Arsenate Adsorption by Unsaturated Alluvial Sediments

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Arsenic can occur naturally in excess of drinking water standards. Earlier a field-scale recharge pond experiment in the Antelope Valley ground water basin, Mohave Desert, California, was performed to determine the effectiveness of naturally occurring minerals in the unsaturated zone to treat high As water. The extent to which the remediation can be continued on any site is unknown and depends on the As adsorption properties and capacity of the sediments. Therefore, arsenate adsorption reactions as a function of solution As concentration and solution pH were investigated on five alluvial sediments obtained from various depths of a borehole adjacent to the recharge pond. Arsenate adsorption increased with increasing solution pH, exhibited a maximum around pH 4 to 5, and then decreased with increasing pH. The constant capacitance model was able to fit arsenate adsorption on the sediments as a function of solution As concentration and solution pH. A general regression model was used to predict arsenate surface complexation constants from routinely measured chemical parameters. The predicted arsenate constants were used to predict adsorption on the sediments, thereby providing a completely independent evaluation of the ability of the model to describe arsenate adsorption. The prediction equations were able to satisfactorily predict arsenate adsorption on one of the five sediments whose chemical properties fell into the range for the set of soils used to develop the prediction equations. Equimolar phosphate concentrations did not affect the extent of arsenate adsorption indicating that the extent of arsenate remediation by the sediments will be unaffected by the low amounts of native phosphate.

Abbreviations: ICP–OES, inductively coupled plasma–optical emission spectrometry; IOC, inorganic carbon; OC, organic carbon, TC, total carbon.

Arsenic is a trace element that is toxic to animals. Elevated concentrations of As in soils and waters can occur as a result of application of arsenical pesticides, geothermal discharge, mine drainage, disposal of fly ash, and mineral oxidation and dissolution (Smedley and Kinniburgh, 2002). In soil solution, the dominant inorganic As species are arsenate, As(V), under oxidizing conditions and arsenite, As(III), under more reducing conditions (Adriano, 1986). Arsenate is considered to be the less toxic oxidation state (Penrose, 1974). Redox transformation rates for inorganic As species are slow so that both As(V) and As(III) often co-exist in soil solution (Masscheleyn et al., 1991).

Arsenic adsorption has been investigated on a wide range of surfaces including Al and Fe oxides, clay minerals, sediments, and whole soils. Soil constituents that are significantly positively correlated with As adsorption include extractable Al and Fe oxides and clay minerals (Wauchope, 1975; Livesey and Huang, 1981; Yang et al., 2002). Arsenate adsorption on various Al and Fe oxides and the clay minerals: kaolinite, montmorillonite, and illite increased with increasing solution pH at low pH, exhibited adsorption maxima in the pH range 3 to 7, and then

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decreased at high pH (Xu et al., 1988; Manning and Goldberg, 1996a, 1996b; Goldberg and Johnston, 2001; Goldberg, 2002). Arsenite adsorption on amorphous Al and Fe oxides and the clay minerals: kaolinite, montmorillonite, and illite also increased with increasing pH at low solution pH and decreased at high solution pH; however, the adsorption maxima were found at the higher pH range of 7 to 9 (Manning and Goldberg, 1997; Jain and Loeppert, 2000; Goldberg and Johnston, 2001; Goldberg, 2002). Arsenate has been observed to adsorb to a much greater extent than As(III) on amorphous oxides at solution pH < 7; while As(III) adsorbed to a greater extent at high solution pH (Jain and Loeppert, 2000; Goldberg and Johnston, 2001).

Analogous to the behavior on Fe and Al oxides and clay minerals, As(V) adsorption on soils from California, Iowa, and Oklahoma (Goldberg and Glaubig, 1988; Goldberg et al., 2005), lake bed sediments (Gao et al., 2006), and clastic mine sediments (Borgnino et al., 2012) increased with increasing pH at low solution pH, exhibited adsorption maxima near pH 7, and then decreased at high solution pH. Arsenic added to harbor and river sediments became associated with Fe and Al compounds (Brannon and Patrick, 1987). Arsenate adsorption by both field soils and lake sediments from the Mississippi River Delta flood plain region was significantly positively correlated with clay content and extractable Fe and Al content (Wauchope and McDowell, 1984). Binding intensity values for As(V) adsorption on lake sediments agreed well with those obtained on amorphous Fe hydroxides (Belzile and Tessier, 1990). The extent of adsorption on sediments is strongly related to mineralogy, with smectitic sediments adsorbing more As(V) than sediments rich in quartz and/or illite (Borgnino et al., 2012).

Arsenate adsorption on soils, soil minerals, and sediments has been described using various chemical surface complexation modeling approaches. Such models include the constant capacitance model (Goldberg, 1986, 2002; Goldberg and Glaubig, 1988; Manning and Goldberg, 1996a, 1996b; Goldberg and Johnston, 2001, Gao and Mucci, 2001, 2003; Gao et al., 2006; Goldberg et al., 2005, 2008; Chakraborty et al., 2007; Borgnino et al., 2012), the diffuse layer model (Dzombak and Morel, 1990; Swedlund and Webster, 1999; Lumsdon et al., 2001; Dixit and Hering, 2003; Sharif et al., 2011), the triple layer model (Hsia et al., 1992; Khaodhiar et al., 2000; Arai et al., 2004; Salazar-Camacho and Villalobos, 2010), and the CD-MUSIC model (Hiemstra and van Riemsdijk, 1999; Gustafsson, 2001, 2006; Weerasooriya et al., 2004; Antelo et al., 2005; Stachowicz et al., 2006, 2008). All of the surface complexation modeling studies postulated inner-sphere surface complexes for As(V) absorption. Chemical surface complexation models define specific surface species, chemical reactions, mass balances, and charge balances and contain molecular features that can be given thermodynamic significance (Sposito, 1983).

