Sorption processes affecting arsenic solubility in oxidized surface sediments from Tulare Lake Bed, California

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Abstract

Elevated concentrations of arsenic (As) in shallow groundwater in Tulare Basin pose an environmental risk because of the carcinogenic properties of As and the potential for its migration to deep aquifers that could serve as a future drinking water source. Adsorption and desorption are hypothesized to be the major processes controlling As solubility in oxidized surface sediments where arsenate [As(V)] is dominant. This study examined the relationship between sorption processes and arsenic solubility in shallow sediments from the dry Tulare Lake bed by determining sorption isotherms, pH effect on solubility, and desorption-readsorption behavior (hysteresis), and by using a surface complexation model to describe sorption. The sediments showed a high capacity to adsorb As(V). Estimates of the maximum adsorption capacity were 92 mg As kg\(^{-1}\) at pH 7.5 and 70 mg As kg\(^{-1}\) at pH 8.5 obtained using the Langmuir adsorption isotherm. Soluble arsenic \([\geq 97\% \text{ As(V)}]\) did not increase dramatically until above pH 10. In the native pH range (7.5–8.5), soluble As concentrations were close to the lowest, indicating that As was strongly retained on the sediment. A surface complexation model, the constant capacitance model, was able to provide a simultaneous fit to both adsorption isotherms (pH 7.5 and 8.5) and the adsorption envelope (pH effect on soluble As), although the data ranges are one order of magnitude different. A hysteresis phenomenon between As adsorbed on the sediment and As in solution phase was observed in the desorption–readsorption processes and differs from conventional hysteresis observed in adsorption–desorption processes. The cause is most likely due to modification of adsorbent surfaces in sediment samples upon extensive extractions (or desorption). The significance of the hysteresis phenomenon in affecting As solubility and mobility may be better understood by further microscopic studies of As interaction mechanisms with sediments subjected to extensive leaching in natural environments.

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1. Introduction

The Tulare Basin is a hydrologically closed system located in the southern one-third of the San Joaquin Valley, California, USA. It contains approximately 324,000 ha where the water table is within 6 m of the
land surface (Fujii and Swain, 1995). Subsurface drainage systems have been used to sustain irrigated agriculture and to prevent accumulation of salts in the root zone. Drainage water and shallow groundwater (<60 m) quality in this region is generally poor with high salinity and high concentrations of trace elements such as Se, As, U, B, and Mo (Swain and Duell, 1993; Beard et al., 1994; Fujii and Swain, 1995). Elevated concentrations of As in shallow groundwater in the Tulare Basin have been of concern due to its carcinogenic properties and its potential downward migration to contaminate the deep aquifer that could serve as a future drinking water source. The source of As in the Tulare basin was primarily from sediments derived from marine sedimentary formation in the mountains surrounding the basin.

Our previous study determined the amount of adsorbed As on Tulare Lake bed sediments using an isotopic dilution method and the potential contribution to groundwater using successive extraction methods (Gao et al., 2004). Results indicated that 24–28% of total As (24 mg kg$^{-1}$) in the oxidized sediment zone was isotopically exchangeable (or adsorbed) and only a portion (~60%) of the adsorbed As (dominated by As(V)) was released to the soluble phase through successive extractions. This adsorbed portion, however, could be a significant source of As contamination to groundwater. The actual amount of As contribution to groundwater depends on As mobility in the cycle of desorption–sorption processes and other factors such as transport and leaching rates dependent on sediment characteristics. In this study, we focused on examining As solubility behavior in sorption processes in sediment samples containing high levels of As.

Important chemical parameters affecting As(V) sorption include pH, the adsorbent’s surface charge and As speciation (Crecelius et al., 1986; Xu et al., 1988; Korte and Fernando, 1991). The sorption of As(V) in soils was correlated with amorphous Fe and Al oxides (Jacobs et al., 1970; Livesey and Huang, 1981). The maximum adsorption of As(V) on goethite ($\propto$-FeOOH) and gibbsite ($\gamma$-Al(OH)$_3$) occurred across a wide pH range but mostly below pH 8.0 (Manning and Goldberg, 1996b). Removal of carbonate greatly reduced As(V) sorption at higher pHs indicating the importance of carbonate in As adsorption by a calcareous soil containing 14.7% calcium carbonate equivalent (Goldberg and Glaubig, 1988). For clay minerals, montmorillonite adsorbed more As(V) than kaolinite. Arsenate adsorption on kaolinite and montmorillonite was high at low pH, peaked between pH 4 to 6, and decreased at pH greater than 6 (Frost and Griffin, 1977).

