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Chemical Equilibrium and Reaction Modeling of Arsenic and Selenium in Soils

Sabine Goldberg

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High concentrations of the trace elements arsenic (As) and selenium (Se) in soils pose a threat to agricultural production and the health of humans and animals. As is toxic to both plants and animals. Se, despite being an essential micronutrient for animal nutrition, is potentially toxic because the concentration range between deficiency and toxicity in animals is narrow. Seleniferous soils release enough Se to produce vegetation toxic to grazing animals. Such soils occur in the semiarid states of the western United States (Lakin, 1961). Concentrations of As and Se in soils and waters can become elevated as a result of discharge from petroleum refineries, disposal of fly ash, mining activities, geothermal discharge, and mineral oxidation and dissolution. Enrichment of As can also occur through the application of arsenical pesticides (Wauchope, 1983) and poultry manures from chickens fed the arsenical additive, roxarsone (Garbarino et al., 2003). Elevated concentrations of As and Se are found in agricultural drainage waters from some soils in arid regions. In recognition of the hazards that these trace elements pose to the welfare of humans and animals, the U.S. Environmental Protection Agency (EPA) has set the drinking water standard at 10 ppb for As and 50 ppb for Se.

The concentrations of As and Se in soil solution may be affected by various chemical processes and soil factors. These include soil solution chemistry, methylation and volatilization reactions, precipitation–dissolution reactions,

oxidation–reduction reactions, and adsorption–desorption reactions. The objective of this chapter is to discuss the soil factors and chemical processes that may control soil solution concentrations of the trace elements As and Se.

Inorganic Chemistry of As and Se in Soil Solution

The dominant inorganic As solution species are As(III) (arsenite) and As(V) (arsenate), while Se(IV) (selenite) and Se(VI) (selenate) are the dominant inorganic Se species in soil solution (Adriano, 1986). For both elements, toxicity depends on the oxidation state, with the lower redox state considered more toxic: that is, arsenite is more toxic than arsenate (Penrose, 1974) and selenite is more toxic than selenate (Harr, 1978).

At most natural pHs, arsenite is present in solution predominantly as H_3AsO_3 because the pK_a values for arsenious acid are high: $\text{pK}_a^1 = 9.2$, $\text{pK}_a^2 = 12.7$. Solution arsenate occurs as H_2AsO_4^- and HAsO_4^{2-} because the pK_a values for arsenic acid are $\text{pK}_a^1 = 2.3$, $\text{pK}_a^2 = 6.8$, and $\text{pK}_a^3 = 11.6$. Solution selenite occurs as HSeO_3^- and SeO_3^{2-} because the pK_a values for selenious acid are $\text{pK}_a^1 = 2.5$ and $\text{pK}_a^2 = 7.3$. Selenate is present in solution as SeO_4^{2-} because the pK_a values for selenic acid are low: $\text{pK}_a^1 \approx -3$ and $\text{pK}_a^2 = 1.9$. Because the kinetics of As and Se redox transformations are relatively slow, both oxidation states are often found in soil solution, regardless of redox conditions (Masscheleyn, Delaune, and Patrick, 1990, 1991a). Under highly reducing conditions, Se occurs in solution primarily as HSe^- because the pK_a values for hydrogen selenide are $\text{pK}_a^1 = -1.1$ and $\text{pK}_a^2 = 15.0$ (Elrashidi et al., 1987).

In typical waters, As forms few aqueous arsenite or arsenate complexes (Cullen and Reimer, 1989). The formation of metal arsenate ion-pairs has been suggested from ion chromatography but their role is expected to be minor (Lee and Nriagu, 2007). In anaerobic aquatic environments, arseno-carbonate solution complexes $\text{As}(\text{CO}_3)_2^-$, $\text{As}(\text{CO}_3)^+$, and $\text{As}(\text{CO}_3)(\text{OH})_2^-$ were proposed to be the most stable inorganic As species (Kim et al., 2000). Subsequently, Neuberger and Helz (2005) showed that As(III) carbonate solution complexes would be negligible at carbonate concentrations found in most natural waters but could be significant, although minor, in extremely carbonate-rich, high ionic strength waters, such as those of evaporative basins. Solution complexes of selenite and selenate appear to make minor contributions to dissolved Se in agricultural soils (Elrashidi et al., 1987).

Methylation and Volatilization Reactions

Methylation reactions involve the addition or substitution of methyl groups, $-\text{CH}_3$, to substrates. Methylated compounds of As that can form in

soils include monomethylarsenic acid ($\text{CH}_3\text{AsO}_3\text{H}_2$), dimethylarsenic acid ($(\text{CH}_3)_2\text{AsO}_2\text{H}$), trimethylarsine oxide, $(\text{CH}_3)_3\text{AsO}$, and the methylarsines: monomethylarsine (CH_3AsH_2), dimethylarsine, $(\text{CH}_3)_2\text{AsH}$, and trimethylarsine $(\text{CH}_3)_3\text{As}$. The various arsine compounds, including arsine (AsH_3), are volatile and tend to escape to the atmosphere (Gao, Tanji, and Goldberg, 1998). Methylated Se compounds are primarily the volatile species dimethylselenide (DMSe) and dimethyldiselenide (DMDS₂Se) (Séby et al., 1998), although the nonvolatile dimethylselenium ion (DMSe^{+•}-R) has been detected in surface waters (Cooke and Bruland, 1987).

Historically, various organic arsenicals have been used as herbicides on cotton and other agricultural crops and on lawns, golf courses, and highway rights-of-way. These herbicides include monosodium methanearsonate (MSMA), disodium methanearsonate (DSMA), calcium acid methanearsonate (CAMA), and cacodylic acid, which is dimethylarsenic acid. Due to toxicity concerns, the U.S. Environmental Protection Agency cancelled all agricultural uses of arsenical herbicides except MSMA as of September 30, 2009. Use of MSMA on golf courses, sod farms, and highway rights-of-way will be prohibited after December 31, 2013. Use of MSMA on cotton, where no alternative herbicide presently exists, will be permitted and reviewed beginning in 2013.

Speciation studies of As and Se in reservoir sediment suspensions under controlled redox and pH conditions found no evidence of organic arsenicals; however, methylated Se compounds were detected under oxidizing and moderately reducing conditions (Masscheleyn et al., 1991b). In soils, bacteria, fungi, and algae can convert organic and inorganic arsenicals to form volatile arsines. Microorganisms can also mineralize organic As forms to produce inorganic As via demethylation reactions. The relative rates of these transformations can control As cycling and accumulation in soils and are functions of As form, As concentration, soil moisture, soil temperature, and availability of organic carbon energy sources for the microbial population (Gao and Burau, 1997).

Organic and inorganic selenium forms can be methylated to the volatile forms, DMSe and DMDS₂Se, by microbial action in soils under both aerobic and anaerobic conditions (Doran and Alexander, 1977). Addition of a supplemental carbon energy source resulted in gaseous release of indigenous Se from soils high in Se (Francis, Duxbury, and Alexander, 1974). Proteins were found to dramatically stimulate Se biomethylation in evaporation pond water, indicating that the process is protein peptide-limited rather than ammonium-, amino acid-, or carbon-limited (Thompson-Eagle and Frankenberger, 1990). The rate of gaseous Se evolution from soil is highly dependent on Se content, soil moisture, soil temperature, aeration status, and availability of organic carbon (Frankenberger and Karlson, 1992).

