 2013), adsorb relatively large amounts of As. Iron/Mn binary oxides have also been found to significantly affect As adsorption because of Mn oxidation (Nesbitt et al. 1998; Manning et al. 2002a; Deschamps et al. 2003; Ying et al. 2012). Previous studies have tended to be focused on removal of As by natural or synthetic Fe/Mn (hydr)oxide minerals since As can undergo ligand exchange with OH^+ or OH^{2+} on the surface of Fe (hydr)oxides to produce stable inner sphere Fe-O-As complexes on the mineral surfaces (Fendorf et al. 1997; Manning et al. 2002b; Guo et al. 2013).

Surface charges of Fe/Mn (hydr)oxide minerals are pH-dependent, that is, the properties and the magnitudes of the surface charges can be changed by changing the pH (Kosmulski 2009). Iron(III) (hydr)oxides are the main As-bearing minerals in aquifer sediments, which are predominantly positively charged at pH 3.0–7.0 and predominantly negatively charged at pH 8.0–10.0 (Guo et al. 2014). Therefore, an increase in pH to >8.2 will drastically decrease the amount of As adsorbed onto Fe (hydr)oxides (Qiao et al. 2012; Mamindy-Pajany et al. 2011) due to the electrostatic repulsion.

Electrostatic selectivity affects adsorption of different As species. Arsenic (V) is predominantly present as oxyanions (H_2AsO_4^- and HAsO_4^{2-}) at neutral pH values (Smedley and Kinniburgh 2002), but As(III) exists as a neutral form (H_3AsO_3). Therefore, As(III) is difficultly captured by aquifer sediments and easily mobilized in groundwater systems due to unionized state (Ravenscroft et al. 2009). Inorganic As species can be converted from one to another, which can be brought about by Fe/Mn minerals (Islam et al. 2004; Campbell et al. 2006; Tufano et al. 2008). In contrast, a number of studies, including X-ray absorption spectroscopy analysis, showed that As(III) could be oxidized into As(V) by Mn oxide minerals (Nesbitt et al. 1998; Manning et al. 2002a; Deschamps et al. 2003; Ying et al. 2012) or in Fe(II)-Fe(III) and Fe(II)- O_2 systems (Hug and Leupin 2003; Robert et al. 2004; Katsoyiannis et al. 2008; Ona-Nguema et al. 2010; Amstaetter et al. 2010; Guo et al. 2013). Although impacts of pH, As species, and Fe/Mn minerals have been evaluated (Huang et al. 2013), adsorption of As onto aquifer sediments would

be promoted or impeded by coupling interactions among pH, As species, and Fe/Mn minerals. However, little is known about detailed impacts of these interactions on As adsorption and fractions.

The release and mobility of As are governed by fractions of As bound onto the solid phase. Sequential extraction technique has been widely used to assess the geochemical partitioning and chemical binding of As in solids (Han et al. 2004; Devesa-Rey et al. 2008; Doušová et al. 2008; Qi and Donahoe 2008; Costagliola et al. 2013; Kim et al. 2014), and to evaluate adsorption fraction and desorption (Zhang and Selim 2005; Osorio-López et al. 2014). This method offers a great promise to distinguish effects of interacting factors and to understand the roles of the interacting factors in chemical binding of adsorbed As.

The aims of the work were to investigate As adsorption onto aquifer sediments, to characterize fractions of adsorbed As, and to assess the controlling factors on As adsorption and fractionation. Effect of pH and As species on As adsorption kinetics and isotherms models were firstly investigated by batch experiments on two homologous sediment samples. Secondly, fractions of adsorbed As, sediment Fe, and Mn minerals were assessed to figure out characteristics of As binding after adsorption. Finally, adsorption isotherm parameters as a function of the increase in the sequentially extracted As fraction relative to pristine sediment were employed to evaluate effect of pH, As species, and contents of extracted-Fe/Mn minerals on adsorption fractions.

2 Materials and Methods

2.1 Sample Collection and Preparation

The Beijing plain is widely covered by Quaternary sediments and composed of several huge alluvial-proluvial fans and depressions. A sediment sample was collected from an aquifer at a depth of 30 m below the land surface (bls) at the Astronomy and Earth Sciences Park of the Chinese Academy of Sciences, Chaoyang District, Beijing, China (40.00° N, 116.38° E). The sampling site was located in the middle of the Yongding River alluvial fan. The groundwater table was approximately 25 m bls.

The sample was dried at room temperature ($20 \pm 5^\circ\text{C}$) and then passed through a 0.613 mm nylon sieve to remove large particles. Part of the sieved sample was

retained and labeled as fine sediment (later referred to as FS) (with the grain size <0.613 mm). The other part of the sieved sample was screened using a 0.0374 mm nylon sieve with the aid of water, and then washed using the shock and ultrasonic method, to remove clay particles and colloids stuck to large particles. The residue in the sieve was dried and labeled as coarse sediment (later referred to as CS) (with the grain size between 0.0374 and 0.613 mm). The sediment samples were stored in sealed plastic flasks at 4°C .

A 0.2-g aliquot of each ground (to give particle sizes of <0.147 mm) sediment sample was digested in a $\text{HNO}_3\text{-HCl-HF}$ mixture in a 50-mL polytetrafluoroethylene crucible. Arsenic concentrations in the extracts were analyzed by atomic fluorescence spectrometry (AFS-9800, KCHG, China). Iron and Mn concentrations were determined by flame atomic absorption spectrometry (ContrAA 700, Analytik Jena, Germany). Calcium and Al concentrations were measured via inductively coupled plasma optical emission spectrometry (Optima 5300DV, Perkin-Elmer, USA). The recovery of determined elements in a stream sediment reference material (GBW07307) was between 90.5 and 108.4% .

Total carbon (TC), organic carbon (TOC), and total sulfur (TS) concentrations were measured by infrared absorption carbon-sulfur spectroscopy (CS-902, WLDY Q, China). Total inorganic carbon (TIC) concentration was defined as the difference between the TC and TOC concentrations (a hydrochloric acid digestion was used to remove the TIC for TOC determination).

The morphological analysis of the sediment samples was achieved using scanning electron microscopy (SEM) using a Zeiss SUPRA 55 microscope (at 3 kV) and energy dispersive spectroscopy (EDS) (SUPRA 55 SAPHIRE, Zeiss, Germany, model). The particle size distribution and the average particle size were determined using a laser granularity analyzer (Mastersizer 2000, Malvern Instruments, UK), with water as the dispersing agent and a $5\pm0.5\%$ laser shading angle. The pH and ORP of the sediment samples were monitored by a pH/ORP meter (S400 SevenExcellence, METTLER TOLEDO, China) in a suspension of the sediment (at a solid-to-liquid ratio of $1:5$).