Total As [e.g., As(V)] adsorption on soils or minerals can be quantified using the distribution coefficient and empirical equations such as Langmuir or Freundlich equations. Their use, however, is limited because they do not provide information about the specific mechanisms of sorption or surface reactions and the parameters obtained are considered as curve-fitting (Sposito, 1982). Spectroscopic techniques that may provide direct evidence of surface reaction configuration have been developing rapidly and assist in interpretation of mechanisms in sorption processes. The ligand exchange theory is supported by evidence that most arsenic replaced two singly coordinated surface OH groups to form binuclear bridging complexes (Sun and Doner, 1996) and that HASO$_4$ ions displaced singly coordinated surface OH groups in forming binuclear species (Lumsdon et al., 1984). Surface complexation models have been used as tools to indirectly identify the chemical reactions and associated equilibrium constants for adsorption. One such model, the constant capacitance model, has been successfully used to describe adsorption of anions on minerals including Fe- and Al- oxyhydroxides, clay minerals, and some soils (Goldberg, 1993). This constant capacitance model was applied to arsenate adsorption including competitive adsorption with other anions (e.g., P, Si) (Goldberg, 1986; Goldberg and Glaubig, 1988; Manning and Goldberg, 1996a,b, 1997). Use of this model to examine As sorption behavior on natural sediments that contain high As concentrations may help us to better describe sorption processes in nature.

Most microscopic studies of As adsorption have focused on oxide minerals. A number of studies using microscopic methods such as X-ray absorption spectroscopy (XAS) (Waychunas et al., 1993; Fendorf et al., 1997; Grossl et al., 1997; Sherman and Randall, 2003) or Fourier transform infrared spectroscopy (FTIR) (Sun and Doner, 1996; Goldberg and Johnston, 2001) have shown that As(V) is strongly adsorbed on metal oxide surfaces such as iron oxides (goethite, ferrihydrite, and hematite) by forming inner-sphere complexes. The inner-sphere surface complexes of As on iron oxides include monodentate, bidentate mononuclear, and bidentate binuclear complexes, and their proportions depend on the degree of surface coverage (Waychunas et al., 1993; Fendorf et al., 1997; Grossl et al., 1997). Using extended X-ray absorption fine structure (EXAFS) spectroscopy, Sherman and Randall (2003) found that the bidentate corner-sharing complex was substantially more favored energetically over the edge-sharing bidentate complex for As(V) sorption to hematite, goethite, lepidocrocite, and ferrihydrite. Goldberg and Johnston (2001) showed...
that arsenate formed inner-sphere complexes on both Fe and Al oxides using Raman and FTIR spectroscopic methods combined with sorption experiments. EXAFS analysis indicated that the molecular environment of adsorbed arsenate on goethite did not change over time in samples either from adsorption or desorption experiments (O’Reilly et al., 2001).

The objective of this study was to examine the relationship between sorption and desorption processes and arsenic solubility in shallow sediments that contain high As concentrations from the dry Tulare Lake bed by determining sorption isotherms, pH effect on releasing As to the soluble phase, and sorption hysteresis phenomenon, and by surface complexation modeling of As sorption.

2. Materials and methods

2.1. Sampling and characterization

Sediment samples used in this study were collected from the Tulare Lake bed area. Detailed characterization of the samples was reported in Gao et al. (2004). Selected properties are shown in Table 1. The samples were taken at a depth of 2–4 m from the land surface where oxidizing conditions were indicated by high redox potential (+300 mV relative to H$_2$/H$^+$) and low soluble Fe and Mn concentrations. The pore water contained a total As concentration of 588 μg L$^{-1}$, dominated by As(V) (96%) with ∼4% of As(III) and negligible amounts of organic As. Pore water pH was 8.5 and a nearby well water had a pH of 7.5. Both pH conditions were examined in the sorption and desorption experiments. Sediments were sterilized using gamma-radiation to prevent microbial transformation of As during the course of the experiments. The sediment samples contained a total As concentration of 24 mg kg$^{-1}$, which was determined by using acid (HNO$_3$–HCl–HClO$_4$–H$_2$SO$_4$–HF) digestion and hydride generation atomic absorption spectrometry method modified from Welsch et al. (1990).