Precipitation–Dissolution Reactions

Precipitation and dissolution reactions of As and Se solid phases are processes that may influence the soil solution concentrations of these elements. Under oxidizing conditions, $\text{Ca}_3(\text{AsO}_4)_2$ and $\text{Mn}_3(\text{AsO}_4)_2$ are the most stable As minerals in alkaline soils, while in acid soils $\text{Fe}_3(\text{AsO}_4)_2$, FeAsO_4 , and AlAsO_4 are the least soluble minerals (Sadiq, 1997). Soils that had been contaminated historically with lead arsenate were found to be supersaturated with $\text{Pb}_3(\text{AsO}_4)_2$ and $\text{Mn}_3(\text{AsO}_4)_2$ (Hess and Blanchar, 1976). In reduced, anoxic sediments, As(III) sulfides (i.e., As_2O_3 and FeAsS) are the most stable As minerals (Welch et al., 2000). Speciation calculations of As in reservoir sediment suspensions under controlled redox and pH conditions found that they were undersaturated by several orders of magnitude with respect to FeAsO_4 , AlAsO_4 , $\text{Ca}_3(\text{AsO}_4)_2$, and $\text{Mn}_3(\text{AsO}_4)_2$, and As solubility was not limited by the formation of As_2O_3 and FeAsS (Masscheleyn et al., 1991b). Chemical speciation calculations of As in shallow groundwater in the Carson Desert (Nevada) found undersaturation with respect to As minerals (Welch and Lico, 1998).

Selenate minerals are much too soluble to persist in aerated soils (Elrashidi et al., 1987). In acid soils, MnSeO_3 is the most stable selenite mineral, while PbSeO_3 is the least soluble mineral in alkaline soil (Elrashidi et al., 1987). Speciation calculations of Se in reservoir sediment suspensions under controlled redox and pH conditions found undersaturation with respect to metal selenates and selenites (Masscheleyn et al., 1991b). Selenium solubility is governed by precipitation reactions of metal selenides: FeSe and FeSe_2 and elemental Se under reducing conditions (Séby et al., 1998). Under reducing conditions, elemental Se is thermodynamically stable over a wide solution pH range (Masscheleyn et al., 1991b). Elemental Se exists as three allotropes: the red and black forms are amorphous and are more likely to occur in soils than the gray hexagonal crystalline form (Geering et al., 1968).

Oxidation–Reduction Reactions

Under oxic conditions, arsenate is the thermodynamically stable and dominant As species in soil solution, while arsenite is the thermodynamically stable and most abundant solution form under anoxic conditions. At intermediate pH and suboxic conditions, both As(III) and As(V) redox states coexist (Sadiq, 1997). Under highly reducing conditions, arsine (AsH_3) may be formed (Korte and Fernando, 1991). Under oxidizing conditions, selenate is the thermodynamically stable and dominant species of Se in soil solution, while selenite is the thermodynamically stable and most abundant form under

reducing conditions (Séby et al., 1998). Under highly reducing conditions, the thermodynamically stable form of Se is selenide (Elrashidi et al., 1987).

Most oxidation–reduction reactions are mediated by microorganisms. Microbes act as kinetic reaction mediators but cannot promote thermodynamically unfavorable reactions (Séby et al., 1998). Oxidation of arsenite to arsenate was observed by bacteria isolated from soil such as *Alcaligenes* (Osborne and Ehrlich, 1976). Various bacteria isolated from river water have been shown to reduce arsenate to arsenite (Freeman, 1985). Reduction of arsenate to arsenite was also achieved by a *Clostridium* species isolated from an As-contaminated soil (Langner and Inskeep, 2000).

Under anaerobic conditions in sediments, bacteria can reduce selenate to selenite and elemental Se (Oremland et al., 1990). The capacity for selenate reduction was found to be widespread and to occur in diverse sediments, including those uncontaminated with Se (Steinberg and Oremland, 1990). Selenate-reducing bacterial communities exhibit broad phylogenetic diversity (Lucas and Hollibaugh, 2001). Oxidation of refractory Se(0) into soluble selenate upon reexposure to air was observed for contaminated sediments that had been deposited under strongly reducing conditions and/or previously ponded (Tokunaga, Pickering, and Brown, 1996; Zawislanski and Zavarin, 1996).

Oxidation of arsenite to arsenate in some aquatic systems can occur predominantly via abiotic processes (Oscarson, Huang, and Liaw, 1980). Removal of manganese oxides from lake sediments indicated that these minerals were responsible for As(III) oxidation (Oscarson, Huang, and Liaw, 1981). As(III) oxidation rates in aquifer samples increased with increasing manganese oxide content and were unaffected by anaerobic and sterile conditions (Amirbahman et al., 2006). Similarly, abiotic oxidation of selenite occurs on the surfaces of the synthetic manganese oxide, birnessite (Scott and Morgan, 1996). Abiotic reduction of Se(VI) to Se(IV) and Se(0) can occur in the presence of a mixed Fe(II,III) oxide called green rust that is present in many sub-oxic soils and sediments (Myneni, Tokunaga, and Brown, 1997).

Adsorption–Desorption Reactions

Adsorption is the accumulation of a chemical species at the solid–solution interface to form a two-dimensional molecular surface. Adsorption reactions on soil surfaces often control the concentration of As and Se in soil solution. Arsenic adsorption is significantly positively correlated with the clay, Al and Fe oxide, organic carbon, and inorganic carbon content of soils (Wauchope, 1975; Livesey and Huang, 1981; Elkhatib, Bennett, and Wright, 1984; Yang et al., 2002). Selenium adsorption is also significantly positively correlated with these same soil constituents (Lévesque, 1974; Elsokkary, 1980; Vuori et al., 1989, 1994).

For both As and Se, adsorption behavior in soils is determined by redox state. As(V) and As(III) both adsorb on soil surfaces. As(V) adsorption is greater than As(III) adsorption in the acid pH range, while at alkaline pH values, As(III) adsorption exceeds As(V) adsorption (Raven, Jain, and Loeppert, 1998; Goldberg and Johnston, 2001). Selenite adsorbs strongly on soil surfaces, while Se(VI) adsorbs weakly or not at all (Neal and Sposito, 1989). In contrast, Se(VI) adsorption at very high Se additions was consistently higher than Se(IV) adsorption on various soils (Singh, Singh, and Relan, 1981).

Specific adsorption of anions forms strong surface complexes that contain no water molecules between the adsorbing ion and the surface site and are called inner-sphere surface complexes. Outer-sphere surface complexes, on the other hand, contain at least one water molecule between the adsorbing anion and the surface site. Outer-sphere complexes are less strong than inner-sphere complexes. Arsenate has been observed to form inner-sphere complexes on goethite, maghemite, hematite, gibbsite, and amorphous Al and Fe oxides using various spectroscopic techniques (Waychunas et al., 1993; Fendorf et al., 1997; Goldberg and Johnston, 2001; Catalano et al., 2007; Morin et al., 2008). Similarly, arsenite was observed to form inner-sphere complexes on goethite, lepidocrocite, maghemite, hematite, and amorphous Fe oxide (Manning, Fendorf, and Goldberg, 1998; Ona-Nguema et al., 2005; Morin et al., 2008). A mixture of inner-sphere and outer-sphere surface complexes was observed for As(V) adsorption on hematite (Catalano et al., 2008) and As(III) adsorption on γ -Al₂O₃ (Arai, Elzinga, and Sparks, 2001).