Evidence of specific adsorption of As(V) as a strong inner-sphere surface complex containing no water between the adsorbing ion and the surface functional group has been provided by point of zero charge, PZC, shifts observed using electrophoretic mobility measurements for goethite (Antelo et al., 2005; Lakshmipathiraj et al., 2006) and for amorphous Al and Fe oxide (Hsia et al., 1994; Suarez et al., 1998; Goldberg and Johnston, 2001). Additional macroscopic evidence for inner-sphere surface complex formation of As(V) was found in its lack of ionic strength dependence of adsorption behavior as seen for amorphous Al and Fe oxide (Hsia et al., 1994; Goldberg and Johnston, 2001), gibbsite (Weerasooriya et al., 2004), and goethite (Antelo et al., 2005). Direct spectroscopic evidence for specific inner-sphere surface complexation of As(V) has been observed on amorphous Fe oxide, goethite, akageneite, lepidocrocite, hematite, maghemite, feroxyhyte (Waychunas et al., 1993; Fendorf et al., 1997; Catalano et al., 2007; Morin et al., 2008; Loring et al., 2009; Müller et al., 2010), amorphous Al oxide (Goldberg and Johnston, 2001), and gibbsite (Ladeira et al., 2001).

Application of the surface complexation modeling approach to describe As(V) adsorption on sediments has so far been restricted to the constant capacitance model. With this model, As(V) adsorption on Tulare Lake bed sediments was successfully described both as a function of solution pH and solution As(V) concentration (Gao et al., 2006). Arsenate adsorption constants obtained from this application were in excellent agreement with those previously obtained for amorphous Al and Fe oxides (Goldberg and Johnston, 2001), suggesting that these constituents play an important role in the As(V) adsorption capacity of sediments. Using the constant capacitance model, Borgnino et al. (2012) were able to describe As(V) adsorption on sediments dominant in phyllosilicates using initial parameter values previously obtained for illite and montmorillonite (Avena and De Pauli, 1998).

Phosphate, due to its chemical similarity to As(V), is a highly competitive ion for As(V) adsorption sites on oxides, clay minerals, and soil surfaces at equimolar and higher solution concentrations (Manning and Goldberg, 1996a, 1996b; Livesey and Huang, 1981; Smith et al., 2002). Phosphate was adsorbed even more strongly than As(V) by lake sediments from the Mississippi Delta at equivalent concentrations (Wauchope and McDowell, 1984). Gao et al. (2004) recommended addition of phosphate and subsequent extraction as a method to determine the potential amount of As(V) that could be released from sediments into ground water.

As demonstrated by Izbicki et al. (2008) in the Mojave Desert of California, infiltration through recharge ponds can be used to recharge aquifers in areas having thick, heterogeneous unsaturated zones and containing low-permeability clay layers. During the recharge experiment total dissolved As concentrations decreased from a median of 9.2 $\mu g\ L^{-1}$ (approaching the drinking water standard of 10 $\mu g\ L^{-1}$) in the infiltrating water to median values of $<2\ \mu g\ L^{-1}$ at 6 m below the land surface. Izbicki et al. (2008) attributed the removal of As in the unsaturated zone to sorption on Al, Fe, and Mn oxides present on mineral grain surfaces. A field-scale study in the Antelope Valley, western Mojave Desert, California, is underway to evaluate the effectiveness of using naturally occurring Al, Fe, and Mn oxides in the unsaturated zone to remediate high-As waters through immobilization during recharge. Inorganic phosphate concentrations in the ground waters associated with these sediments are <0.02 mg L^{-1} (Izbicki, personal communication, 2012).

The objectives of the present study were: (i) to determine As(V) adsorption on samples of unsaturated alluvium from various depths obtained through a borehole adjacent to the Antelope Valley recharge pond as a function of solution pH and solution As concentration; (ii) to evaluate the competitive effect of phosphate on As(V) adsorption on these sediments; and (iii) to test the ability the constant capacitance model to describe As(V) adsorption on the sediments.

MATERIALS AND METHODS

Arsenate adsorption behavior was studied on five sediments obtained from various depths of one borehole adjacent to the Antelope Valley recharge pond, located in the northwestern part of the Lancaster subbasin approximately 16 miles northwest of Lancaster, CA. The Antelope Valley ground water basin near Lancaster consists of alluvial and lacustrine deposits that are predominantly granitic in origin. The <2-mm fractions of the unsaturated alluvial deposits were used for the experiments. Chemical and physical characteristics and mineralogy are provided in Table 1. X-ray diffraction analyses were performed using powder amounts of the <50-µm fractions. Cation exchange capacities of the sediments were measured using Na saturation and Mg extraction as described by Rhoades (1982). Surface areas were determined using ethylene glycol monoethyl ether adsorption as described in the protocol of Cihacek and Bremner (1979). Particle size analysis was determined using the basic hydrometer method (Gee and Bauder, 1986). Coulometry was used for determining C contents: inorganic carbon (IOC) by acidification and heating, total carbon (TC) by combustion at 950°C, and organic carbon (OC) by difference between TC and IOC. Extraction of free Fe and Al oxides was accomplished using a Na citrate–citric acid buffer combined with Na hydrosulfite as described by Coffin (1963). Soluble Fe and Al concentrations in the extractant solutions were determined with inductively coupled plasma–optical emission spectrometry (ICP–OES).