Adsorbed As on the sediment determined by an isotopic dilution method was 6.7 mg As kg$^{-1}$ at pH 7.5 and 5.7 mg As kg$^{-1}$ at pH 8.5 (Gao et al., 2004). The method used $^{73}$As to exchange the abundant $^{75}$As on the sediment. A sediment suspension was prepared initially and pH was adjusted to 7.5 or 8.5. A trace amount of $^{73}$As was added to a known volume of the suspension with a final sediment : solution ratio of 1 : 10 (w : v). Five replicates and blanks were conducted. After 24 h of equilibration, the supernatant was obtained by centrifuging the suspension and filtering through 0.22-μm filter membranes. The radioactivity of $^{73}$As in the supernatant was counted. The blank supernatant was analysed for total As and speciation ($^{73}$As added to the sediment was negligible, <0.002 μg As L$^{-1}$). By assuming at equilibrium, the distribution coefficients ($K_d$) of the two isotopes are equal:

\[
K_d = \frac{\text{As}_{solid}}{\text{As}_{solute}} = \frac{73\text{As}_{solid}}{75\text{As}_{solute}}\]

The isotopically exchangeable (or adsorbed) As on the sediments is obtained from:

\[
\text{Asexch} = \frac{m_l}{m_s} \left( \frac{A_{total}}{A_1} - 1 \right)
\]

where

- $m_l$ = the liquid volume (mL)
- $m_s$ = the mass of the solids (g)
- $\text{Asexch}$ = the concentration of As on the solid that is isotopically exchangeable (mg As kg$^{-1}$)
- $\text{As}_{i}$ = the concentration of As in solution phase in the control (mg As L$^{-1}$)
- $A_{total}$ = the total radioactivity added (μCi)
- $A_1$ = the total radioactivity in solution at equilibrium (μCi)

A solution having a chemical composition similar to the sediment pore water was used for all the experiments in this study. The solution was prepared by dissolving 0.638 g NaHCO$_3$, 0.877 g NaCl, 0.06 g MgSO$_4$, 0.987 g
Na$_2$SO$_4$, and 0.075 CaSO$_4$ into 1 L distilled deionized water (DD water). Similar to the pore water extracted from the sediment, the solution contained Na, Ca, Mg, Cl and SO$_4$ of 839, 22, 13, 532, and 768 mg L$^{-1}$, respectively, and had an EC of 4.0 dS/m, an alkalinity of 760 mg L$^{-1}$ CaCO$_3$, and a pH of 8.5. When other pHs were required, the solution pH was adjusted with HCl or NaOH.

2.2. Adsorption isotherm determination

Sediment samples equivalent to 2 g oven-dry weight were suspended in the artificial pore water at a solid:water ratio of 1:9.5 (w:v) in 50-mL Nalgene polypropylene tubes. The pH of the artificial pore water was adjusted previously to either pH 7.5 or pH 8.5. The samples were shaken on a reciprocal shaker for 24 h and the pH was readjusted if it deviated from the desired values. A variable amount of As(V) (0.25–1.0 mL of 10, 100, or 1000 mg L$^{-1}$) and DD water was then added to each tube to reach a solid:water ratio of 1:10 (w:v). After shaking for another 24 h, the suspensions were centrifuged at 12,000 g RCF (relative centrifugal force) for 20 min and filtered through a 0.22-μm filter membrane.

Total As concentrations as well as As(V) and As(III) species were determined. Calculations of adsorbed As were based on As concentration changes in the solution phase and the As adsorbed on the original sediment samples that was determined using isotopic dilution technique as stated above.

2.3. pH effect on soluble As (Envelope)

Sediment suspension was prepared initially in a 2-L plastic bottle containing moist sediment (equivalent to 120 g oven-dry basis) and 1140 mL artificial pore water of pH=7.5 [solid:sediment ratio = 1:9.5 (w:v)]. The suspension was shaken on a reciprocal shaker for 24 h. The suspension pH was 7.7 without additional acid or base added. When HCl was added and pH was adjusted to 7.2, the pH shifted 0.2 U up within 24 h indicating that a longer time is needed to obtain a stable pH of the suspension. The suspension was then partitioned by taking 19 mL of the suspension into 50-mL Nalgene polypropylene tubes. To obtain a pH range of 2.5 to 12, variable amounts of 0.1 N NaOH or 0.1 N HCl and DD water were added to the suspension to reach a final solid:solution ratio of 1:10 (w:v). The suspensions were shaken for 72 h. The pH was monitored every 24 h and little or no pH change was observed after 48 h. Final pHs of the suspensions were used to process the data. The supernatant was obtained by centrifuging the suspension at 11,720 g RCF for 20 min and filtering through a 0.22-μm filter. Total As concentration, as well as, As(V) and As(III) species were determined. The amount of adsorbed As at each pH was calculated based on the adsorbed As concentration at pH 7.5 and 8.5 (determined using isotopic dilution method) and solution As concentrations released from the sediment (taking into account the difference from those at pH 7.5 and 8.5 when determining adsorbed As by isotope dilution).