2.2 Batch Experiments

A stock 500 mg L^{-1} As(III) solution and a stock 500 mg L^{-1} As(V) solution were prepared from NaAsO_2 (Sigma-Aldrich, USA) and $\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$

(Sigma-Aldrich, USA), respectively, in deionized water. Effect of solution pH on As adsorption was studied by performing batch experiments at initial pH values of 5 , 7 , and 9 . The pH was adjusted using 0.1 M HCl and 0.1 M NaOH . All of the experiments were conducted in 50-mL polypropylene shaking flasks. A 25-mL aliquot of the appropriate As solution was added to 0.2 g (accurately weighed) of the sediment sample and the flasks were placed in a shaking incubator that was held at 25°C and shaken at 180 rpm for a specified period. The mixture was then centrifuged at $2000\times g$ -force for 10 min , filtered through a $0.22\text{ }\mu\text{m}$ membrane filter, acidified with 1 M HNO_3 to $\text{pH}<2.0$, and analyzed within 24 h .

The kinetic rate of As adsorption on each sediment sample was investigated using adsorption kinetics experiments with different reaction times. A 5 mg L^{-1} solution of As(III) or As(V) was allowed to react with a sediment sample for a period of time ranging between 0.5 and 24 h . The reaction period required for isothermal adsorption experiments was determined from the kinetics experiments. The isothermal adsorption experiments were performed using initial As(III) or As(V) concentrations ranging from 0.2 to 10 mg L^{-1} , with contact time of 8 h .

2.3 Sequential Extraction of Adsorbed As

A sequential extraction procedure was employed to investigate the amounts of As retained in different phases in the sediment samples which were subject to the isothermal adsorption experiments. The As-loaded sediment samples from the isothermal adsorption experiments with initial As(III) and As(V) concentrations of 1 mg L^{-1} were used. Since some dissolved As in sediment solution remained within the wet sediment samples, both the dissolved and water-soluble As were removed by shaking the sample at 180 rpm with 25 mL deionized water for 5 min three times. After that, the samples were freeze-dried for subsequent experiments to avoid redistribution among As fractions and speciation (Huang et al. 2015).

Five-step sequential extraction was carried out according to the method described by Wenzel et al. (2001). The extractants used and the adsorbed As extracted in each step are described below. Step (i) was the extraction of non-specifically sorbed As (As_{F1}) using $0.05\text{ M }(\text{NH}_4)_2\text{SO}_4$; step (ii) was the extraction of specifically sorbed As (As_{F2}) using $0.05\text{ M NH}_4\text{H}_2\text{PO}_4$; step (iii) was the extraction of As associated with amorphous and

poorly crystalline (hydr)oxides (later referred to As associated with amorphous (hydr)oxides) (As_{F3}) using a 0.2 M NH_4 -oxalate buffer in the dark; step (iv) was the extraction of As associated with well-crystallized (hydr)oxides (later referred to As associated with crystalline (hydr)oxides) (As_{F4}) using 0.2 M NH_4 -oxalate and 0.1 M ascorbic acid; and step (v) was the extraction of residual As (As_{F5}) by digesting the residue with HNO_3 and H_2O_2 . The water-soluble As (As_{F0}) was calculated using the equation:

$$[As_{F0}] = Q_e - [As_{F1}] - [As_{F2}] - [As_{F3}] - [As_{F4}] - [As_{F5}],$$

Where $[As_{Fi}]$ is As concentration in the fraction extracted in step i and Q_e is the amount of adsorbed As at equilibrium.

2.4 Speciation of Adsorbed As

The different As species were extracted from the sediment samples following the method described by Giral et al. (2010). The samples were the same as used in the sequential As extraction experiments. A 10-mL aliquot of the extraction solution (1 M phosphoric acid and 0.5 M ascorbic acid, with or without a standard As species solution) was added to 0.2 g (accurately weighed) of a sample in a closed microwave tube (MARS6, CEM, USA). The mixture was then maintained at 80 W during 10 min in the microwave system (MARS6). The sample was cooled to room temperature, diluted by a factor of 20 with 30 mM phosphate buffer, filtered through a 0.22 μm membrane filter, and then analyzed for the As species.

The As species were determined by high-performance liquid chromatography hydride generation atomic fluorescence spectrophotometry (PSA-10.825, PS Analytical, UK). The As species were separated using anion exchange chromatography, a PRP-X100 column (Hamilton, USA) and a guard cartridge system (SAX, USA), with a 30 mM phosphate buffer (at pH 6.0) as mobile phase at a flow rate of 1.0 mL min^{-1} . The recoveries of standard additions of As(III) and As(V) were 90.2 and 93.8 %, respectively.

2.5 Sequential Extraction of Fe Minerals

The sequential extraction of Fe minerals was achieved using a method described by Poulton and Canfield (2005). Each sample was treated to separate seven

fractions as described below. Step (i) was the extraction of the exchangeable Fe (Fe(II)) using 1.0 M $MgCl_2$; step (ii) was the extraction of Fe associated with carbonate (Fe_{carb}), including siderite and ankerite, using 1.0 M NaOAc; step (iii) was the extraction of easily reducible Fe (Fe_{ox1}), including ferrihydrite and lepidocrocite, using a 1.0 M hydroxylamine-HCl solution in 25 %v/v acetic acid; step (iv) was the extraction of reducible Fe (Fe_{ox2}), including goethite, hematite, and akaganeite, using a 50 g L^{-1} sodium dithionite solution buffered to pH 4.8 with 0.35 M acetic acid and 0.2 M sodium citrate; step (v) was the extraction of magnetite (Fe_{mag}) using a 0.2 M ammonium oxalate and 0.17 M oxalic acid solution; step (vi) was the extraction of poorly reactive sheet silicate Fe (Fe_{PRS}) by digesting the residue in HCl; and step (vii) was the extraction of the residual Fe (Fe_r) by digesting the residue in a HNO_3 -HCl-HF mixture.

Sequential extraction As, sequential extraction Fe minerals, and extracted As species were performed in duplicate, with the relative standard deviations of the duplicated samples less than 6.8 %. The other experiments were performed at least in triplicate.