Arsenate adsorption experiments on the sediments were performed in batch systems to determine adsorption isotherms [amount of As(V) adsorbed as a function of equilibrium solution As(V) concentration] and adsorption envelopes [amount of As(V) adsorbed as a function of solution pH per fixed total As(V) concentration]. For the As(V) adsorption isotherms, 1.0-g samples of air-dried sediments were added to a 50-mL polypropylene centrifuge tubes and equilibrated with 25 mL of a 0.1 M NaCl solution on a reciprocating shaker. The temperature of reaction was 23.4±0.1°C and the pressure was atmospheric. The equilibrating solution also contained As(V) concentrations of 0, 0.05, 0.1, 0.2, 0.5, 0.75, 1.0, 1.5, 2.0, 3.0, 4.0, and 5.0 mg L^{-1}. After reacting for 2 h, the samples were centrifuged, decanted, analyzed for pH, filtered through 0.45-µm membrane filters, and analyzed for As concentration using ICP–OES. The 2 h reaction time had been used in two prior surface complexation modeling studies of As(V) adsorption by soils (Goldberg and Glaubig, 1988; Goldberg et al., 2005) including the experiments used to develop the surface complexation model prediction equations (Goldberg et al., 2005). Amount of As(V) adsorption was determined as the difference between the initial electrolyte solution As concentration and the final equilibrium As concentration. The Langmuir adsorption isotherm equation:

$$\mathrm{As}_{\mathrm{ads}} = \frac{K\mathrm{As}_{\mathrm{eq}}M}{1+K\mathrm{As}_{\mathrm{eq}}} \qquad [\mathbf{1}]$$

where $\mathrm{As}_{\mathrm{ads}}$ is the As adsorption (mg kg^{-1}), $\mathrm{As}_{\mathrm{eq}}$ is the equilibrium As concentration (mg L^{-1}), M is the maximum As adsorption (mg kg^{-1}), and K is a parameter (L mg^{-1}) was fit to the As adsorption data.

For the As(V) adsorption envelopes, 1.0 g sediment samples were also equilibrated with 25 mL of a 0.1 M NaCl solution in centrifuge tubes on a reciprocating shaker. The reaction time was 2 h at a temperature of 24.2±0.4°C. In this case the equilibrating solution contained 1.5 mg As(V) L^{-1} and had been adjusted to the desired pH range with 0.5 mL of solutions of varying combinations of 1 M HCl, 1 M NaCl, and 1 M NaOH. After reaction, the samples were also centrifuged, decanted, analyzed for pH, filtered, and analyzed for As concentration using ICP–OES. Arsenate adsorption envelopes were also obtained in

Table 1. Chemical and physical characteristics and mineralogy of sediments.

Sample	Depth	Clay	pH	CEC†	SA	IOC	OC	Fe	Al
Description and mineralogy	m	%		cmol$_c$ kg^{-1}	m^2 g^{-1}	%			
Silty sand with gravel mica, feldspar, vermiculite, kaolinite	3.0–4.6	2.15	7.4	2.02	5.89	0.0029	0.072	0.135	0.0091
Clay mica, feldspar	8.5–9.7	29.1	8.0	24.3	112	0.0016	0.092	0.515	0.0484
Silty sand mica, feldspar	14.6–15.5	7.50	6.9	7.24	29.7	0.0028	0.187	0.190	0.0149
Red palposol sand with gravel mica, feldspar, kaolinite	20.7–22.2	2.95	6.7	3.09	15.1	0.0011	0.074	0.093	0.0086
Gray sand/silt mica, feldspar, kaolinite	25.2–25.8	2.36	4.7	7.37	15.9	0.0078	0.016	0.176	0.0122

† CEC, cation exchange capacity; SA, surface area; IOC, inorganic carbon; OC, organic carbon.

the presence of equimolar and 10 times equimolar phosphate concentrations under identical experimental conditions.

The theory and assumptions of the constant capacitance surface complexation model are discussed in detail in Goldberg (1992). In the application of the model to As(V) adsorption on sediments, the following surface complexation constants are considered:

$$\mathrm{SOH_{(s)} + H^+_{(aq)} \leftrightarrow SOH^+_{2(s)}} \qquad [2]$$

$$\mathrm{SOH_{(s)} \leftrightarrow SO^-_{(s)} + H^+_{(aq)}} \qquad [3]$$

$$\mathrm{SOH_{(s)} + H_3AsO_{4(aq)} \leftrightarrow SH_2AsO_{4(s)} + H_2O} \qquad [4]$$

$$\mathrm{SOH_{(s)} + H_3AsO_{4(aq)} \leftrightarrow SHAsO^-_{4(s)} + H^+_{(aq)} + H_2O} \qquad [5]$$

$$\mathrm{SOH_{(s)} + H_3AsO_{4(aq)} \leftrightarrow SAsO^{2-}_{4(s)} + 2H^+_{(aq)} + H_2O} \qquad [6]$$

where $\mathrm{SOH_{(s)}}$ represents reactive surface hydroxyl groups on oxides and aluminol groups on clay minerals contained in the sediments. Although, by convention, anion surface complexation reactions in the constant capacitance model are written in terms of the completely undissociated acids, the model application, nevertheless, contains the aqueous speciation reactions for As(V). Arsenate surface species are defined as monodentate because an improved fit of monodentate over bidentate surface species had been obtained in the model application to a large set of soils (Goldberg et al., 2005).