Extended x-ray absorption fine structure spectroscopy investigations have observed selenate to form inner-sphere complexes on goethite (Manceau and Charlet, 1994) and hematite (Peak and Sparks, 2002). Various spectroscopic investigations have similarly observed selenite to form inner-sphere complexes on goethite, hematite, gibbsite, and amorphous Al and Fe oxide (Manceau and Charlet, 1994; Papelis et al., 1995; Peak, 2006; Catalano et al., 2006). A mixture of inner-sphere and outer-sphere surface complexes was observed for Se(IV) adsorption on corundum (Peak, 2006) and for Se(VI) adsorption on goethite, corundum, and amorphous Fe and Al oxide (Wijnja and Schulthess, 2000; Peak and Sparks, 2002; Peak, 2006). Predominantly outer-sphere surface complexes were observed for Se(VI) adsorption on γ -Al₂O₃ (Wijnja and Schulthess, 2000) and amorphous Al oxide (Peak, 2006).

Modeling of Adsorption by Soils: Empirical Models

Adsorption reactions by soils have historically been described using empirical adsorption isotherm equations. The most popular adsorption isotherms are the linear, Freundlich, and Langmuir equations. Typically, these equations

are very good at describing experimental data despite their lack of theoretical basis. Their popularity stems in part from their simplicity and from the ease of estimation of their adjustable parameters.

The adsorption isotherm equation is a linear function and is written in terms of the distribution coefficient, K_d :

$$x = K_d c \quad (3.1)$$

where x is the amount of ion adsorbed per unit mass of soil and c is the equilibrium solution ion concentration. Because of the linear assumption, this equation usually describes adsorption data only over a very restricted solution concentration range. The linear adsorption isotherm equation has been used to describe As(V) adsorption by contaminated and uncontaminated Belgian soils (De Brouwere, Smolders, and Merckx, 2004) and Se(IV) adsorption by a calcareous soil from China (Wang and Liu, 2005).

The Freundlich adsorption equation is a nonlinear isotherm whose use implies heterogeneity of adsorption sites. The Freundlich isotherm equation is

$$x = K c^\beta \quad (3.2)$$

where K is an affinity parameter and β is a heterogeneity parameter; the smaller the value of β , the greater the heterogeneity (Kinniburgh, 1985). When $\beta = 1$, the Freundlich equation reduces to a linear adsorption isotherm. Although the Freundlich equation is strictly valid only for ion adsorption at low solution ion concentration (Sposito, 1984), it has often been used to describe ion adsorption by soils over the entire concentration range investigated. The Freundlich adsorption isotherm equation has been used to describe As(III) (Elkhatib, Bennett, and Wright, 1984) and As(V) adsorption (Zhang and Selim, 2005) by soils and Se(IV) adsorption by alluvium, sediment, and basalt (Del Debbio, 1991).

The Langmuir adsorption isotherm equation was originally developed to describe gas adsorption onto clean surfaces. The Langmuir isotherm equation is

$$x = \frac{x_m K c}{1 + K c} \quad (3.3)$$

where x_m is the maximum ion adsorption per unit mass of soil and K is an affinity parameter related to the bonding energy of the ion to the surface. The Langmuir isotherm can be derived theoretically based on evaporation and condensation rates, assuming a finite number of uniform adsorption sites and the absence of any lateral interaction between adsorbed species

(Adamson, 1976). Despite the fact that these assumptions are violated in soils, the Langmuir isotherm has often been used to describe ion adsorption reactions by soils. In many studies, the Langmuir equation is only able to describe adsorption for low solution ion concentrations. The Langmuir adsorption isotherm equation has been used to describe As(V) adsorption by Chinese soils (Jiang et al., 2005) and Se(IV) and Se(IV) adsorption by diverse soils (Singh, Singh, and Relan, 1981).

Modeling of Adsorption by Soils: Constant Capacitance Model

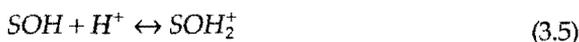
The constant capacitance model is a chemical surface complexation model that was developed to describe ion adsorption at the oxide–solution interface (Schindler et al., 1976; Stumm, Kummert, and Sigg, 1980). As is characteristic of surface complexation models, this chemical model explicitly defines surface species, chemical reactions, equilibrium constants, mass balances, charge balance, and electrostatic potentials. The reactive surface site is defined as SOH, an average reactive surface hydroxyl ion bound to a metal, S, in the oxide mineral. The constant capacitance model has been extended to describe the adsorption of trace element anions on soil surfaces. The applications of the model to predict arsenate and selenite adsorption by soils will be presented (Goldberg et al., 2005, Goldberg, Lesch, and Suarez, 2007).

The constant capacitance model contains the following assumptions: (1) all surface complexes are inner-sphere; (2) anion adsorption occurs via ligand exchange with reactive surface hydroxyl groups; (3) no surface complexes are formed with background electrolyte ions; (4) the relationship between surface charge, σ ($\text{mol}_c\text{L}^{-1}$), and surface potential, ψ (V), is linear and is given by

$$\sigma = \frac{CSa}{F} \psi \quad (3.4)$$

where C (F.m^{-2}) is the capacitance, S ($\text{m}^2.\text{g}^{-1}$) is the surface area, a (g.L^{-1}) is the solid concentration, and F (C.mol_c^{-1}) is the Faraday constant. The structure of the solid–solution interface for the constant capacitance model is depicted in Figure 3.1.

In the constant capacitance model, the protonation and dissociation reactions of the reactive surface site are



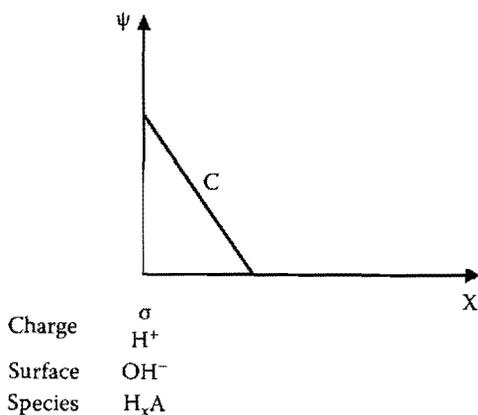
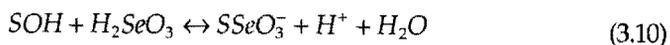
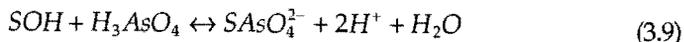
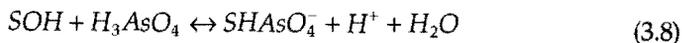
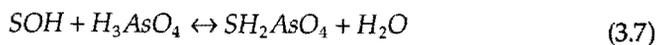


FIGURE 3.1
Structure of the solid-solution interface for the constant capacitance model.