3 Results and Discussion

3.1 Sediments Characteristics

Physical and chemical characteristics of FS and CS are shown in Table 1. The average particle size of CS was 70.0 μm , which is greater than the average particle size of 17.6 μm in FS due to the screening and washing. Since clay minerals, such as gibbsite, kaolinite, and montmorillonites, typically contain Al (Teppen et al. 1998), the lower Al content in CS (by around 50 %) than in FS would indicate removal of clay minerals and their colloids during screening and washing. Relative to FS, decreases in concentrations of Fe, Mn, and As in CS were 26.6, 17.1, and 21.9 %, respectively. It showed that As may be associated with Fe/Mn oxide minerals (Goldberg and Johnstonm 2001; Mohan and Pittman 2007; Guo et al. 2014) rather than Al (Kim et al. 2014) in the sediment used in this study. The decreases in TIC and Ca were 0.53 and 0.60 mol kg^{-1} , respectively, which indicated that $CaCO_3$ was partly present in fine particles (<0.0374 mm). TOC concentrations in FS and CS were both low when compared to the wide range

Table 1 Characteristics of the sediments used in the adsorption experiments

Item	FS	CS
As ($\mu\text{g g}^{-1}$)	7.35 $\pm$ 0.13	5.74 $\pm$ 0.28
Fe ($\mu\text{g g}^{-1}$)	13,675 $\pm$ 560	11,340 $\pm$ 258
Mn ($\mu\text{g g}^{-1}$)	402 $\pm$ 13	295 $\pm$ 7.2
Al ($\mu\text{g g}^{-1}$)	13,235 $\pm$ 1678	6512 $\pm$ 389
Ca ($\mu\text{g g}^{-1}$)	51,369 $\pm$ 1076	27,184 $\pm$ 447
TC (%)	1.69 $\pm$ 0.08	0.99 $\pm$ 0.03
TOC (%)	0.12 $\pm$ 0.00	0.06 $\pm$ 0.00
TIC (%)	1.57 $\pm$ 0.08	0.93 $\pm$ 0.03
TS (‰)	0.32 $\pm$ 0.02	0.30 $\pm$ 0.02
pH	8.33 $\pm$ 0.05	8.69 $\pm$ 0.03
ORP (mV)	126.2 $\pm$ 5.78	128.1 $\pm$ 6.21
Average particle size (μm)	17.6 $\pm$ 0.8	70.0 $\pm$ 2.7

found in natural sediments. TS concentrations, pH values, and ORPs were kept relatively constant.

The SEM images, EDS patterns, and laser granularity plots (showing the microscopic morphologies, surface compositions, and particle size distributions, respectively) of sediment samples are shown in Fig. 1. FS had coarsely surfaced and heterogeneously sized particles (Fig. 1a), while CS had smoothly surfaced and uniformly sized particles (Fig. 1b). The EDS analyses showed that FS contained more Fe, Al, Mg, and C than CS, while CS contained more Si and O than FS (Fig. 1c). It indicated that organic and Al-containing colloidal particles being present in FS had been removed from CS, and silicate materials were retained. These results were consistent with the results described above. In summary, a large amount of organic matter and CaCO_3 and approximately 20 % of the Fe, Mn, and As in the clay particles and colloids with sizes of 1–20 μm had been removed from CS relative to FS (Fig. 1d). In contrast, pH and ORP were the same in FS and CS because of the homology of the sediments.

3.2 Characteristics of Fe and Mn Minerals in the Sediments

Extraction procedures provide insight into the dominant phases of Fe/Mn minerals in solids (Giral et al. 2010). According to the results, exposing the sediment samples to As(III) and As(V) solutions at different pH values for a short reaction time did not transform Fe and Mn fractions in the sediments significantly. Average Fe

and Mn concentrations in Fe sequential extraction fractions are shown in Table 2.

In the step (i) of sequential Fe extraction, concentrations of Fe(II) in FS and CS had similar low values. Although this fraction was active, low contents led to a limited effect on As adsorption. Concentrations of Fe_{carb} , Fe_{mag} , and Fe_{PRS} in FS (214, 693, and 1936 $\mu\text{g/g}$) were similar to those in CS (186, 655, and 2182 $\mu\text{g/g}$), respectively (Table 2). Concentrations of Fe_{ox1} and Fe_{ox2} were quite different between two sediments, with around 40 % higher in FS than CS. The (easily) reducible Fe (including ferrihydrite, lepidocrocite, goethite, hematite, and akaganeite) would be the major cause for the difference in As adsorption in two sediments. Although concentration of Fe_r was high, this Fe fraction would have been fixed in the mineral lattice and relatively inactive.

Active Mn fractions (except Mn- Fe_r) were two to three times higher in FS than in CS (Table 2). Since MgCl_2 and NaOAc extractants were similar to reagents used in the first two Tessier sequential extraction procedure fractions (Tessier et al. 1979), the Mn in the Fe(II) and Fe_{carb} (Mn-Fe(II) and Mn- Fe_{carb}) fractions could be defined as the exchangeable Mn and Mn carbonates, respectively. The Mn carbonates accounted for around 70 % of active Mn, which was in line with sediments from the Baltic Sea studied with an EXAFS, XANES, and LA-ICP-MS (Lenz et al. 2014). Most of the active Mn was extracted in the first three extraction steps, indicating that Mn was quite active in both FS and CS. However, the Mn could not play a crucial role in As adsorption because active Fe was much more than active Mn.

As mentioned above, the two samples had similar pH and ORP, but different Fe/Mn minerals. Therefore, the effect of Fe/Mn minerals on As adsorption could be investigated by using these two samples.

3.3 Adsorption Kinetics

The adsorption kinetics for FS and CS with different initial pH values and As species are shown in Fig. 2. The results showed that rapid adsorption occurred at the beginning, with the adsorption maximum being reached within 8 h, which is similar to adsorbents mainly composed of silicate or carbonate, including dolomitic sorbents (Salameh et al. 2010), modified montmorillonite (Ramesh et al. 2007), and Fe oxide-coated sand (Gupta et al. 2005). The adsorption equilibrium time was confirmed as 8 h. In addition to the equilibrium time, three conclusions were obtained briefly as follows: (1) a low

Fig. 1 SEM images of the sediment samples (a) and (b), EDS spectra for particle surfaces (c) and particle size distributions (d)

pH value was conducive to As adsorption onto sediments, (2) As(V) was more readily adsorbed than As(III) on the sediment samples, and (3) FS had a stronger ability than CS to adsorb As because it had more adsorption sites.

The experimental data were fitted to pseudo-first-order (Ho 2004) and pseudo-second-order (Ho and McKay 1999) models using a nonlinear regression method, to evaluate the kinetic mechanisms. The models can be written as Eqs. (1) and (2), respectively. These are

well fitted, as shown in Fig. 2, and the kinetic parameters are listed in Table 4.

$$q_t = q_e (1 - e^{-k_1 t}) \quad (1)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (2)$$

Where K_1 (h^{-1}) and K_2 ($\text{g}(\mu\text{g h})^{-1}$) are the rate constants for the pseudo-first-order and pseudo-second-order models, respectively; q_e is the amount of

Table 2 The Fe and Mn concentrations in the fractions extracted from the sediment samples in the sequential Fe extraction

		Fe(II)	Fe _{carb}	Fe _{ox1}	Fe _{ox2}	Fe _{mag}	Fe _{PRS}	Fe _r
Fe($\mu\text{g g}^{-1}$)	FS	0.09±0.03	214±20	1070±44	1492±100	693±38	1936±179	9052±992
	CS	0.00±0.00	186±19	660±25	964±53	655±42	2182±163	7351±711
Mn($\mu\text{g g}^{-1}$)	FS	21±0.80	142±2.8	20±1.1	8.9±0.67	5.0±0.18	7.1±0.36	214±27
	CS	5.0±0.25	70±1.5	12.6±0.23	6.4±0.08	2.0±0.25	0.51±0.04	224±21

Fig. 2 Effect of contact time on the As adsorption from As(III) solution (a) and As(V) solution (b) by sediments (dosage=8 g L⁻¹; initial As concentration=5.0 mg L⁻¹; initial pH of 5, 7, or 9; at 25 °C)

adsorbed ($\mu\text{g g}^{-1}$) at equilibrium; q_t is the amount of the adsorption ($\mu\text{g g}^{-1}$) at any time t (h).