Equilibrium constant expressions for the surface complexation reactions are:

$$K_+(\mathrm{int}) = \frac{[\mathrm{SOH_2^+}]}{[\mathrm{SOH}][\mathrm{H^+}]}\exp(\mathrm{F}\psi/\mathrm{R}T) \qquad [7]$$

$$K_-(\mathrm{int}) = \frac{[\mathrm{SO^-}][\mathrm{H^+}]}{[\mathrm{SOH}]}\exp(-\mathrm{F}\psi/\mathrm{R}T) \qquad [8]$$

$$K^1_{\mathrm{As}}(\mathrm{int}) = \frac{[\mathrm{SH_2AsO_4}]}{[\mathrm{SOH}][\mathrm{H_3AsO_4}]} \qquad [9]$$

$$K^2_{\mathrm{As}}(\mathrm{int}) = \frac{[\mathrm{SHAsO_4^-}][\mathrm{H^+}]}{[\mathrm{SOH}][\mathrm{H_3AsO_4}]}\exp(-\mathrm{F}\psi/\mathrm{R}T) \qquad [10]$$

$$K^3_{\mathrm{As}}(\mathrm{int}) = \frac{[\mathrm{SAsO_4^{2-}}][\mathrm{H^+}]^2}{[\mathrm{SOH}][\mathrm{H_3AsO_4}]}\exp(-2\mathrm{F}\psi/\mathrm{R}T) \qquad [11]$$

where F is the Faraday constant (C $\mathrm{mol_c^{-1}}$), ψ is the surface potential (V), R is the molar gas constant (J $\mathrm{mol^{-1}\ K^{-1}}$), T is the absolute temperature (K), and square brackets represent concentrations (mol $\mathrm{L^{-1}}$). The exponential terms can be viewed as solid-phase activity coefficients that correct for any charge on the surface complexes. Mass balance of the surface functional groups is defined as:

$$[\mathrm{SOH}]_\mathrm{T} = [\mathrm{SOH}] + [\mathrm{SOH_2^+}] + [\mathrm{SO^-}] + [\mathrm{SH_2AsO_4}] + [\mathrm{SHAsO_4^-}] + [\mathrm{SAsO_4^{2-}}] \qquad [12]$$

and the charge balance equation is:

$$\sigma = [\mathrm{SOH_2^+}] - [\mathrm{SO^-}] - [\mathrm{SHAsO_4^-}] - 2[\mathrm{SAsO_4^{2-}}] \qquad [13]$$

where σ is the surface charge ($\mathrm{mol_c\ L^{-1}}$).

The computer program FITEQL 4.0 (Herbelin and Westall, 1999) was used to fit As(V) surface complexation constants to the experimental adsorption data. The program uses a nonlinear least squares optimization routine to fit equilibrium constants to experimental data and contains several surface complexation models of adsorption including the constant capacitance model. The FITEQL code can also be used to predict ion solution and surface speciation with previously determined equilibrium constant values. In the present application, As(V) surface complexation constants were determined using the assumption that adsorption takes place on one composite set of reactive surface functional groups. This is clearly a simplification since sediments are complex multisite mixtures containing a variety of surface sites. Therefore, the surface complexation constants obtained for the sediments become average composite values that include competing ion effects and mineralogical characteristics.

In addition to surface area, input parameter values for the model application to sediments were those that had been used by Goldberg et al. (2005) for soils: capacitance: C = 1.06 F $\mathrm{m^{-2}}$ (considered optimum for Al oxide by Westall and Hohl, 1980), protonation constant: $\log K_+(\mathrm{int}) = 7.35$, dissociation constant: $\log K_-(\mathrm{int}) = -8.95$ (averages of a literature compilation for Al and Fe oxides from Goldberg and Sposito, 1984), and total number of reactive surface hydroxyl groups: $[\mathrm{SOH}]_T$ = 21 μmol $\mathrm{L^{-1}}$ (Goldberg et al., 2005). Goodness-of-fit of the model application was evaluated using the overall variance V in Y:

$$V_Y = \frac{\mathrm{SOS}}{\mathrm{DF}} \qquad [14]$$

where SOS is the weighted sum of squares of the residuals and DF is the degrees of freedom.

RESULTS AND DISCUSSION

Arsenate adsorption as a function of solution As(V) concentration is indicated in Fig. 1 for all five sediment materials. The Langmuir adsorption isotherm equation was fit to the experimental data using nonlinear least-squares optimization as described by Kinniburgh (1986). The Langmuir equation provided good fits to the experimental adsorption data. The regression coefficients were statistically significant at the 99% level of confidence for all materials. Langmuir parameters for all five sediments are presented in Table 2. Not surprisingly, the maximum adsorption was greatest for the material having the highest clay content, depth 8.5 to 9.7 m. Native adsorbed As originally present in the sediments was determined from the 0 As addition and found to range from 0.02 to 0.03 mg $\mathrm{kg^{-1}}$.