2.4. Readsorption

In natural environments, sediment As is subject to natural leaching or desorption and sorption reactions. To observe the effects of these processes on As behavior, sediment samples that had previously gone through successive extractions (desorption) with an artificial pore water were used to observe As(V) adsorption near the native As concentration range. We refer to this process as “readsorption”. The previous desorption procedure is briefly described below (details in Gao et al., 2004). Sediment samples were extracted in 250 mL bottles that contain about 20 g dry sediment at a solid:solution ratio of 1:10 (w:v). The sediment was initially equilibrated with the artificial pore water at a fixed pH (7.5 or 8.5). After 24 h extraction, the sediment suspension was centrifuged and filtered through 0.22-μm filter membranes. The supernatant was collected for total As and species analysis. Sediments collected on the filter paper were placed back into the extraction tubes with a spatula whenever possible. The sediment was extracted again following the same procedures. The amount of adsorbed As after each extraction was calculated based on the adsorbed As concentration at pH 7.5 and 8.5 (determined using isotopic dilution method), adsorbed As removed by releasing As to the solution, and the amount of adsorbed As removed from the previous extraction steps. The amount of As in the solution remaining with the sediment after removing supernatant from the previous step was corrected for each calculation. Sediment samples were extracted 14 times at pH 7.5 and 5 times at pH 8.5. Cumulative As removed from the successive extraction was 3.9 mg kg$^{-1}$ at pH 7.5 (∼57% of adsorbed on the sediment) and 2.1 mg kg$^{-1}$ at pH 8.5 (∼37% of adsorbed on the sediment). The former could be considered extensively desorbed. The final sediments from each of the successive extraction (desorption) experiments at pH 7.5 and 8.5 were separately collected, air-dried and mixed thoroughly. These sediments were then partitioned and samples equivalent to 2 g dry weight were suspended in the artificial pore water at a solid:solution ratio of 1:9.5 (w:v) in 50-mL Nalgene centrifuge tubes. The artificial pore
water was previously adjusted to pH 7.5 or 8.5 and allowed to equilibrate with the As desorbed sediments for 24 h. Variable amounts (0.1–2.0 mL) of 10 mg L\(^{-1}\) As(V) concentration and DD water [to reach a final solid:water ratio of 1:10 (w:v)] were added to the suspension in the concentration range of As removed by successive extractions. After shaking for 24 h, the suspension was centrifuged at 12,000 g RCF for 20 min and filtered through a 0.22 μm syringe filter. Suspension pH was monitored and varied within 0.2 U from the desired pH. Total As concentration as well as As(V) and As(III) species were determined. Adsorbed As was calculated by summing the adsorbed As on the sediment before readsorption (end of successive extraction) and the amount of As lost from solution due to adsorption.

2.5. Analysis of total As and speciation

Throughout this study, total As and As species (III and V) in solution samples were determined using a modified method of Glaubig and Goldberg (1988). Detailed analyses and QA/QC procedures can be found in Gao et al. (2004). Arsenic(V) was dominant in all the analyses (>97% of total As) because of the oxidized nature of the sediment and As(III) was present in trace amounts (<3%). Thus the As referred to in the Results and discussion section was mainly As(V).

2.6. Complexation model for As(V) adsorption

Surface complexation theory, which describes adsorption in terms of chemical reactions between surface functional groups and dissolved chemical species, has been applied to interfacial adsorption phenomena (Davis and Kent, 1990). The constant capacitance model (Stumm et al., 1980), a surface complexation model, considers adsorbed ions to form inner-sphere complexes located in a surface plane with the protons and hydroxyl ions associated with the solid. The surface functional group (XOH) is considered as an average reactive surface hydroxyl ion bound to a metal such as Al or Fe in oxide minerals or an alumino group on the clay mineral edges. The surface reactions for As(V) adsorption via ligand exchange mechanisms were defined by Goldberg (1986, 1993) (Table 2). Consistent with previous studies, the computer program FITEQQL 3.2 (Herbelin and Westall, 1996) was used to fit three monodentate intrinsic As surface complexation constants. The capacitance was set at 1.06 F m\(^{-2}\) as in previous studies. The protonation dissociation constants (log \(K_p\) (int) = 7.20 and log \(K_p\) (int) = −11.24) were obtained by optimizing potentiometric titration data on the sediments at ionic strength of 0.1, 0.01, and 0.001 M.