The pseudo-second-order model was better applied to the whole adsorption process (Chang and Juang 2004), including (1) diffusion across the liquid film surrounding the solid particles, (2) intra-particle diffusion, and (3) physical or chemical adsorption at a site (Kumar et al. 2005). The pseudo-first-order model was suitable for describing the initial adsorption stage (Ho and McKay 1999). The equilibrium adsorption capacity ($q_e(\text{exp})$) for the experiment closer matched $q_e(\text{cal})$ the pseudo-first-order model, in comparison with the pseudo-second-order model (Table 3). This

showed that As adsorption appeared to be controlled by the initial step in the adsorption process, which would probably be diffusion through the external film, exhibiting constraint on adsorption. The correlation coefficient (R^2) for the pseudo-second-order model was a little higher for FS than for CS. It seemed that the complicated and tight adsorption may play a more prominent role in FS than CS.

3.4 Adsorption Isotherms

Langmuir and Freundlich isotherm models were used to provide more quantitative information for describing the

Table 3 Correlation coefficients and kinetic parameters for the pseudo-first-order and pseudo-second-order models and equilibrium adsorption capacity found in the experiments (dosage=8 g L⁻¹; initial As concentration=5.0 mg L⁻¹; initial pH of 5, 7, or 9; at 25 °C)

As		Pseudo-first-order model			Pseudo-second-order model			$q_e(\text{exp}) \mu\text{g g}^{-1}$
		R^2	$K_1 \text{ h}^{-1}$	$q_e(\text{cal}) \mu\text{g g}^{-1}$	R^2	$K_2 \text{ g}(\mu\text{g h})^{-1}$	$q_e(\text{cal}) \mu\text{g g}^{-1}$	
As(III)	FS pH=5	0.964	0.73	27.2	0.969	0.035	29.3	28.4
	FS pH=7	0.934	0.92	21.3	0.974	0.060	22.8	21.8
	FS pH=9	0.959	0.88	17.7	0.971	0.070	18.9	18.0
	CS pH=5	0.963	0.86	17.2	0.960	0.072	18.3	17.3
	CS pH=7	0.974	0.77	15.4	0.982	0.067	16.6	15.6
	CS pH=9	0.981	0.75	13.6	0.969	0.074	14.7	13.7
As(V)	FS pH=5	0.973	0.63	47.9	0.980	0.017	52.1	48.5
	FS pH=7	0.975	0.58	41.9	0.984	0.017	45.9	42.3
	FS pH=9	0.977	0.68	34.0	0.982	0.024	37.2	34.4
	CS pH=5	0.991	0.40	23.3	0.967	0.018	26.4	23.0
	CS pH=7	0.992	0.52	16.4	0.971	0.037	18.2	16.3
	CS pH=9	0.979	0.47	13.0	0.960	0.042	14.4	12.9

effect of As concentration on the surface loadings of As(III) and As(V) on the sediment samples. The Langmuir model assumes that monolayer adsorption occurs on a homogeneous adsorbent surface with a finite number of identical sites, and the Freundlich model is empirical in nature and allows multilayer adsorption. The nonlinear forms of the Langmuir and Freundlich models are given as Eqs. (3) and (4), respectively.

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (3)$$

$$Q_e = K_F C_e^n \quad (4)$$

Where C_e is the residual As concentration in the solution ($\mu\text{g ml}^{-1}$), Q_e is the As equilibrium adsorption concentration in the solid adsorbent ($\mu\text{g g}^{-1}$), Q_m is the monolayer maximum adsorption capacity ($\mu\text{g g}^{-1}$), b is a constant related to the energy of adsorption in the Langmuir model ($\text{ml } \mu\text{g}^{-1}$), K_F is a constant related to the adsorption capacity ($(\mu\text{g g}^{-1})(\text{ml } \mu\text{g}^{-1})^n$), n is a constant related to the energy of adsorption in the Freundlich model. Values of $1 < n < 10$ show favorable adsorption of As onto adsorbents (Namasivayam and Senthilkumar 1998).

Plots of the Langmuir and Freundlich isotherms are shown in Fig. 3, and the parameters that were obtained from those isotherms are shown in Table 4. The correlation coefficients were higher for the Langmuir model ($R^2=0.952\text{--}0.999$) than for the Freundlich model ($R^2=0.851\text{--}0.980$). Therefore, Langmuir isotherm yielded better fit to the experimental data, denoting unconsolidated monolayer adsorption of As onto sediments. The Q_m , b , and K_F parameters generally matched the conclusions that were drawn in the previous section. The n

value was in the range 1.6–2.3, which was evidence for the adsorption process being favorable.

3.5 Fractions of Adsorbed Arsenic

Five sequential As extraction steps were performed on sediment samples loaded with As immediately after the adsorption isotherm experiments, to determine the fractions of the adsorbed As. The total amounts of As extracted in this experiment are shown in Fig. 4. Most of the As in the pristine sediment was As associated with amorphous (hydr)oxides (25.3–26.7 %), As associated with crystalline (hydr)oxides (29.3–29.5 %), and residual As (36.6–39.7 %). A small percentage of the As was adsorbed non-specifically or specifically onto the surface of the sediments. The proportions of the As found in each fraction agreed with the results of previous studies on soils (Wenzel et al. 2001; Kim et al. 2014) and sediments (Javed et al. 2013; Keon et al. 2001).

After As adsorption, water-soluble As, which is the most labile fraction, formed a relatively high proportion (43.7–66.7 %) of the total As content. This As fraction diffused to the surface of the sediment, and became the most unstable adsorption mode. Some of the As on the surface of the sediment would also have been held in a diffuse electric double layer surface by Coulombic interactions and become specifically adsorbed. The relatively weak forms of adsorption, including water-soluble As and non-specifically sorbed As, accounted for 59.3–79.1 % of the total amount of adsorbed As, which matches adsorption kinetics.