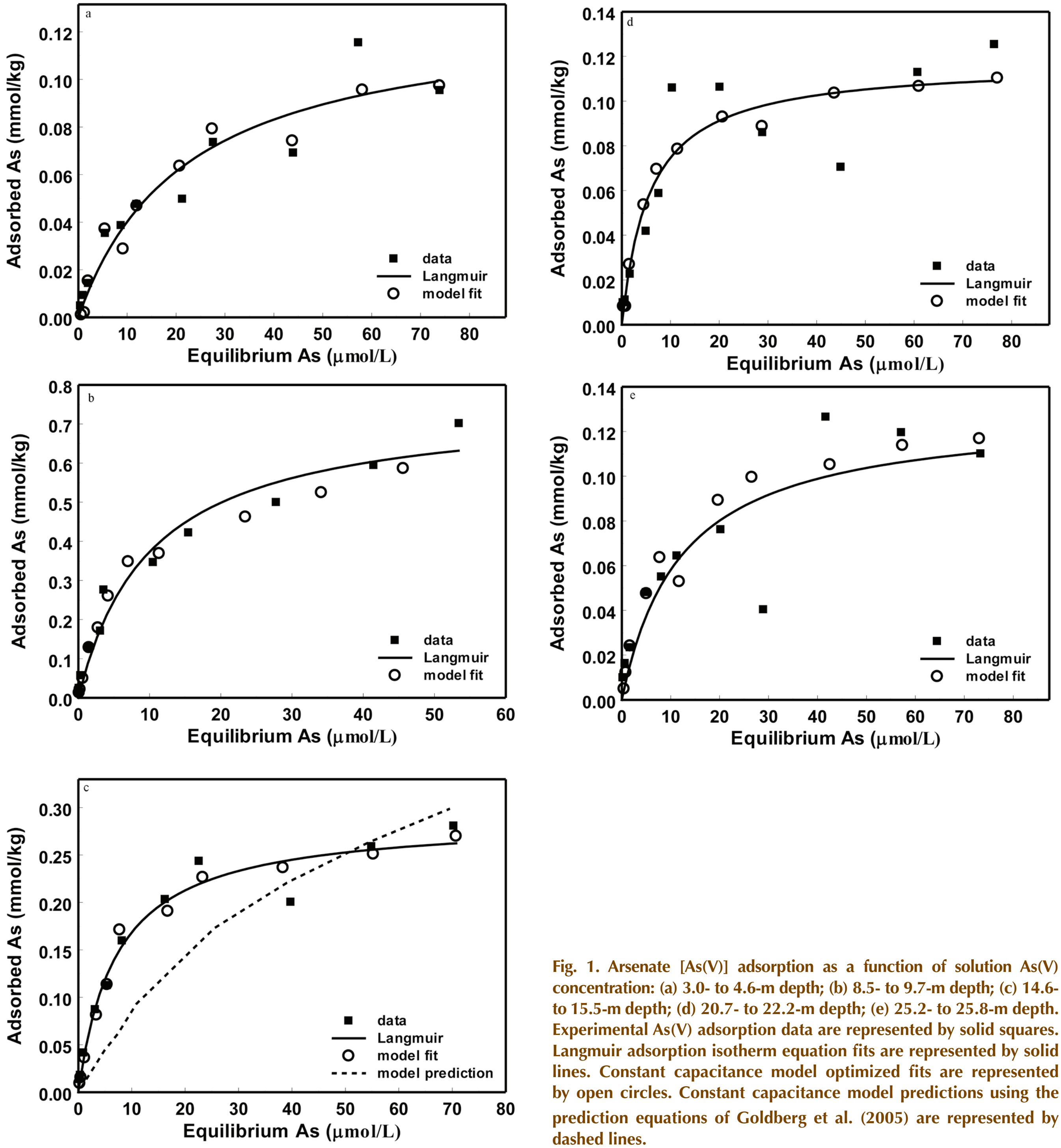

Fig. 1. Arsenate [As(V)] adsorption as a function of solution As(V) concentration: (a) 3.0- to 4.6-m depth; (b) 8.5- to 9.7-m depth; (c) 14.6- to 15.5-m depth; (d) 20.7- to 22.2-m depth; (e) 25.2- to 25.8-m depth. Experimental As(V) adsorption data are represented by solid squares. Langmuir adsorption isotherm equation fits are represented by solid lines. Constant capacitance model optimized fits are represented by open circles. Constant capacitance model predictions using the prediction equations of Goldberg et al. (2005) are represented by dashed lines.

This represents 1% of the As adsorbed from the lowest As treatment of 50 μg L^{-1}. For this reason, correction of the adsorption data for native adsorbed As was not needed.

The constant capacitance model was fit to the experimental As(V) adsorption data initially optimizing three monodentate surface complexation constants: log $K^{1}_{\mathrm{As}}(\mathrm{int})$, log $K^{2}_{\mathrm{As}}(\mathrm{int})$, and log $K^{3}_{As}(\mathrm{int})$ as had been done in the application of the constant capacitance model to describe As(V) adsorption on Tulare Lake Bed sediments (Gao et al., 2006). Figure 1 presents the ability of the constant capacitance model to fit As(V) adsorption isotherm data on

Table 2. Langmuir adsorption isotherm parameters.

Sample	Depth	*K*†	*M*	R^2
	m	L mg^{-1}	mg kg^{-1}	
Silty sand with gravel	3.0–4.6	0.00082	8.96±0.62	0.975**
Clay	8.5–9.7	0.00159	50.7±3.9	0.965**
Silty sand	14.6–15.5	0.00149	22.7±1.2	0.977**
Red palposol sand with gravel	20.7–22.2	0.00110	11.5±2.1	0.801**
Grey sand/silt	25.2–25.8	0.00127	10.2±1.0	0.929**

** Indicates statistical significance at the 99% level of confidence for the coefficient of determination, R^2, resulting from nonlinear least squares fitting of the Langmuir adsorption isotherm to the experimental adsorption data.