For soils, the SOH reactive site is generic, representing reactive hydroxyl groups including aluminol and silanol groups on the edges of clay mineral particles. The surface complexation reactions for the adsorption of arsenate and selenite are



The equilibrium constants for the above reactions are

$$K_+(int) = \frac{[SOH_2^+]}{[SOH][H^+]} \exp(F\Psi / RT) \quad (3.11)$$

$$K_{-}(\text{int}) = \frac{[\text{SO}^-][\text{H}^+]}{[\text{SOH}]} \exp(-F\psi / RT) \quad (3.12)$$

$$K_{As}^1(\text{int}) = \frac{[\text{SH}_2\text{AsO}_4]}{[\text{SOH}][\text{H}_3\text{AsO}_4]} \quad (3.13)$$

$$K_{As}^2(\text{int}) = \frac{[\text{SHAsO}_4^-][\text{H}^+]}{[\text{SOH}][\text{H}_3\text{AsO}_4]} \exp(-F\psi / RT) \quad (3.14)$$

$$K_{As}^3(\text{int}) = \frac{[\text{SAsO}_4^{2-}][\text{H}^+]^2}{[\text{SOH}][\text{H}_3\text{AsO}_4]} \exp(-2F\psi / RT) \quad (3.15)$$

$$K_{Se}(\text{int}) = \frac{[\text{SSeO}_3^-][\text{H}^+]}{[\text{SOH}][\text{H}_2\text{SeO}_3]} \exp(-F\psi / RT) \quad (3.16)$$

In the constant capacitance model, charged surface complexes create an average electric potential field at the solid surface. These coulombic forces provide the dominant contribution to the solid-phase activity coefficients because the contribution from other forces is considered equal for all surface complexes. In this manner, the exponential terms can be considered solid-phase activity coefficients that correct for the charges on the surface complexes (Sposito, 1983).

The mass balance of the surface reactive site for arsenate adsorption is

$$\begin{aligned} [\text{SOH}]_T &= [\text{SOH}] + [\text{SOH}_2^+] + [\text{SO}^-] + [\text{SH}_2\text{AsO}_4] \\ &+ [\text{SHAsO}_4^-] + [\text{SAsO}_4^{2-}] \end{aligned} \quad (3.17)$$

and for selenite adsorption is

$$[\text{SOH}]_T = [\text{SOH}] + [\text{SOH}_2^+] + [\text{SO}^-] + [\text{SSeO}_3^-] \quad (3.18)$$

where SOH_T is the total number of reactive sites. Charge balance for arsenate adsorption is

$$\sigma = [\text{SOH}_2^+] - [\text{SO}^-] - [\text{SHAsO}_4^-] - 2[\text{SAsO}_4^{2-}] \quad (3.19)$$

and for selenite adsorption it is

$$\sigma = [\text{SOH}_2^+] - [\text{SO}^-] - [\text{SSeO}_3^-] \quad (3.20)$$

The above systems of equations can be solved using a mathematical approach. The computer program FITEQL 3.2 (Herbelin and Westall, 1996) is an iterative nonlinear least squares optimization program that was used to fit equilibrium constants to experimental adsorption data using the constant capacitance model. The FITEQL 3.2 program was also used to predict chemical surface speciation using previously determined equilibrium constant values. The stoichiometry of the equilibrium problem for the application of the constant capacitance model to arsenate and selenite adsorption is shown in Table 3.1. The assumption that arsenate and selenite adsorptions take place on only one set of reactive surface sites is clearly a gross simplification because soils are complex multisite mixtures of a variety of reactive sites. Therefore, the surface complexation constants determined for soils will

TABLE 3.1
Stoichiometry of the Equilibrium Problem
for the Constant Capacitance Model

Species	Components			
	SOH	e ^{Fw/RT}	H _x A ^a	H ⁺
H ⁺	0	0	0	1
OH ⁻	0	0	0	-1
SOH ₂ ⁺	1	1	0	1
SOH	1	0	0	0
SO ⁻	1	-1	0	-1
H ₃ AsO ₄	0	0	1	0
H ₂ AsO ₄ ⁻	0	0	1	-1
HAsO ₄ ²⁻	0	0	1	-2
AsO ₄ ³⁻	0	0	1	-3
H ₂ SeO ₃	0	0	1	0
HSeO ₃ ⁻	0	0	1	-1
SeO ₃ ²⁻	0	0	1	-2
SH ₂ AsO ₄	1	0	1	0
SHAsO ₄ ⁻	1	-1	1	-1
SAsO ₄ ²⁻	1	-2	1	-2
SSeO ₃ ⁻	1	-1	1	-1

^a A is an anion and x is the number of protons in the undissociated form of the acid.

be average composite values that include soil mineralogical characteristics and competing ion effects.

The total number of reactive surface sites, SOH_T (mol.L^{-1}), is an important input parameter in the constant capacitance model. It is related to the reactive surface site density, N_s (sites.nm^{-2}):

$$\text{SOH}_T = \frac{S_a 10^{18}}{N_A} N_s \quad (3.21)$$

where N_A is Avogadro's number. Values of surface site density can be determined using a wide variety of experimental methods, including potentiometric titration and maximum ion adsorption. Site density results can vary by an order of magnitude between methods. The ability of the constant capacitance model to describe anion adsorption is dependent on the reactive site density (Goldberg, 1991). A surface site density value of 2.31 sites per nm^{-2} was recommended for natural materials by Davis and Kent (1990). This value has been used in the constant capacitance model to describe selenite adsorption by soils. A reactive surface site number of $21.0 \mu\text{mol.L}^{-1}$ was used to describe arsenate adsorption by soils.

For application of the constant capacitance model to soils, the capacitance value was chosen from the literature. To describe arsenate and selenite adsorption, the capacitance was set at 1.06 F.m^{-2} , considered optimum for aluminum oxide by Westall and Hohl (1980). For the development of self-consistent parameter databases, a constant value of capacitance is necessary.

Protonation and dissociation constant values were obtained from the literature for arsenate adsorption and by computer optimization for selenite adsorption. To describe arsenate adsorption, the protonation constant, $\log K_a$, was set to 7.35 and the dissociation constant, $\log K$, was set to -8.95 . These values are averages of a literature compilation of protonation–dissociation constants for aluminum and iron oxides obtained by Goldberg and Sposito (1984).

Surface complexation constants for arsenate and selenite adsorption by soils were obtained using computer optimization. An evaluation of the goodness of model fit can be obtained from the overall variance V in Y :

$$V_y = \frac{\text{SOS}}{DF} \quad (3.22)$$

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

Recently, general prediction models have been developed to obtain anion surface complexation constants from easily measured soil chemical properties—cation exchange capacity, surface area, organic carbon, inorganic carbon, Fe oxide, and Al oxide content—that correlate with soil adsorption

capacity for trace element anions. This approach has been successfully applied to predict adsorption of arsenate (Goldberg et al., 2005) and selenite (Goldberg, Lesch, and Suarez, 2007) adsorption by soils. In this approach, arsenate and selenite adsorption behavior by soils is predicted independently of experimental adsorption measurements using the general prediction models.

Trace element adsorption was investigated using 53 surface and subsurface samples from soils belonging to 6 different soil orders chosen to provide a wide range of soil chemical properties. Soil chemical characteristics are listed in Table 3.2. Soils Altamont to Yolo constitute a set of 21 soil series from the southwestern United States, primarily California. This set of soils consists mainly of alfisols and entisols. Soils Bernow to Teller constitute a set of 17 soil series from the midwestern United States, primarily Oklahoma. This set of soils consists mainly of mollisols.

Soil pH values were measured in 1:5 soil:deionized water extracts (Thomas, 1996). Cation exchange capacities were obtained by sodium saturation and magnesium extraction (Rhoades, 1982). Ethylene glycol monoethyl ether adsorption was used to determine surface areas (Cihacek and Bremner, 1979). Free Fe and Al oxides were extracted with citrate buffer and hydrosulfite (Coffin, 1963); Al and Fe concentrations were measured using inductively coupled plasma optical emission spectrometry (ICP-OES). Carbon contents were obtained using a carbon coulometer. Organic C was calculated as the difference between total C measured by combustion at 950°C and inorganic C determined by acidification and heating (Goldberg et al., 2005, Goldberg, Lesch, and Suarez, 2007).