3. Results and discussion

3.1. Adsorption isotherms

The adsorption isotherms at pH 7.5 and 8.5 are shown in Fig. 1. Because the sediment contained natural high concentration of As, data from desorption experiments were processed as described above and used in constructing the adsorption isotherms at the low concentration range. Overall, the sediment showed a high capacity to adsorb As (V) and greater sorption occurred at pH 7.5 than at pH 8.5. The maximum sorption capacity was not observed even when sorbed As concentrations reached about 65 mg kg\(^{-1}\) at pH 7.5 or 54 mg kg\(^{-1}\) at pH 8.5, and the solution As concentrations reached 19–22 mg L\(^{-1}\). The adsorption maxima were extrapolated by using a Langmuir adsorption isotherm. Calculations resulted in estimates of adsorption maxima of 92 mg As kg\(^{-1}\) at pH 7.5 and 70 mg As kg\(^{-1}\) at pH 8.5. To fit the adsorption data more closely, a multiple-site adsorption model of the Langmuir equation was actually applied indicating a multi-component adsorbent system in the sediment and the predicted adsorption isotherms are also indicated in Fig. 1.

Mineral precipitation did not appear to be important in controlling solution As concentrations in this sediment. The speciation model Visual MINTEQ (developed by J.P. Gustafsson and available at http://www.lwr.kth.se/English/OurSoftware/vminteq/index.html), a Windows version of MINTEQA2 (Allison et al., 1991), was used for solution speciation. Saturation indices (SI = log [IAP/\(K_{eq}\)]) where IAP is the ion activity product and \(K_{eq}\) is the equilibrium constant) were computed for the highest solution As concentration (~21 mg L\(^{-1}\)) in the adsorption isotherm experiment. Available SIs for Ca\(_3\)(AsO\(_4\))\(_2\)·4H\(_2\)O were −26.9 at pH 7.5 and −24.8 at pH 8.5. SI values for As\(_2\)O\(_5\) were −60.8 at pH 7.5 and −64.6 at pH 8.5. Because the sediment was under oxidizing conditions, soluble Fe, Mn and Al concentrations in the pore water were below detection limit (1 mg L\(^{-1}\). By assuming total dissolved concentrations of Fe and Al at the maximum 1 mg L\(^{-1}\), the SIs for AlAsO\(_4\)\(_2\)H\(_2\)O and FeAsO\(_4\)\(_2\)H\(_2\)O ( scorodite) were −19.4 and −22.0, at pH 7.5, and −22.3 and −23.2 at pH 8.5, respectively. These negative SI values indicate that the solution was undersaturated with respect to these arsenic minerals. EXAFS spectroscopy showed that an As-bearing surface precipitate or solid solution was not formed when high adsorbed amounts [0.25 mol As(V)
Table 2
Surface complexation reactions and constant capacitance model intrinsic surface complexation constants obtained by fitting sorption isotherm and envelope data