† *K* = parameter, *M* = maximum As adsorption.

Table 3. Surface complexation constants for the constant capacitance model.

Sample depth	Optimized				From prediction equations			
	log K^1_{As}	log K^2_{As}	log K^3_{As}	V_Y	log K^1_{As}	log K^2_{As}	log K^3_{As}	V_Y
m								
3.0–4.6		3.56±0.66	–4.49±0.89	0.04	9.09	2.14	–5.40	3.8
	9.46±0.05		–4.57±0.13	1.5				
8.5–9.7	10.36±0.15	3.20±0.33		0.5	10.04	3.15	–4.54	20.9
	10.07±0.05	2.73±0.71	–3.72±0.09	22.3				
14.6–15.5	10.23±0.13		–3.37±0.53	0.2	9.36	2.64	–4.97	7.5
	9.49±0.04		–4.87±0.09	7.7				
20.7–22.2	8.26±6.46	3.81±0.19		0.2	9.11	2.29	–5.33	3.0
	9.27±0.08		–4.15±0.14	1.8				
25.2–25.8	10.10±0.36	3.33±0.64		0.2	9.54	2.15	–5.42	2.8
	9.24±0.66		–5.20±0.25	1.1				
Average	9.61±0.66	3.33±0.41	–4.34±0.64					
Weighted average	9.64±0.04	3.46±0.06	–4.37±0.10					

the sediments. In all cases, the model fit provided a quantitative description of the adsorption data. Simultaneous optimization of all three As(V) constants was possible for only one material: the clay sample from the 8.5- to 9.7-m depth. Optimized values of the As(V) surface complexation constants are listed in Table 3. The constant values are in close agreement to those obtained for As(V) adsorption on Al and Fe oxides for the same monodentate As(V) surface species (Goldberg, 1986; Goldberg and Johnston, 2001). This finding is in agreement with the positive correlations previously observed between As(V) adsorption and extractable Al and Fe content of sediments (Wauchope and McDowell, 1984). The average values of the As(V) surface complexation constants optimized in this study of cored sediments are not statistically significantly different at the 95% level of confidence from the average values of these constants determined for surface samples of 44 soils by Goldberg et al. (2005): log $K^1_{\mathrm{As}}(\mathrm{int})$ = 10.31±0.99, log $K^2_{\mathrm{As}}(\mathrm{int})$ = 3.59±1.01, and log $K^3_{\mathrm{As}}(\mathrm{int})$ = –3.76±0.92. The average values of the optimized constants are presented for comparison purposes only and are not used to describe the experimental adsorption data. Table 3 also presents averages and standard deviations weighted to consider the uncertainties in the FITEQL optimized log *K* values using the method of Dzombak and Morel (1990). The applicability of either set of average surface complexation constants to describe As(V) adsorption on new sediments remains to be investigated.

The ability of the constant capacitance model to describe the adsorption isotherm data is very comparable in quality to that of the Langmuir adsorption isotherm equation (compare the constant capacitance model fit depicted by open circles to the solid line representing the Langmuir fit in Fig. 1). Both model applications contain two adjustable parameters. However, the constant capacitance model defines specific surface species and has the ability to predict changes related to solution pH. Therefore, it contains additional chemical information over the Langmuir equation without any increase in the number of adjustable parameters.

Arsenate adsorption as a function of solution pH is presented in Fig. 2 for all five sediments. Arsenate adsorption envelopes increased with increasing solution pH, exhibited a maximum around pH 4 to 5 and then decreased with increasing solution pH. Similar pH-dependent adsorption behavior had been observed previously for As(V) on the clay minerals: kaolinite, montmorillonite, and illite by Goldberg (2002). This observed similarity is not surprising since mica predominates the mineralogy of the sediments (see Table 1). Despite the variability in the experimental data, the constant capacitance model was able to describe As(V) adsorption as a function of solution pH by optimizing two or three of the As(V) surface complexation constants. These optimized results are presented as fits in Fig. 2.

The ability of the constant capacitance model to predict As(V) adsorption on the sediments as a function of solution pH and solution As(V) concentration was also evaluated using the general regression model developed for soils by Goldberg et al. (2005). In this approach, the As(V) surface complexation constants used in the model are predicted from easily measured soil chemical properties: cation exchange capacity (CEC), IOC content, OC content, Fe content, and surface area (SA) using the following equations:

$$\begin{aligned}\mathrm{Log}K^1_{\mathrm{As}} = {} & 10.639 - 0.107\ln(\mathrm{CEC}) + 0.078\ln(\mathrm{IOC}) - 0.365\ln(\mathrm{OC}) \\ & + 1.087\ln(\mathrm{Fe}) + 0.094\ln(\mathrm{SA})\end{aligned} \quad [15]$$

$$\begin{aligned}\mathrm{Log}K^2_{\mathrm{As}} = {} & 3.385 - 0.083\ln(\mathrm{CEC}) - 0.002\ln(\mathrm{IOC}) - 0.400\ln(\mathrm{OC}) \\ & + 1.360\ln(\mathrm{Fe}) + 0.018\ln(\mathrm{SA})\end{aligned} \quad [16]$$

$$\begin{aligned}\mathrm{Log}K^3_{\mathrm{As}} = {} & -2.579 - 0.296\ln(\mathrm{CEC}) + 0.115\ln(\mathrm{IOC}) - 0.570\ln(\mathrm{OC}) \\ & + 1.382\ln(\mathrm{Fe}) - 0.004\ln(\mathrm{SA})\end{aligned} \quad [17]$$

The predicted surface complexation constants are then used in the constant capacitance model to predict As(V) adsorption. The predicted values of the surface complexation constants are presented in Table 3. Using this procedure, the model predictions are independent of any experimental measurement of As(V) adsorption on the material and zero model parameters are optimized.