Adsorption experiments were carried out in batch systems to determine adsorption envelopes, the amount of ion adsorbed as a function of solution pH at fixed total ion mass. One-gram samples of soil were equilibrated with 25 mL of 0.1 M NaCl background electrolyte solution on a shaker for 2 hours. The equilibrating solution contained 20 $\mu\text{mol}\cdot\text{L}^{-1}$ of As(V) or Se(IV) and had been adjusted to the desired pH range of 2 to 10 using 1 M HCl or 1 M NaOH. After reaction, the samples were centrifuged, decanted, analyzed for pH, filtered, and analyzed for As or Se concentration using ICP-OES. Additional experimental details are provided in Goldberg et al. (2005) for As(V) and in Goldberg, Lesch, and Suarez (2007) for Se(IV) adsorption.

Arsenate adsorption envelopes were determined for 27 southwestern and 22 midwestern soil samples. Arsenate adsorption increased with increasing solution pH, exhibited an adsorption maximum in the pH range 6 to 7, and decreased with further increases in solution pH, as can be seen in Figure 3.2. Selenite adsorption envelopes were determined for 23 southwestern and 22 midwestern soil samples. Selenite adsorption decreased with increasing solution pH over the pH range 2 to 10, as can be seen in Figure 3.3.

The constant capacitance model was fit to the As(V) adsorption envelopes by optimizing the three As(V) surface complexation constants ($\log K^1_{As}$, $\log K^2_{As}$, and $\log K^3_{As}$) simultaneously. The protonation constant was fixed at \log

TABLE 3.2

Chemical Characteristics of Soils

Soil Series	Depth cm	pH	CEC mmol _c kg ⁻¹	S m ² .g ⁻¹	IOC g.kg ⁻¹	OC g.kg ⁻¹	Fe g.kg ⁻¹	Al g.kg ⁻¹
Altamont	0-25	5.90	152	103	0.0099	9.6	7.7	0.58
	25-51	5.65	160	114	0.011	6.7	8.2	0.64
	0-23	6.20	179	109	0.12	30.8	9.2	0.88
Arlington	0-25	8.17	107	61.1	0.30	4.7	8.2	0.48
	25-51	7.80	190	103	0.16	2.8	10.1	0.60
Avon	0-15	6.91	183	60.1	0.083	30.8	4.3	0.78
Bonsall	0-25	5.88	54	15.7	0.13	4.9	9.3	0.45
	25-51	5.86	122	32.9	0.07	2.1	16.8	0.91
Chino	0-15	10.2	304	159	6.4	6.2	4.7	1.64
Diablo	0-15	7.58	301	190	0.26	19.8	7.1	1.02
	0-15	7.42	234	130	2.2	28.3	5.8	0.84
Fallbrook	0-25	6.79	112	68.3	0.023	3.5	6.9	0.36
	25-51	6.35	78	28.5	0.24	3.1	4.9	0.21
Fiander	0-15	9.60	248	92.5	6.9	4.0	9.2	1.06
Haines	20	9.05	80	59.5	15.8	14.9	1.7	0.18
Hanford	0-10	8.40	111	28.9	10.1	28.7	6.6	0.35
Holtville	61-76	8.93	58	43.0	16.4	2.1	4.9	0.27
Imperial	15-46	8.58	198	106	17.9	4.5	7.0	0.53
Nohili	0-23	8.03	467	286	2.7	21.3	49.0	3.7
Pachappa	0-25	6.78	39	15.1	0.026	3.8	7.6	0.67
	25-51	7.02	52	41.0	0.014	1.1	7.2	0.35
	0-20	8.98	122	85.8	0.87	3.5	5.6	0.86
Porterville	0-7.6	6.83	203	137	0.039	9.4	10.7	0.90
Ramona	0-25	5.89	66	27.9	0.02	4.4	4.5	0.42
	25-51	6.33	29	38.8	0.018	2.2	5.9	0.40
Reagan	Surface	8.39	98	58.8	18.3	10.1	4.6	0.45
Ryepatch	0-15	7.98	385	213	2.5	32.4	2.6	0.92
Sebree	0-13	5.99	27	21.2	0.0063	2.2	6.0	0.46
Wasco	0-5.1	5.01	71	30.9	0.009	4.7	2.4	0.42
Wyo		6.26	155	53.9	0.014	19.9	9.5	0.89
Yolo	0-15	8.43	177	73.0	0.23	11.5	15.6	1.13
Bernow	B	4.15	77.6	46.4	0.0028	3.8	8.1	1.1
Canisteo	A	8.06	195	152	14.8	34.3	1.7	0.44
Dennis	A	5.27	85.5	40.3	0.0014	18.6	12.9	1.7
	B	5.43	63.1	72.4	0.0010	5.2	30.0	4.1
Dougherty	A	4.98	3.67	241	0.0010	7.0	1.7	0.28
Hanlon	A	7.41	142	58.7	2.6	15.1	3.7	0.45
Kirkland	A	5.05	154	42.1	0.014	12.3	5.6	0.80
Luton	A	6.92	317	169	0.099	21.1	9.1	0.99
Mansic	A	8.32	142	42.2	16.7	10.1	2.7	0.40
	B	8.58	88.1	35.5	63.4	9.0	1.1	0.23

TABLE 3.2 (Continued)

Chemical Characteristics of Soils

Soil Series	Depth cm	pH	CEC					
			mmol _c kg ⁻¹	S m ² ·g ⁻¹	IOC g·kg ⁻¹	OC g·kg ⁻¹	Fe g·kg ⁻¹	Al g·kg ⁻¹
Norge	A	3.86	62.1	21.9	0.0010	11.6	6.1	0.75
Osage	A	6.84	377	134	0.59	29.2	15.9	1.4
	B	6.24	384	143	0.0100	18.9	16.5	1.3
Pond Creek	A	4.94	141	35.4	0.0023	16.6	5.2	0.70
	B	6.78	106	59.6	0.016	5.0	5.1	0.81
Pratt	A	5.94	23.9	12.3	0.0026	4.2	1.2	0.18
	B	5.66	23.3	117	0.0007	2.1	0.92	0.13
Richfield	B	7.12	275	82.0	0.040	8.0	5.4	0.76
Summit	A	7.03	374	218	0.25	26.7	16.2	2.3
	B	6.23	384	169	0.0079	10.3	17.8	2.5
Taloka	A	4.88	47.4	87.0	0.0021	9.3	3.6	0.62
Teller	A	4.02	43.1	227	0.0008	6.8	3.2	0.53

Source: Adapted from Goldberg, S., S.M. Lesch, D.L. Suarez, and N.T. Basta. 2005. *Soil Sci. Soc. Am. J.* 69: 1389–1398; Goldberg, S., S.M. Lesch, and D.L. Suarez. 2007. *Geochim. Cosmochim. Acta* 71: 5750–5762.

$K_c = 7.35$ and the dissociation constant was fixed at $\log K_c = -8.95$. The ability of the model to describe the As(V) adsorption data was very good. Figure 3.2 shows some model fits for surface horizons. Values of the optimized As(V) surface complexation constants are provided in Table 3.3. For the Bernow, Canisteo, Summit B, and Nohili soils, only two surface complexation constants were optimized because $\log K_{As}^2$ did not converge.