Ligand exchange of As(III) and As(V) with OH^+ or OH^{2+} (through Lewis acid-base interactions) can occur

Fig. 3 Adsorption of As(III) (a) and As(V) (b) onto sediments (dosage=8 g L⁻¹, initial As concentration 0.2–10 mg L⁻¹, contact time=8 h, pH of 5, 7, or 9, at 25 °C)

Table 4 Correlation coefficients and isotherm parameters for the Langmuir isotherm and Freundlich isotherm models (dosage=8 g L⁻¹, initial As concentration 0.2–10 mg L⁻¹, contact time=8 h, pH of 5, 7, or 9, at 25 °C)

As		Langmuir isotherm			Freundlich isotherm		
		R^2	Q_m ($\mu\text{g g}^{-1}$)	b ($\text{ml } \mu\text{g}^{-1}$)	R^2	K_F ($\mu\text{g g}^{-1}$) ($\text{ml } \mu\text{g}^{-1}$) ⁿ	n
As(III)	FS pH=5	0.962	41.5	0.49	0.880	12.6	2.1
	FS pH=7	0.990	37.8	0.33	0.947	9.2	1.9
	FS pH=9	0.975	29.6	0.33	0.901	7.1	1.9
	CS pH=5	0.969	26.0	0.39	0.890	7.0	2.0
	CS pH=7	0.967	24.5	0.30	0.895	5.6	1.8
	CS pH=9	0.974	24.0	0.30	0.904	5.4	1.8
As(V)	FS pH=5	0.992	68.3	0.61	0.940	24.0	2.3
	FS pH=7	0.974	60.2	0.46	0.888	17.7	2.1
	FS pH=9	0.961	46.4	0.51	0.864	14.7	2.2
	CS pH=5	0.952	32.4	0.54	0.851	10.6	2.2
	CS pH=7	0.997	29.1	0.27	0.962	6.3	1.8
	CS pH=9	0.999	30.1	0.18	0.980	4.7	1.6

on the surfaces of Fe oxides, which would allow monodentate mononuclear and bidentate binuclear corner-sharing complexes to be formed (Fendorf et al. 1997; Manning et al. 2002b; Guo et al. 2013) in the inner part of the electric double layer. Part of these corner-sharing complexes, which can be readily replaced by phosphate, was defined as specifically sorbed As. The concentration of the specifically sorbed As increased from 1.00 to 2.96 $\mu\text{g g}^{-1}$ after the adsorption process. This increase was higher than the increase in the non-specifically sorbed As (0.65–1.20 $\mu\text{g g}^{-1}$), showing that the As readily formed Lewis acid-base interactions with functional groups rather than forming Coulombic interactions.

Sediments with silicate as the principal component have poor adsorption capacity because they have less Fe/Mn minerals adsorption sites than natural (artificial) Fe/Mn minerals. Therefore, concentration of As associated with amorphous (hydr)oxides increased only a little (0.08–0.60 $\mu\text{g g}^{-1}$) during the adsorption process. The ratio between the amount of chemically adsorbed As and the total adsorbed As ranged from 20.8 to 40.3 %. The stable As fractions (As associated with crystalline (hydr)oxides and residual As) did not change. The As had more Lewis acid-base interactions with FS than with CS, showing that Fe/Mn minerals play the important role in the chemically adsorbed As.

Fig. 4 Arsenic concentrations in sequentially extracted fractions from the sediment samples before and after the samples had been used in the adsorption isotherm experiments (dosage=8 g L⁻¹, initial As(III) or As(V) concentration=1 mg L⁻¹, contact time=8 h, pH of 5, 7, or 9, at 25 °C). PFS and PCS stand for pristine fine sediment and coarse sediment, respectively

3.6 Arsenic Species

Coexistence and transformation of As species on sediments complicate the adsorption process. Therefore, As species were extracted from As-loaded sediments to determine the transformation between species that may have occurred during the adsorption process. Concentrations of As species in the pristine and the As-loaded sediment samples are shown in Fig. 5. The initial As(III)/As(V) ratios for the two sediment samples were different, being 1:4 for FS and 1:3 for CS, indicating that the As(V) had a stronger affinity than the As(III) for the fine particles.

After As adsorption, the ratios changed to a similar extent. For FS, the proportion of As(III) that was oxidized to As(V) (13.3–28.5 %) was a little higher than the proportion of As(V) that was reduced to As(III) (7.9–12.7 %), which suggested that FS would cause both oxidation and weakly reduction. However, As(III) was stably preserved on CS. The As(III)-treated CS did not contain a detectable increase in concentrations of As(V). Nevertheless, 32.8–49.4 % of the As(V) was reduced in the As(V)-adsorbing CS. Therefore, it is believed that CS had a strong ability to reduce As(V).

Under reducing conditions with the reduction of As(V) predominated, adsorbed As(V) is expected to be reduced to As(III) (Mukherjee et al. 2012). This reduction appeared to decrease the quantity of the As(V) adsorption, because As(III) has a lower affinity for mineral surfaces than As(V) (Manning et al. 1998; Guo et al. 2007). In contrast, the As(III) oxidation that

occurred on FS could have increased the As(III) adsorption. This was probably because FS contained more Mn oxides than CS, as mentioned above, which can promote As(III) oxidation (Nesbitt et al. 1998; Manning et al. 2002a; Deschamps et al. 2003; Ying et al. 2012). The other investigation showed that carbonate and silicate minerals hardly oxidized As(III) (Oscarson et al. 1981). However, the Fe(II) in FS appeared to play a role in the oxidation of As(III), because Fe(II)-Fe(III) and Fe(II)-O₂ systems rapidly oxidize As(III) to As(V) (Hug and Leupin 2003; Robert et al. 2004; Katsoyiannis et al. 2008; Amstaetter et al. 2010; Ona-Nguema et al. 2010; Guo et al. 2013). In this study, water-soluble As was not analyzed because of the difficulty in distinguishing it from dissolved As. However, it is likely that the water-soluble As would have contained more As(III) than As(V) due to the weak affinity between the As(III) and the sediments.

3.7 Factors Influencing Arsenic Fractions

It has been reported that the Langmuir maximum (Q_e) is linearly related to the amount of ammonium oxalate-extractable Fe (Livesey and Huang 1981) and citrate-bicarbonate-dithionite (CBD)-extractable Fe (Zhang and Selim 2005) in sediments. Similarly, some researchers have found that the Freundlich K_F for As adsorption on soils correlates significantly with the amounts of CBD-extractable Fe (Zhang and Selim 2005), total Fe, and ammonium oxalate-extractable Fe (Osorio-López et al. 2014). Although those studies suggested that As adsorption was closely correlated with Fe content of sediment samples, effects of variables such as

Fig. 5 Arsenic species, extracted with 1 M H₃PO₄ and 0.5 M C₆H₈O₆, in the sediment samples before and after the adsorption isotherm experiments (dosage=8 g L⁻¹, initial As(III) or As(V) concentration=1 mg L⁻¹, contact time=8 h, pH of 5, 7, or 9, at 25 °C). PFS and PCS stand for pristine fine sediment and coarse sediment, respectively

Fig. 6 Freundlich K_F as a function of the increase in the sequentially extracted As fraction relative to pristine sediment (ΔQ s), including water-soluble As (a), non-specifically sorbed As (b), specifically sorbed As (c), and As associated with amorphous (hydr)oxides (d)

pH and As species were ignored on As adsorption fractions.