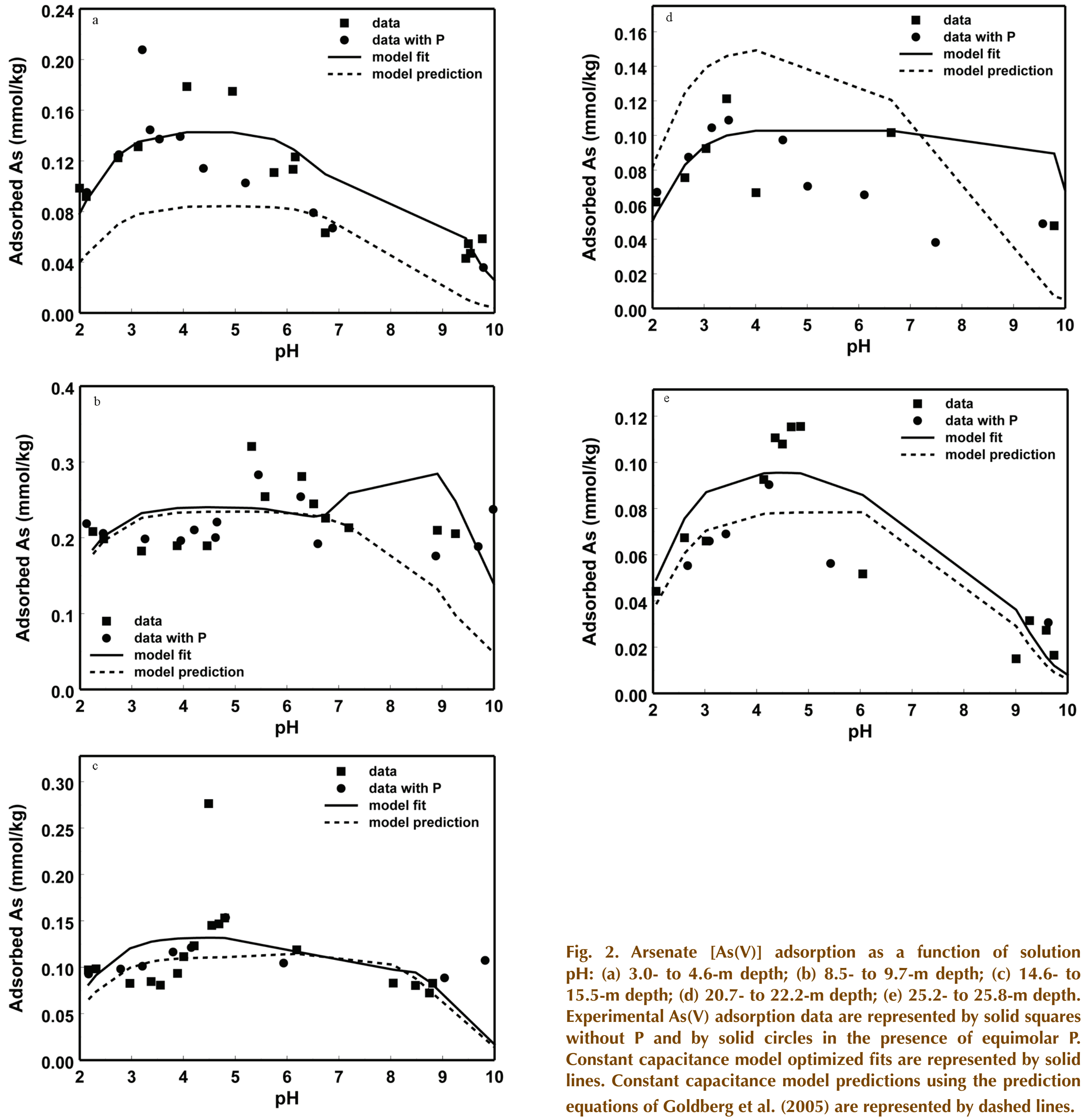

Fig. 2. Arsenate [As(V)] adsorption as a function of solution pH: (a) 3.0- to 4.6-m depth; (b) 8.5- to 9.7-m depth; (c) 14.6- to 15.5-m depth; (d) 20.7- to 22.2-m depth; (e) 25.2- to 25.8-m depth. Experimental As(V) adsorption data are represented by solid squares without P and by solid circles in the presence of equimolar P. Constant capacitance model optimized fits are represented by solid lines. Constant capacitance model predictions using the prediction equations of Goldberg et al. (2005) are represented by dashed lines.