The constant capacitance model was fit to the Se(IV) adsorption envelopes by optimizing the Se(IV) surface complexation constant ($\log K_{Se}^2$) because $\log K_{Se}^1$ converged for only five of the soils. Subsequently, to improve the model fit, the protonation constant ($\log K_a$) and the dissociation constant ($\log K_c$) were simultaneously optimized with $\log K_{Se}^2$. Because initial optimizations indicated that the deprotonated surface species was present in only trace amounts ($\log K_c < -39$), it was omitted from the final optimizations. The ability of the model to describe the Se(IV) adsorption data was very good. Figure 3.3 shows some model fits for surface horizons. Values of the optimized Se(IV) surface complexation constants are provided in Table 3.4. Optimized constants are not listed for soils having >1% inorganic C because the model could not converge $\log K_{Se}^2$ and $\log K_c$ simultaneously.

A general regression modeling approach was used to relate the constant capacitance model As(V) and Se(IV) surface complexation constants to the following soil chemical properties: cation exchange capacity, surface area, inorganic carbon content, organic carbon content, iron oxide content, and aluminum oxide content. An exploratory data analysis revealed that the As(V) and Se(IV) surface complexation constants were linearly related to

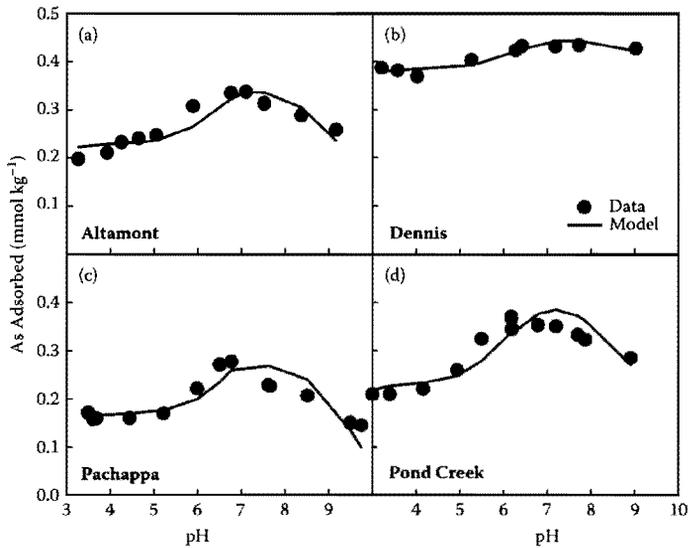


FIGURE 3.2

Fit of the constant capacitance model to As(V) adsorption on southwestern soils (a, c) and mid-western soils (b, d): (a) Altamont soil, (b) Dennis soil, (c) Pachappa soil, and (d) Pond Creek soil. Circles represent experimental data. Model fits are represented by solid lines. (Source: Adapted from Goldberg, S., S.M. Lesch, D.L. Suarez, and N.T. Basta. 2005. *Soil Sci. Soc. Am. J.* 69: 1389–1398.)

each of the log transformed chemical properties. Therefore, the following initial regression model was specified for each of the As(V) and Se(IV) surface complexation constants:

$$\begin{aligned} \text{Log}K_j = & \beta_{0j} + \beta_{1j}(\ln \text{CEC}) + \beta_{2j}(\ln \text{SA}) + \beta_{3j}(\ln(\text{IOC})) \\ & + \beta_{4j}(\ln \text{OC}) + \beta_{5j}(\ln \text{Fe}) + \beta_{6j}(\ln \text{Al}) + \epsilon \end{aligned} \quad (3.23)$$

where the β_{ij} represent regression coefficients, ϵ represents the residual error component, and $j = 1, 2$ for southwestern and midwestern soils, respectively.

For As(IV) and Se(IV), an initial analysis of the regression model presented by Equation (3.23) yielded rather poor results when the two sets of soils were considered together. Additional statistical analyses revealed that the mid-western and southwestern soils represented two distinct populations exhibiting different soil property and surface complexation constant relationships. A multivariate analysis of covariance established a common intercept and common $\ln(\text{CEC})$ term for the general regression prediction equations for As(V) adsorption. For Se(IV) adsorption, a multivariate analysis of covariance established a common $\ln(\text{SA})$ term for $\log K_{\text{Se}}^2$ and a common $\ln(\text{Fe})$ term for $\log K_{\text{Se}}$.

TABLE 3.3

Constant Capacitance Model Surface Complexation Constants for As(V) Adsorption

Soil Series	Depth (cm)	Optimized LogK ¹ _{As}	Optimized LogK ² _{As}	Optimized LogK ³ _{As}	Predicted LogK ¹ _{As}	Predicted LogK ² _{As}	Predicted LogK ³ _{As}
Altamont	0-25	9.99	3.92	-3.89	9.88	3.56	-4.10
	25-51	10.09	4.41	-3.69	9.98	3.56	-4.08
Arlington	0-25	9.57	2.04	-4.59	9.99	3.20	-4.15
	25-51	9.95	2.92	-4.24	10.20	3.33	-4.10
Avon	0-15	9.29	3.02	-4.52	9.38	3.22	-4.42
Bonsall	0-25	9.50	2.77	-4.64	9.92	3.20	-4.15
	25-51	10.90	3.64	-3.27	10.47	3.56	-3.82
Diablo	0-15	9.26	3.14	-4.45	9.90	3.51	-3.96
Fallbrook	0-25	10.02	3.00	-4.20	9.93	3.30	-4.27
	25-51	9.56	2.84	-4.62	9.68	2.85	-4.57
Fiander	0-15	10.08	2.10	-4.76	10.14	3.06	-4.14
Haines	20	9.43	2.39	-4.01	9.33	2.60	-4.45
Hanford	0-10	9.83	3.04	-4.16	9.53	2.92	-4.28
Holtville	61-76	10.32	3.66	-3.88	9.97	2.67	-4.26
Imperial	15-46	10.23	3.77	-3.77	10.10	2.98	-4.08
Nohili	0-23	12.82		-2.21	10.74	4.04	-3.17
Pachappa	0-25	9.67	3.55	-4.15	9.91	3.26	-4.15
	25-51	10.03	3.06	-4.44	10.05	3.16	-4.33
Porterville	0-7.6	10.36	3.89	-3.60	10.14	3.68	-3.84
Ramona	0-25	9.58	2.79	-4.37	9.55	3.02	-4.59
	25-51	9.96	2.99	-4.46	9.93	3.19	-4.18
Reagan	Surface	9.66	2.94	-4.07	9.74	2.84	-4.18
Ryepatch	0-15	9.40	3.07	-4.70	9.50	3.11	-4.26
Sebree	0-13	9.64	3.28	-4.70	9.76	3.11	-4.41
Wasco	0-5.1	9.65	3.31	-4.45	9.46	3.04	-4.59
Wyo		10.36	3.67	-3.80	9.79	3.62	-4.06
Yolo	0-15	10.00	3.96	-3.86	10.09	3.51	-3.93
Bernow	B	12.84		-1.78	11.21	5.29	-2.40
Canisteco	A	10.54		-3.70	9.39	2.21	-5.11
Dennis	A	10.99	5.02	-2.57	11.06	5.28	-2.77
	B	12.51	6.93	-0.73	12.50	6.97	-0.83
Dougherty	A	9.49	3.23	-4.21	9.69	3.21	-4.13
Hanlon	A	10.11	3.18	-4.17	10.35	3.61	-3.66
Kirkland	A	10.44	5.25	-3.14	10.42	4.26	-3.60
Luton	A	10.46	4.46	-3.31	10.96	4.66	-3.23
Mansic	A	9.71	3.05	-4.24	10.26	3.34	-3.65
	B	10.21	2.58	-3.65	9.47	2.19	-4.53
Norge	A	10.31	3.90	-3.99	10.37	4.46	-3.47
Osage	A	11.75	5.08	-2.63	11.55	5.27	-2.49
	B	12.26	5.97	-1.86	11.43	5.50	-2.66