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Equilibrium Expressions and Constants</th>
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<tr>
<td><strong>Surface hydrolysis reactions</strong></td>
<td></td>
</tr>
<tr>
<td>XOH + H(^+) = XO(^-) + H(^2)OH (^*)</td>
<td>(K_+(\text{int}) \equiv \frac{[\text{XOH}^-][\text{H}^+]}{[\text{XOH}][\text{H}^2\text{OH}]} \exp \left(\frac{F\psi}{RT}\right) = 10^{7.35})</td>
</tr>
<tr>
<td>XOH = XO(^-) + H(^+)</td>
<td>(K_-(\text{int}) \equiv \frac{[\text{XO}^-][\text{H}^+]}{[\text{XOH}]} \exp \left(-\frac{F\psi}{RT}\right) = 10^{-8.95})</td>
</tr>
<tr>
<td><strong>Formation of inner-sphere surface complexes</strong></td>
<td></td>
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<tr>
<td>XOH + H(_2)AsO(_4) = XH(_2)AsO(_4) + H(_2)O</td>
<td>(K_1(\text{int}) \equiv \frac{[\text{XH}_2\text{AsO}_4]}{[\text{XOH}][\text{H}_2\text{AsO}_4]} = 10^{9.05})</td>
</tr>
<tr>
<td>XOH + H(_2)AsO(_4) = XHAsO(_4)(^-) + H(_2)O + H(^+)</td>
<td>(K_2(\text{int}) \equiv \frac{[\text{XHAsO}_4^\text{-}][\text{H}^+]}{[\text{XOH}][\text{H}_2\text{AsO}_4]} \exp \left(-\frac{F\psi}{RT}\right) = 10^{2.23})</td>
</tr>
<tr>
<td>XOH + H(_2)AsO(_4) = XAsO(_4)(^2\text{-}) + H(_2)O + 2H(^+)</td>
<td>(K_3(\text{int}) \equiv \frac{[\text{XAsO}_4^\text{2-}][\text{H}^+]^2}{[\text{XOH}][\text{H}_2\text{AsO}_4]} \exp \left(-\frac{2F\psi}{RT}\right) = 10^{-5.36})</td>
</tr>
<tr>
<td><strong>Mass balance</strong></td>
<td></td>
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<tr>
<td>([\text{XOH}]_T = [\text{XOH}] + [\text{XOH}^2\text{OH}] + [\text{XO}^-] + [\text{XH}_2\text{AsO}_4] + [\text{XHAsO}_4^\text{-}] + [\text{XAsO}_4^\text{2-}])</td>
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<tr>
<td><strong>Charge balance</strong></td>
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<tr>
<td>(\sigma = [\text{XOH}^2\text{OH}] - [\text{XO}^-] - [\text{XHAsO}_4^\text{-}] - 2[\text{XAsO}_4^\text{2-}])</td>
<td></td>
</tr>
</tbody>
</table>

Where \(X\) denotes a metal ion Al or Fe on the solid surface of the sediments.

* Equilibrium constant values obtained for simultaneous optimization of sorption and envelope data by FITEQL 3.2. For fitting two isotherms only: \(K_1(\text{int}) = 10^{8.78}\); \(K_2(\text{int})\) did not converge and \(K_3(\text{int}) = 10^{-5.36}\). For fitting the envelope only: \(K_1(\text{int}) = 10^{9.14}\); \(K_2(\text{int}) = 10^{6.60}\), and \(K_3(\text{int}) = 10^{-4.56}\).

mol\(^{-1}\) of Fe (synthesized ferrihydrite) were studied (Waychunas et al., 1993). The results support the conclusion that sorption–desorption processes rather than precipitation–dissolution processes were controlling As partitioning between the solution and the solid phase in the sediment.

The relatively high oxalate extractable (amorphous or active) Al and Fe (795 and 860 mg kg\(^{-1}\), respectively) and citrate-dithionite extractable (total or “free”) Al and Fe (600 and 2636 mg kg\(^{-1}\), respectively) amounts in the sediment samples may indicate the importance of Fe- and Al-oxides in As(V) adsorption on the sediments. Because of the high clay content (51%) and dominance of 2:1 minerals (Table 1), clay minerals in As adsorption may also be important. Inorganic carbonate was unlikely to be important in As adsorption because CaCO\(_3\) content was only 1.7%. A calcareous soil of much higher CaCO\(_3\) content (14.7%) where carbonate was determined to play an important role in As(V) adsorption had a maximum of As(V) adsorption near pH 10.5 (Goldberg and Glauzibig, 1988). Such a maximum was not observed in Fig. 2.

3.2. Effects of pH on Soluble Arsenic

Soluble arsenic concentrations ranged (with a slightly increasing trend) from 400 to 500 μg L\(^{-1}\) between pH 2 and 6, then decreased to 400 μg L\(^{-1}\) around pH 8 (Fig. 2). Between pH 8 and 10, solution As concentration increased to 550 μg L\(^{-1}\). From pH 10 to 12, As concentrations increased dramatically to 980 μg L\(^{-1}\). At the native pH range (7.5–8.5), the relatively low solution concentrations may indicate that As is strongly retained on the sediment. Under ambient conditions, the easily desorbed As may have been lost from the sediments by leaching over long equilibration times.