The relative precision and absolute accuracy statistics for the independent predictions of the five sediments are given in Table 4. The average root mean square error, ARMSE, is:

$$\mathrm{ARMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\mathrm{Ads_e} - \mathrm{Ads_p}\right)^2} \qquad [18]$$

where N is the number of data points, $\mathrm{Ads_e}$ is the experimentally determined As(V) adsorption, and $\mathrm{Ads_p}$ is the As(V) adsorption predicted using the regression equations of Goldberg et al. (2005). This statistic represents the square root of both prediction variances in the average squared bias effects (Myers and Montgomery, 2002) which reflect the relative precision and

Table 4. Relative precision and absolute accuracy statistics for experimentally derived vs. constant capacitance model predicted arsenate [As(V)] adsorption levels for the sediments using the prediction equations of Goldberg et al. (2005).

Depth	Correlation coefficient	ARMSE†	CIp
m		mmol kg^{-1}	%
3.0–4.6	0.864	0.051	20.88
8.5–9.7	–0.322	0.126	15.74
14.6–15.5	0.108	0.072	19.62
20.7–22.2	0.784	0.049	20.27
25.2–25.8	0.803	0.029	14.50

† ARMSE = average root mean square error, CIp, coefficient-of-imprecision.

absolute accuracy between the experimental and the predicted As(V) adsorption data. The coefficient-of-imprecision, CIp, is a coefficient-of-variation type statistic:

$$\mathrm{CIp} = \frac{100\mathrm{ARMSE}}{\left(\overline{Y_e}+\overline{Y_p}\right)/2} \qquad [19]$$

where $\overline{Y_e}$ is the mean experimental As(V) adsorption and $\overline{Y_p}$ is the mean predicted As(V) adsorption. The CIp statistic values for sediments (Table 4) are smaller than the average value (CIp = 33.3%) obtained for the 44 calibration soils used to develop the prediction equations see Table 5 of Goldberg et al. (2005).

Quantitative prediction of the adsorption isotherm data was achieved only for the 14.6- to 15.5-m depth, if the outlier data point at pH 4.5 is discounted (see Fig. 1c). The failure of the predictive model of Goldberg et al. (2005) to accurately predict As(V) adsorption on these materials is not entirely surprising since the OC contents for the other four sediments fall below the OC content range of the soils used to develop the prediction equations. Nevertheless, for the adsorption envelope data, the model predictions always predicted the pH values of the adsorption maxima and for the most part the shapes of the adsorption envelopes as a function of solution pH. For the 8.5- to 9.7-m depth below pH 7 and the 14.6- to 15.5- and 25.2- to 25.8-m depths, the predicted As(V) adsorptions were comparable in quality to those obtained from optimized model fitting (compare the model fits depicted by solid lines to the model predictions represented by dashed lines). This is also evidenced by the smaller values of the CIp statistic for these three depths (Table 4). Values of the goodness-of-fit criterion, V_Y, were also very comparable for the optimized fits and the model predictions (see Table 3). The chemical properties of the 8.5- to 9.7- and 25.2- to 25.8-m depths fall out of range of the soil properties only for OC content; while the Al and Fe oxide contents for the 3.0- to 4.6- and 20.7- to 22.2-m depths were also below those for the range of soils used to develop the prediction equations. This circumstance may explain the poor quality of the model predictions for these two sediments.

It is encouraging that the prediction approach developed by Goldberg et al. (2005) for soils was able to quantitatively predict As(V) adsorption as a function of solution As(V) concentration and solution pH on a sediment whose chemical properties fell within the soil ranges, the 14.6- to 15.5-m depth. Given this result, the adsorption prediction, which is independent of any experimental measurement of As(V) adsorption on the sediment, is suitable for transport modeling applications and will be used to describe As movement in soil columns packed with these sediment materials.

Inorganic phosphate competes so strongly with As(V) that it has been recommended as an extractant to determine potential As(V) release from sediments to ground water (Gao et al., 2004). For this reason, As(V) adsorption envelopes were additionally determined in the presence of equimolar (0.02 mmol L^{-1} equivalent to 1.9 mg PO_4 L^{-1}) phosphate concentrations. As evident from Fig. 2, As(V) adsorption was unaffected by the presence of equimolar phosphate concentrations throughout the pH range investigated (compare the solid squares with the solid circles). Depression of As(V) adsorption was observed in the presence of phosphate at 10 times the molar As(V) concentration, especially at low solution pH (data not shown). However, inorganic phosphate concentrations in the ground waters associated with these sediments are very low, <0.02 mg PO_4 L^{-1} (Izbicki, personal communication, 2012). Therefore, the native phosphate concentrations (<0.21 μmol L^{-1}) will not interfere with the effectiveness of the sediments to adsorb As(V) and thereby remediate high-As waters during recharge.

The constant capacitance surface complexation model was able to fit As(V) adsorption as a function of solution As concentration and solution pH on five alluvial sediments. The quality of the fit of the chemical surface complexation model to the experimental adsorption isotherm data was comparable to that of the empirical Langmuir equation using the same number of adjustable parameters. For one of the sediments the constant capacitance model was able to accurately predict As(V) adsorption using the prediction equations of Goldberg et al. (2005). Prediction of As(V) adsorption was not good for the other sediments, likely because their chemical properties fell outside of the range for the soils used to develop the prediction equations. Arsenate adsorption on the sediments was unaffected by equimolar phosphate concentrations indicating that low amounts of native phosphate will not interfere with the effectiveness of As(V) remediation by the sediments during recharge. The chemical properties, especially the organic matter content, of most sediments are outside the range of soil chemical properties used to develop the prediction equations of Goldberg et al. (2005). Therefore, additional data for samples that fall within the range for unconsolidated sediments are required to be able to develop prediction equations.

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