—continued

TABLE 3.3 (Continued)

Constant Capacitance Model Surface Complexation Constants for As(V) Adsorption

Soil Series	Depth (cm)	Optimized $\text{LogK}^1_{\text{As}}$	Optimized $\text{LogK}^2_{\text{As}}$	Optimized $\text{LogK}^3_{\text{As}}$	Predicted $\text{LogK}^1_{\text{As}}$	Predicted $\text{LogK}^2_{\text{As}}$	Predicted $\text{LogK}^3_{\text{As}}$
Pond Creek	A	10.02	4.44	-3.86	10.09	4.04	-4.05
Pond Creek	B	10.85	4.98	-3.01	10.73	4.53	-3.09
Pratt	A	9.14	2.56	-4.78	9.09	2.73	-4.75
Pratt	B	9.26	2.55	-4.64	9.17	2.69	-4.87
Richfield	B	10.00	3.85	-4.17	10.62	4.34	-3.45
Summit	A	11.65		-2.57	11.58	5.34	-2.51
Summit	B	13.14		-1.61	11.73	5.85	-2.24
Taloka	A	10.25	4.11	-3.89	10.09	3.88	-3.92
Teller	A	10.20	3.61	-4.34	10.10	3.87	-3.99

Source: Adapted from Goldberg, S., S.M. Lesch, D.L. Suarez, and N.T. Basta. 2005. *Soil Sci. Soc. Am. J.* 69: 1389–1398.

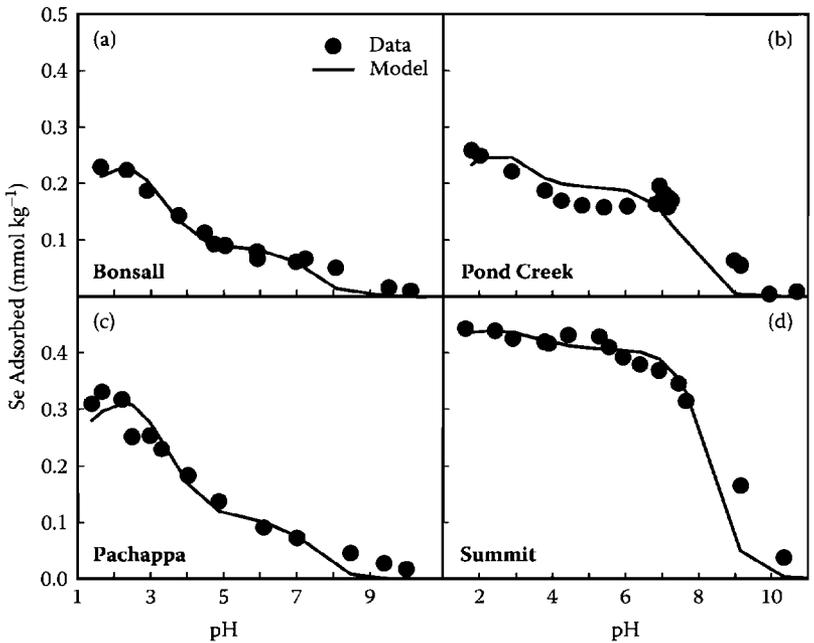


FIGURE 3.3

Fit of the constant capacitance model to Se(IV) adsorption on southwestern soils (a, c) and midwestern soils (b, d): (a) Bonsall soil; (b) Pond Creek soil; (c) Pachappa soil; (d) Summit soil. Circles represent experimental data. Model fits are represented by solid lines. (Source: Adapted from Goldberg, S., S.M. Lesch, and D.L. Suarez. 2007. *Geochim. Cosmochim. Acta* 71: 5750–5762.)

TABLE 3.4

Constant Capacitance Model Surface Complexation Constants for Se(IV) Adsorption

Soil Series	Depth (cm)	Optimized $\text{Log}K_{\text{Se}}^2$	Optimized $\text{Log}K_{\text{t}}$	Predicted $\text{Log}K_{\text{Se}}^2$	Predicted $\text{Log}K_{\text{t}}$
Altamont	0-20	-1.42	2.72	-1.23	2.79
Arlington	0-25	-1.04	2.82	-0.88	2.81
Avon	0-15	-1.24	2.27	-1.21	2.16
Bonsall	0-25	-0.90	2.80	-0.62	2.81
Chino	0-15	-1.57	2.96	-1.42	2.72
Diablo	0-15	-1.57	2.11	-1.47	2.68
	0-15	-1.75	2.85	-1.41	2.77
Fallbrook	25-51	-0.73	2.53	-0.70	2.38
Fiander	0-15	-1.01	3.20	-0.99	3.25
Haines	20			-1.40	2.04
Hanford	0-10	-0.53	2.68	-0.81	3.04
Holtville	61-76			-0.82	2.87
Imperial	15-46			-1.13	3.15
Nohili	0-23			-1.10	4.44
Pachappa	0-25		2.17	-0.69	2.47
	25-51	-0.53	2.50	-0.65	2.35
	0-20	-1.22	3.10	-1.09	2.63
Porterville	0-7.6	-1.04	2.86	-1.26	2.78
Reagan	Surface			-1.09	2.83
Sebree	0-13	-0.47	2.11	-0.53	2.12
Wasco	0-5.1	-0.93	1.28	-1.19	1.45
Wyo		-0.58	2.79	-1.05	2.57
Yolo	0-15	-0.79	3.28	-0.85	3.27
Bernow	B	0.62	2.85	0.59	2.24
Canisteo	A			1.77	1.77
Dennis	A	0.31	2.36	0.38	2.25
	B			1.63	2.19
Dougherty	A	-1.77	2.11	-1.94	2.14
Hanlon	A	-0.92	2.50	-0.96	2.37
Kirkland	A	-0.06	1.76	-0.31	2.21
Luton	A	-0.79	2.33	-0.59	2.41
Mansic	A			-0.97	2.21
	B			-1.78	1.96
Norge	A	-0.24	2.08	0.06	2.33
Osage	A	0.15	2.13	-0.08	2.57
	B	0.22	3.24	0.14	2.65
Pond Creek	A	-0.44	2.07	-0.46	2.26
	B	0.03	1.89	-0.11	2.13
Pratt	A	-0.99	2.56	-0.92	2.23
	B	-1.59	2.00	-1.73	2.29
Richfield	B	-0.77	2.22	-0.40	2.23
Summit	A	-0.14	2.66	-0.20	2.18
	B	0.49	1.54	0.44	2.18
Taloka	A	-0.88	2.38	-0.91	2.08
Teller	A	-1.46	2.15	-1.25	2.11

Source: Adapted from Goldberg, S., S.M. Lesch, and D.L. Suarez. 2007. *Geochim. Cosmochim. Acta* 71: 5750-5762.