Because different fractions of adsorbed As were located in different adsorption layers as discussed above. The Freundlich model, a multilayer adsorption model, is more suitable for assessing effects of factors on As

adsorption fractions. Moreover, based on the fact that As adsorption is a pH-dependent process (Maji et al. 2007; Partey et al. 2008; Stanic et al. 2009), the effect of pH was represented by the Freundlich K_F in this study, because this parameter was clearly different at different pH values. The Freundlich K_F as a function of the

Table 5 Correlation coefficients, slope and intercept for relationships between the Freundlich K_F and the increase in the sequentially extracted As fraction relative to pristine sediment (ΔQ s)

As fraction	FS			CS		
	R^2	Slope	Intercept	R^2	Slope	Intercept
As _{F0}	0.941	0.485	−0.885	0.917	0.531	−0.605
As _{F1}	0.875	0.083	0.185	0.344	0.115	0.224
As _{F2}	0.630	0.057	1.765	0.885	0.104	0.571
As _{F3}	0.788	0.008	0.412	0.275	0.019	0.077

increase in the sequentially extracted As fraction relative to pristine sediment ($\Delta Q\text{-As}_{Fi}$, $i=0, 1, 2$, or 3) was found to be a more direct and explicit way in evaluating effect of pH on the adsorption fractions. Meanwhile, effect of As species and Fe/Mn minerals can be evaluated. A plot of $\Delta Q\text{-As}_{Fi}$ against the Freundlich K_F parameter is shown in Fig. 6 for each sediment. The slope, intercept, and correlation coefficient (R^2) are given in Table 5.

Decreases in correlation coefficient (R^2) and slope indicated that the influence of the pH decreased as the adsorption intensity increased from water-soluble form to amorphous (hydr)oxides associated form. The water-soluble As fraction (As_{F0}) showed a good correlation with the Freundlich K_F (R^2 close to 0.9) for both sediment samples (Fig. 6a), indicating that the pH played a key role in the weak adsorption. Similar slopes were found for FS and CS in the plot of As_{F0} versus K_F , which indicated that the influence of pH was not measurably different for the two sediment samples. These results suggested that an increase in the environment pH should release water-soluble As from solid surfaces.

More As(V) than As(III) was non-specifically adsorbed under all of the test conditions (Fig. 6b), although the As redox reactions on the sediment may decrease the difference. This phenomenon was interpreted by the fact that specifically sorbed As was controlled by the diffuse electric double layer and relied on electrostatic attraction. The R^2 between As_{F1} and K_F for FS was 0.875, showing that the pH affected the non-specific adsorption. However, weak correlation ($R^2=0.346$) between As_{F1} and K_F for CS indicated that effect of the pH was hidden by effect of the As species. These findings showed that the reduction of As(V) would activate the specifically sorbed As.

Good linear relationships (R^2 0.630 for FS and R^2 0.885 for CS) between As_{F2} and K_F were observed for both sediment samples, indicating that the pH did have an effect on the specifically sorbed As (Fig. 6c). The differences in the slopes for the two sediment samples indicated that the pH affected the sediment samples somewhat differently. Furthermore, more As was clearly specifically adsorbed onto FS than onto CS under all of the test conditions. This showed that the characteristics of the sediments (such as Fe/Mn minerals) were the main factors affecting the specific adsorption.

In comparison with the specific adsorption, the influence of sediment Fe/Mn minerals was more significant on amorphous (hydr)oxides associated As. Increases in

this As fraction in FS and CS were 0.46–0.60 and 0.08–0.26 $\mu\text{g g}^{-1}$, respectively (Fig. 6d). Low slopes were found (0.008 for FS and 0.019 for CS), which indicated that the pH had little influence on this adsorption fraction. As mentioned above, As would undergo ligand exchange with OH^+ or OH^{2+} on the surfaces of sediments, and be restricted to the inner electric double layer. The Fe/Mn minerals, which provide numerous ligands in the sediment samples, directly determine the fraction of chemically adsorbed As. The release of chemically adsorbed As depended on chemical transformation of Fe/Mn minerals, such as the reductive dissolution of Fe(III) (hydr)oxides.

4 Conclusions

Arsenic adsorption increased as the pH decreased. Arsenic was readily adsorbed by sediment rich in amorphous Fe, although As(V) was more easily adsorbed than As(III). The experimental data fitted the pseudo-second-order kinetics model and the Langmuir isotherm model well, indicating that As adsorption was controlled by diffusion through the film covering sediment particles and involved a monolayer adsorption process. Sequential extraction experiments showed that soluble As and non-specifically sorbed As were the predominant As fractions in As-adsorbed sediments. Correlation between the Freundlich K_F and the increases in the amounts of As fractions in the sediment samples indicated that the pH played a key role in the weak adsorption, especially the water-soluble As fraction. More As(V) was non-specifically adsorbed than As(III), showing that electrostatic selectivity determined the non-specific adsorption process. The presence of Fe/Mn minerals controlled fractions of chemically adsorbed As, including specifically sorbed As and As associated with amorphous Fe/Mn minerals. Therefore, As occurs as various forms on aquifer sediments, which is influenced by geochemical conditions such as pH, redox, and mineralogy. This study suggested that accurately evaluating As fractions in the solid phase and clearly defining effect of geochemical conditions are important in risk assessments of aquifer As and remediation of As-contaminated groundwater.