Arsenate speciation is pH-dependent, with H\(_2\)AsO\(_4\)\(^\text{-}\), H\(_2\)AsO\(_4\)\(^2\text{-}\), and AsO\(_4\)\(^3\text{-}\) having pK\(_{\text{a1}}\) = 2.24, pK\(_{\text{a2}}\) = 6.96, and pK\(_{\text{a3}}\) = 11.50 (NIST, 2003), respectively. Proton-bearing surface functional groups on metal oxyhydroxides, clay minerals, and organic materials also undergo pH-dependent dissociation. Consequently, amounts of As controlled by adsorption and desorption processes are pH-dependent. Arsenate adsorption...
maxima on goethite ($\alpha$-FeOOH) and gibbsite ($\gamma$-Al(OH)$_3$) occurred over a wide pH range, but were highest at pH values below 8.0 (Manning and Goldberg, 1996b). Arsenate adsorption on oxides and clays was high at low pH and decreased with increasing pH above pH 9 for Al oxides, above pH 7 for Fe oxide and above pH 5 for clays (Goldberg, 2002). In contrast, the As(V) sorption maximum on calcite was between pH 10 and 12 (Goldberg and Glaubig, 1988). Arsenate adsorption on clay minerals such as kaolinite, montmorillonite, and illite, peaked between pH 4 and 6 and decreased at pH greater than 5 (Frost and Griffin, 1977; Goldberg, 2002). For the Tulare Lake Bed sediments (Fig. 2), soluble As(V) appeared to be a function of pH and was controlled by a multi-component adsorbent system, with both clay and Fe-, Al-oxyhydroxides regulating soluble As in the sediments.

3.3. Complexation modeling of arsenic sorption

The constant capacitance model was able to fit the data for the two adsorption isotherms (pH 7.5 and 8.5) and the adsorption envelope (pH effect on soluble As) (Fig. 3). The adsorption isotherm data are for As added to the system; while the adsorption envelope data are for release of adsorbed As from the original sediment samples upon changes in pH. The model was well able to describe both types of adsorption data despite their differing one order of magnitude in adsorbed amount. The modeling parameters used for the data fitting are given in Table 2.

For simultaneous fitting to both adsorption isotherms and envelope data, the surface complexation constants, or intrinsic $K$ values, were obtained using FITEQL 3.2: $K_1$(int) = 10$^{9.05}$, $K_2$(int) = 10$^{2.22}$, and $K_3$(int) = 10$^{-5.36}$. For fitting the two isotherms only, these values were $K_1$(int) = 10$^{9.78}$, $K_2$(int) did not converge, and $K_3$(int) = 10$^{-5.36}$. For fitting the envelope only, these constants were $K_1$(int) = 10$^{10.41}$, $K_2$(int) = 10$^{6.60}$, and $K_3$(int) = 10$^{-4.56}$. Despite some deviations, the constant values are in close agreement to those obtained for arsenate adsorption on Al and Fe oxides $K_1$(int) = 10$^{6.5}$ to 10$^{10.9}$, $K_2$(int) = 10$^{2.6}$ to 10$^{6.5}$ and $K_3$(int) = 10$^{-4.5}$ to 10$^{-0.55}$ for the same monodentate surface species (Goldberg, 1986; Grossl et al., 1997; Goldberg and Johnston, 2001). These results support the conclusion that metal oxides play an important role in As(V) adsorption by this sediment. Our surface complexation constants are also in excellent agreement with those obtained for an arid zone soil: $K_1$(int) = 10$^{11}$, $K_2$(int) = 10$^{3.7}$ and $K_3$(int) = 10$^{-4.2}$ (Goldberg and Glaubig, 1988). This result indicates that these heterogeneous natural materials have similar As adsorbing surfaces.

3.4. Hysteresis phenomenon in desorption and readsorption

A hysteresis phenomenon between As adsorbed on the sediment and As in solution was observed in the desorption–readsorption processes (Fig. 4). Our data differ from traditional hysteresis that is observed in adsorption–desorption process, since the sequence of experimental procedures, i.e., desorption followed by readsorption, was reversed from usual convention. The primary differences in hysteresis at pH 7.5 and 8.5 can be attributed to pH and desorption intensity. In general, the effects of pH on As readsorption followed the general trends observed in the As(V) adsorption.

Fig. 3. As(V) adsorption isotherms on sediment at pH 7.5 and 8.5.