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References

- Amstaetter, K., Borch, T., Karesse-casanova, P., & Kappler, A. (2010). Redox transformation of arsenic by Fe(II)-activated goethite (α -FeOOH). *Environmental Science & Technology*, 44(1), 102–108.
- Anawar, H. M., Akai, J., & Sakugawa, H. (2004). Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in groundwater. *Chemosphere*, 54(6), 753–762.
- Asta, M. P., Cama, J., Martínez, M., & Giménez, J. (2009). Arsenic removal by goethite and jarosite in acidic conditions and its environmental implications. *Journal of Hazardous Materials*, 171(1–3), 965–972.
- Banerjee, K., Amy, G. L., Prevost, M., Nour, S., Jekel, M., Gallagher, P. M., & Blumenschein, C. D. (2008). Kinetic and thermodynamic aspects of adsorption of arsenic onto granular ferric hydroxide (GFH). *Water Research*, 42(13), 3371–3378.
- Campbell, K. M., Malasarn, D., Saltikov, C. W., Newman, D. K., & Hering, J. G. (2006). Simultaneous microbial reduction of iron (III) and arsenic (V) in suspensions of hydrous ferric oxide. *Environmental Science & Technology*, 40(19), 5950–5955.
- Chang, M. Y., & Juang, R. S. (2004). Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay. *Journal of Colloid and Interface Science*, 278(1), 18–25.
- Costagliola, P., Bardelli, F., Benvenuti, M., Benedetto, F. D., Lattanzi, P., Romanelli, M., Paolieri, M., Rimondi, V., & Vaggelli, G. (2013). Arsenic-bearing calcite in natural travertines: evidence from sequential extraction, μ XAS, and μ XRF. *Environmental Science & Technology*, 47(12), 6231–6238.
- Deschamps, E., Ciminelli, V. S. T., Weidler, P. G., & Ramos, A. Y. (2003). Arsenic sorption onto soils enriched in Mn and Fe minerals. *Clays and Clay Minerals*, 51(2), 197–204.
- Devesa-Rey, R., Paradelo, R., Díaz-Fierros, F., & Barral, M. T. (2008). Fractionation and bioavailability of arsenic in the bed sediments of the Anllóns River (NW Spain). *Water, Air, & Soil Pollution*, 195(1), 189–198.
- Doušová, B., Martaus, A., Filippi, M., & Koloušek, D. (2008). Stability of arsenic species in soils contaminated naturally and in an anthropogenic manner. *Water, Air, & Soil Pollution*, 187(1–4), 233–241.
- Fendorf, S., Eick, M. J., Grossl, P., & Sparks, D. L. (1997). Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. *Environmental Science & Technology*, 31(2), 315–320.
- Fendorf, S., Michael, H. A., & van Geen, A. (2010). Spatial and temporal variations of groundwater arsenic in South and Southeast Asia. *Science*, 328(5982), 1123–1127.
- Fritzsche, A., Rennert, T., & Totsche, K. U. (2011). Arsenic strongly associates with ferrihydrite colloids formed in a soil effluent. *Environmental Pollution*, 159(5), 1398–1405.
- Gao, X. B., Su, C. L., Wang, Y. X., & Hu, Q. H. (2013). Mobility of arsenic in aquifer sediments at Datong Basin, northern China: effect of bicarbonate and phosphate. *Journal of Geochemical Exploration*, 135(5), 93–103.
- Giral, M., Zagury, G. J., Deschênes, L., & Blouin, J. (2010). Comparison of four extraction procedures to assess arsenate and arsenite species in contaminated soils. *Environmental Pollution*, 158(5), 1890–1898.
- Goldberg, S., & Johnston, C. T. (2001). Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modelling. *Journal of Colloid and Interface Science*, 234(1), 204–216.
- Gunduz, O., Simsek, C., & Hasozbek, A. (2010). Arsenic pollution in the groundwater of Simav Plain, Turkey: its impact on water quality and human health. *Water, Air, & Soil Pollution*, 205(1), 43–62.
- Guo, H. M., Stüben, D., & Berner, Z. (2007). Adsorption of arsenic(III) and arsenic(V) from groundwater using natural siderite as the adsorbent. *Journal of Colloid and Interface Science*, 315(1), 47–53.
- Guo, H. M., Li, Y., & Zhao, K. (2010). Arsenate removal from aqueous solution using synthetic siderite. *Journal of Hazardous Materials*, 176(1), 174–180.
- Guo, H. M., Ren, Y., Liu, Q., Zhao, K., & Li, Y. (2013). Enhancement of arsenic adsorption during mineral transformation from siderite to goethite: mechanism and application. *Environmental Science & Technology*, 47(2), 1009–1016.
- Guo, H. M., Wen, D. G., Liu, Z. Y., Jia, Y. F., & Guo, Q. (2014). A review of high arsenic groundwater in Mainland and Taiwan, China: Distribution, characteristics and geochemical processes. *Applied Geochemistry*, 41, 196–217.
- Gupta, V. K., Saini, V. K., & Jain, N. (2005). Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. *Journal of Colloid and Interface Science*, 288(1), 55–60.
- Han, F. X., Kingery, W. L., Selim, H. M., Gerard, P. D., Cox, M. S., & Oldham, J. L. (2004). Arsenic solubility and distribution in poultrywaste and long-term amended soil. *Science of the Total Environment*, 320(1), 51–61.
- Ho, Y. S. (2004). Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics*, 59(1), 171–177.
- Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, 34(5), 451–465.
- Huang, G. X., Chen, Z. Y., Wang, J. C., Sun, J. C., Liu, J. T., & Zhang, Y. (2013). Adsorption of arsenite onto a soil irrigated by sewage. *Journal of Geochemical Exploration*, 132, 164–172.
- Huang, G. X., Chen, Z. Y., Sun, J. C., Liu, F., Wang, J., & Zhang, Y. (2015). Effect of sample pretreatment on the fractionation of arsenic in anoxic soils. *Environmental Science and Pollution Research*, 22(11), 8367–8374.
- Hug, S. J., & Leupin, O. (2003). Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environmental Science & Technology*, 37(12), 2734–2742.
- Islam, F. S., Gault, A. G., Boothman, C., Polya, D. A., Charnock, J. M., Chatterjee, D., & Lloyd, J. R. (2004). Role of metal-

- reducing bacteria in arsenic release from Bengal delta sediments. *Nature*, 430(6995), 68–71.
- Javed, M. B., Kachanoski, G., & Siddique, T. (2013). A modified sequential extraction method for arsenic fractionation in sediments. *Analytica Chimica Acta*, 787(17), 102–110.
- Jessen, S., Larsen, F., Koch, C. B., & Avin, E. (2005). Sorption and desorption of arsenic to ferrihydrite in a sand filter. *Environmental Science & Technology*, 39(20), 8045–8051.
- Katsoyiannis, I. A., Ruettimann, T., & Hug, S. J. (2008). pH dependence of Fenton reagent generation and As(III) oxidation and removal by corrosion of zero valent iron in aerated water. *Environmental Science & Technology*, 42(19), 7424–7430.
- Keon, N. E., Swartz, C. H., Brabander, D. J., Harveyand, C., & Hemond, H. F. (2001). Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environmental Science & Technology*, 35(13), 2778–2784.
- Kim, E. J., Yoo, J., & Baek, K. (2014). Arsenic speciation and bioaccessibility in arsenic-contaminated soils: sequential extraction and mineralogical investigation. *Environmental Pollution*, 186, 29–35.
- Kosmulski, M. (2009). Compilation of PZC and IEP of sparingly soluble metal oxides and hydroxides from literature. *Advances in Colloid and Interface Science*, 152(1), 14–25.
- Kumar, K. V., Ramamurthi, V., & Sivanesan, S. (2005). Modeling the mechanism involved during the sorption of methylene blue onto fly ash. *Journal of Colloid and Interface Science*, 284(1), 14–21.
- Lenz, C., Behrends, T., Jilbert, T., Silveira, M., & Slomp, C. P. (2014). Redox-dependent changes in manganese speciation in Baltic Sea sediments from the Holocene Thermal Maximum: An EXAFS, XANES and LA-ICP-MS study. *Chemical Geology*, 370(26), 49–57.
- Liang, Q. Q., & Zhao, D. Y. (2014). Immobilization of arsenate in a sandy loam soil using starch-stabilized magnetite nanoparticles. *Journal of Hazardous Materials*, 271(30), 16–23.
- Livesey, N. T., & Huang, P. M. (1981). Adsorption of arsenate by soils and its relation to selected chemical properties and anions. *Soil Science*, 131(2), 88–94.
- Maji, S. K., Pal, A., Pal, T., & Adak, A. (2007). Adsorption thermodynamics of arsenic on laterite soil. *Journal of Surface Science and Technology*, 22(3–4), 161–176.
- Mamindy-Pajany, Y., Hurel, C., Marmier, N., & Roméo, M. (2011). Arsenic (V) adsorption from aqueous solution onto goethite, hematite, magnetite and zero-valent iron: effects of pH, concentration and reversibility. *Desalination*, 281(17), 93–99.
- Manning, B. A., Fendorf, S. E., & Goldberg, S. (1998). Surface structures and stability of arsenic(III) on goethite: spectroscopic evidence for inner-sphere complexes. *Environmental Science & Technology*, 32(16), 2383–2388.
- Manning, B. A., Fendorf, S. E., Bostick, B., & Suarez, D. L. (2002a). Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. *Environmental Science & Technology*, 36(5), 976–981.
- Manning, B. A., Hunt, M. L., Amrhein, C., & Yarmoff, J. A. (2002b). Arsenic(III) and arsenic(V) reactions with zero valent iron corrosion products. *Environmental Science & Technology*, 36(24), 5455–5461.
- Mohan, D., & Pittman, C. U., Jr. (2007). Arsenic removal from water/wastewater using adsorbents—a critical review. *Journal of Hazardous Materials*, 142(1–2), 1–53.
- Mukherjee, A., Scanlon, B. R., Fryar, A. E., Saha, D., Ghosh, A., Chowdhuri, S., & Mishra, R. (2012). Solute chemistry and arsenic fate in aquifers between the Himalayan foothills and Indian craton (including central Gangetic plain): influence of geology and geomorphology. *Geochimica et Cosmochimica Acta*, 90(1), 283–302.
- Namasivayam, C., & Senthilkumar, S. (1998). Removal of arsenic(V) from aqueous solution using industrial solid waste: adsorption rates and equilibrium studies. *Industrial & Engineering Chemistry Research*, 37(12), 4816–4822.
- Nath, B., Sahu, S. J., Jana, J., Mukherjee-Goswami, A., Roy, S., & Sarkar, M. J. (2008). Hydrochemistry of arsenic-enriched aquifer from rural West Bengal, India: a study of the arsenic exposure and mitigation option. *Water, Air, & Soil Pollution*, 190(1–4), 95–113.
- Nesbitt, H. W., Canning, G. W., & Bancroft, G. M. (1998). XPS study of reductive dissolution of 7 Å-birnessite by H_3AsO_3 , with constraints on reaction mechanism. *Geochimica et Cosmochimica Acta*, 62(12), 2097–2110.
- Ona-Nguema, G., Morin, G., Wang, Y. H., Foster, A. L., Juillot, F., Calas, G., & Brown, G. E. (2010). XANES evidence for rapid arsenic(III) oxidation at magnetite and ferrihydrite surfaces by dissolved O_2 via Fe^{2+} -mediated reactions. *Environmental Science & Technology*, 44(14), 5416–5422.
- Oscarson, D. W., Huang, P. M., & Liaw, W. K. (1981). Role of manganese in the oxidation of arsenite by freshwater lake sediments. *Clays and Clay Minerals*, 29(3), 219–225.
- Osorio-López, C., Seco-Reigosa, N., Garrido-Rodríguez, B., Cutillas-Barreiro, L., Arias-Estévez, M., Fernández-Sanjurjo, M. J., Álvarez-Rodríguez, E., & Núñez-Delgado, A. (2014). As(V) adsorption on forest and vineyard soils and pyritic material with or without mussel shell: kinetics and fractionation. *Journal of the Taiwan Institute of Chemical Engineers*, 45(3), 1007–1014.
- Partey, F., Norman, D., Ndur, S., & Nartey, R. (2008). Arsenic sorption onto laterite iron concretions: temperature effect. *Journal of Surface Science and Technology*, 321(2), 493–500.
- Poulton, S. W., & Canfield, D. E. (2005). Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. *Chemical Geology*, 214(3–4), 209–221.
- Qi, Y. Q., & Donahoe, R. J. (2008). The environmental fate of arsenic in surface soil contaminated by historical herbicide application. *Science of the Total Environment*, 405(1–3), 246–254.
- Qiao, J. L., Jiang, Z., Sun, B., Sun, Y. K., Wang, Q., & Guan, X. H. (2012). Arsenate and arsenite removal by FeCl_3 : effects of pH, As/Fe ratio, initial As concentration and co-existing solutes. *Separation and Purification Technology*, 92(18), 106–114.
- Ramesh, A., Hasegawa, H., Maki, T., & Ueda, K. (2007). Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite. *Separation and Purification Technology*, 56(1), 90–100.
- Ravenscroft, P., Brammer, H., & Richards, K. (2009). *Arsenic pollution: a global synthesis*. Oxford: Wiley-Blackwell.

- Robert, L. C., Hug, S. J., Ruettimann, T., Billah, M. M., Khan, A. W., & Rahman, M. T. (2004). Arsenic removal with iron(II) and iron(III) in waters with high silicate and phosphate concentrations. *Environmental Science & Technology*, 38(1), 307–315.
- Salameh, Y., Al-Lagtah, N., Ahmad, M. N. M., Allen, S. J., & Walker, G. M. (2010). Kinetic and thermodynamic investigations on arsenic adsorption onto dolomitic sorbents. *Chemical Engineering Journal*, 160(2), 440–446.
- Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17(5), 517–568.
- Stanic, T., Dakovic, A., Zivanovic, A., Tomasevic-Canovic, M., Dondur, V., & Milicevic, S. (2009). Adsorption of arsenic(V) by iron III-modified natural zeolitic tuff. *Environmental Chemistry Letters*, 7(2), 161–166.
- Teppen, B. J., Yu, C. H., Newton, S. Q., Miller, D. M., & Schtifer, L. (1998). Ab initio investigations pertaining to aluminum in tetrahedral octahedral sites of clay minerals. *Journal of Molecular Structure*, 445(1–3), 65–88.
- Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51(7), 844–851.
- Tufano, K. J., Reyes, C., Saltikov, C. W., & Fendorf, S. (2008). Reductive processes controlling arsenic retention: revealing the relative importance of iron and arsenic reduction. *Environmental Science & Technology*, 42(22), 8283–8289.
- Wenzel, W. W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., & Adriano, D. C. (2001). Arsenic fractionation in soils using an improved sequential extraction procedure. *Analytica Chimica Acta*, 436(2), 309–323.
- Ying, C., Kocar, B. D., & Fendorf, S. (2012). Oxidation and competitive retention of arsenic between iron- and manganese oxides Samantha. *Geochimica et Cosmochimica Acta*, 96(1), 294–303.
- Zhang, H., & Selim, H. M. (2005). Kinetics of arsenate adsorption-desorption in soils. *Environmental Science & Technology*, 39(16), 6101–6108.