Fig. 2. Effects of pH on soluble As(V) (>97%) in sediment samples.
isotherms (Fig. 1). Prior to readsorption, sediment samples at pH 7.5 were desorbed 14 times (extensively desorbed) compared to 5 times at pH 8.5. The data from the desorption extractions are plotted in the “desorption” isotherm, with the soluble and solid phase As measurements from each successive desorption step plotted separately. As expected, both the soluble and solid phase data from each successive desorption step plots less than the previous step. The impact of desorption intensity on hysteresis behavior was particularly evident at pH 7.5. After adsorbed As was extensively desorbed, added As(V) partitioned differently into solid and solution phase depending on concentration ranges but exhibits a more linear correlation.

The isotherms from desorption are curve-shaped as expected while the “readsorption” isotherm are almost linear (Fig. 4). The results suggest that successive extractions of As from the sediments may have modified the surfaces that adsorb As. To examine the cause for the hysteresis phenomenon, adsorption isotherms at lower concentration ranges for non-extracted sediment samples and the readsorption isotherms for successively extracted sediment samples are plotted in Fig. 5. All the isotherms are linear. The different slopes of the isotherms indicate that the sediment surfaces must have been modified in some way upon successive extraction using the artificial pore water. Steeper slopes in the readsorption isotherms

![Fig. 3. Constant capacitance model fit for simultaneous modeling of As adsorption isotherm (a) and envelope data (b).](image)

![Fig. 4. Successive desorption trends and readsorption isotherm of As for sediment samples at pH 7.5 (a) and 8.5 (b).](image)
than the desorption isotherms suggest that upon repeated extraction, the surface of adsorbent contributing to As adsorption was modified to expose or create more adsorption sites with similar type of energy towards arsenic adsorption. This is evident by the straight and steeper slopes in the readsorption isotherms than the desorption isotherm (Fig. 4) as well as a steeper slope at pH 7.5 (extracted 14 times) than at pH 8.5 (extracted 5 times). The mechanisms causing modification of the solid surfaces upon extractions with artificial pore water are unknown at this point because no characterization of the sediment after extraction was carried out in this research. Further studies are needed to better understand arsenic coordination with sediments that are particularly subject to leaching processes.

Hysteresis is a phenomenon commonly observed in sorption research, with most experiments being designed to investigate adsorption followed by desorption processes. A few examples include adsorption of natural organic matter or organic compounds (Kaiser and Zech, 1999; Fytianos et al., 2000; Lu and Pignatello, 2002), heavy metals such as Cu and Zn (Wu et al., 1999; Pan et al., 1999), and oxyanions such as P (Villapando and Graetz, 2001) onto soils or sediments. In each of these studies, the adsorbate was first added to the system, then fresh solutions were used to desorb the adsorbate. Most of the results were similar, i.e., some of the adsorbed constituents could not be desorbed or were irreversibly adsorbed. The hysteresis could be attributed to entrapment, the diffusion of dissolved ions to adsorption sites within micropores and clay interlayers, and the formation of covalent bonds (Essington, 2004). Hysteresis could also be explained by kinetic control. For example, the rate constants for arsenate desorption from goethite were lower than the rate constants for adsorption, indicating that desorption was the rate-limiting step in the reaction of arsenate with the goethite surface (Grossl et al., 1997). Fuller et al. (1993) similarly indicated that arsenate desorption from ferrihydrite was limited by diffusional processes. In our study, a very different hysteresis phenomenon was observed in the process of desorption followed by readsorption, and we propose that the different experimental procedures resulted in this different behavior. To the best of our knowledge, this is the first study that observed a hysteresis phenomenon in a desorption–readsorption cycle, particularly for sediments that were extensively desorbed. Further confirmation and microscopic studies may provide a better understanding of the mechanisms of As(V) reaction with the sediments in these processes. Nonetheless, these results may have implications of the fate of As in natural systems that are subject to leaching process in natural environment.

4. Conclusions

Adsorption and desorption are important processes affecting arsenic solubility in Tulare Lake bed sediment samples under oxidizing conditions. The sediments effectively adsorbed As across the native pH range (7.5–8.5). The capability of the surface complexation model to describe adsorption data at various conditions with As levels spanning one order of magnitude suggests that metal oxides (Fe and Al) and clay minerals play an important role in As(V) adsorption. Although the sediment demonstrated a very high adsorption capacity for As(V), mechanisms controlling As desorption and adsorption particularly on sediments that are subject to constant leaching and desorption are not well understood and bear further study.

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References