The prediction equations for obtaining As(V) surface complexation constants to describe As(V) adsorption with the constant capacitance model are

$$\begin{aligned} \text{Log}K_{As}^1 &= 10.64 - 0.107 \ln(\text{CEC}) + 0.094 \ln(\text{SA}) + 0.078 \ln(\text{IOC}) \\ &\quad - 0.365 \ln(\text{OC}) + 1.09 \ln(\text{Fe}) \end{aligned} \quad (3.24)$$

$$\begin{aligned} \text{Log}K_{As}^2 &= 3.39 - 0.083 \ln(\text{CEC}) + 0.018 \ln(\text{SA}) - 0.002 \ln(\text{IOC}) \\ &\quad - 0.400 \ln(\text{OC}) + 1.36 \ln(\text{Fe}) \end{aligned} \quad (3.25)$$

$$\begin{aligned} \text{Log}K_{As}^3 &= -2.58 - 0.296 \ln(\text{CEC}) - 0.004 \ln(\text{SA}) + 0.115 \ln(\text{IOC}) \\ &\quad - 0.570 \ln(\text{OC}) + 1.38 \ln(\text{Fe}) \end{aligned} \quad (3.26)$$

for midwestern soils,

$$\begin{aligned} \text{Log}K_{As}^1 &= 10.65 - 0.107 \ln(\text{CEC}) + 0.256 \ln(\text{SA}) + 0.022 \ln(\text{IOC}) \\ &\quad - 0.143 \ln(\text{OC}) + 0.385 \ln(\text{Fe}) \end{aligned} \quad (3.27)$$

$$\begin{aligned} \text{Log}K_{As}^2 &= 3.39 - 0.083 \ln(\text{CEC}) + 0.247 \ln(\text{SA}) - 0.061 \ln(\text{IOC}) \\ &\quad - 0.104 \ln(\text{OC}) + 0.313 \ln(\text{Fe}) \end{aligned} \quad (3.28)$$

$$\begin{aligned} \text{Log}K_{As}^3 &= -2.58 - 0.296 \ln(\text{CEC}) - 0.376 \ln(\text{SA}) + 0.024 \ln(\text{IOC}) \\ &\quad - 0.085 \ln(\text{OC}) + 0.363 \ln(\text{Fe}) \end{aligned} \quad (3.29)$$

and for southwestern soils.

The prediction equations for obtaining Se(IV) surface complexation constants to describe Se(IV) adsorption with the constant capacitance model are

$$\text{Log}K_{Se}^2 = 0.675 - 0.380 \ln(\text{SA}) - 0.083 \ln(\text{OC}) + 0.274 \ln(\text{Fe}) \quad (3.30)$$

$$\text{Log}K_{+} = 3.36 + 0.115 \ln(\text{IOC}) + 0.774 \ln(\text{Fe}) \quad (3.31)$$

for midwestern soils

$$\text{Log}K_{S_e}^2 = 1.18 - 0.380 \ln(\text{SA}) - 0.470 \ln(\text{OC}) + 1.03 \ln(\text{Fe}) \quad (3.32)$$

$$\text{Log}K_s = 0.613 + 0.774 \ln(\text{Fe}) - 0.811 \ln(\text{Al}) \quad (3.33)$$

for southwestern soils.

Surface complexation constants obtained with the prediction equations are provided in Table 3.3 for As(V) and Table 3.4 for Se(IV). A “jack-knifing” procedure was performed on Equations (3.24) to (3.33) to assess their predictive ability. Jack-knifing is a technique where each observation is sequentially set aside, the equation is reestimated without this observation, and the set-aside observation is then predicted from the remaining data using the reestimated equation. A jack-knifing procedure indicated good general agreement between ordinary predictions and jack-knife estimates for both As(V) and Se(IV) surface complexation constants, suggesting predictive capabilities. Additional details on statistical analyses are provided in Goldberg et al. (2005) for As(V) and Goldberg, Lesch, and Suarez (2007) for Se(IV).

The As(V) surface complexation constants were predicted using the prediction Equations (3.24) to (3.26) for midwestern soils and Equations (3.27) to (3.29) for southwestern soils. These surface complexation constants were then used in the constant capacitance model to predict As(V) adsorption on the soils. The ability of the model to predict As(V) adsorption is shown in Figure 3.4 for two soils not used to obtain the prediction equations. Prediction of As(V) adsorption by the Summit soil was good. Prediction of As(V) adsorption by the Nohili soil deviated from the experimental adsorption data by 30% or less, a reasonable result considering that the prediction was obtained without optimization of any adjustable parameters.

The Se(IV) surface complexation constants were predicted using the prediction Equations (3.30) and (3.31) for midwestern soils and Equations (3.32) and (3.33) for southwestern soils. These surface complexation constants were then used in the constant capacitance model to predict Se(IV) adsorption on the soils. The ability of the model to predict Se(IV) adsorption is shown in Figure 3.5 for four soils. For the Pond Creek and Summit soils, the prediction equations provide descriptions of the experimental data that are comparable in quality to the optimized fits (compare Figures 3.3b with 3.5b and 3.3d with 3.5d). For the Bonsall and Pachappa soils, the prediction equations describe the experimental data less closely than the optimized fits (compare Figure 3.3a with 3.5a and Figure 3.3c with 3.5c). However, the model always correctly predicts the shape of the adsorption envelope as a function of solution pH.

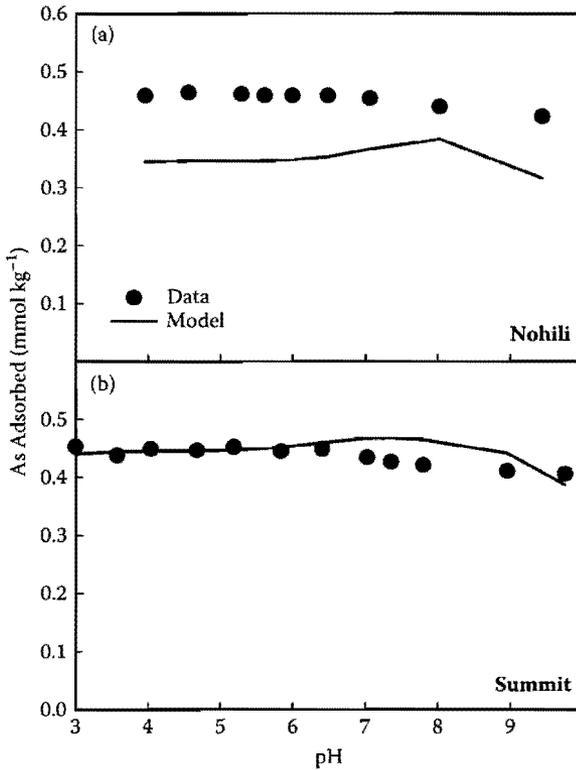


FIGURE 3.4

Constant capacitance model prediction of As(V) adsorption by soils not used to obtain the prediction equations: (a) Nohili soil and (b) Summit soil. Experimental data are represented by circles. Model predictions are represented by solid lines. (Source: Adapted from Goldberg, S., S.M. Lesch, D.L. Suarez, and N.T. Basta. 2005. *Soil Sci. Soc. Am. J.* 69: 1389–1398.)

Predictions of As(V) and Se(IV) adsorption were reasonable for most of the soils. These predictions were obtained independently of any experimental measurement of As(V) or Se(IV) adsorption on these soils, that is, solely from values of a few easily measured chemical properties. Incorporation of these prediction equations into chemical speciation transport models should allow simulation of As(V) and Se(IV) concentrations in soil solution under diverse environmental conditions.

Summary

The chemical processes and soil factors that affect the concentrations of As and Se in soil solution were discussed. Both elements occur in two redox

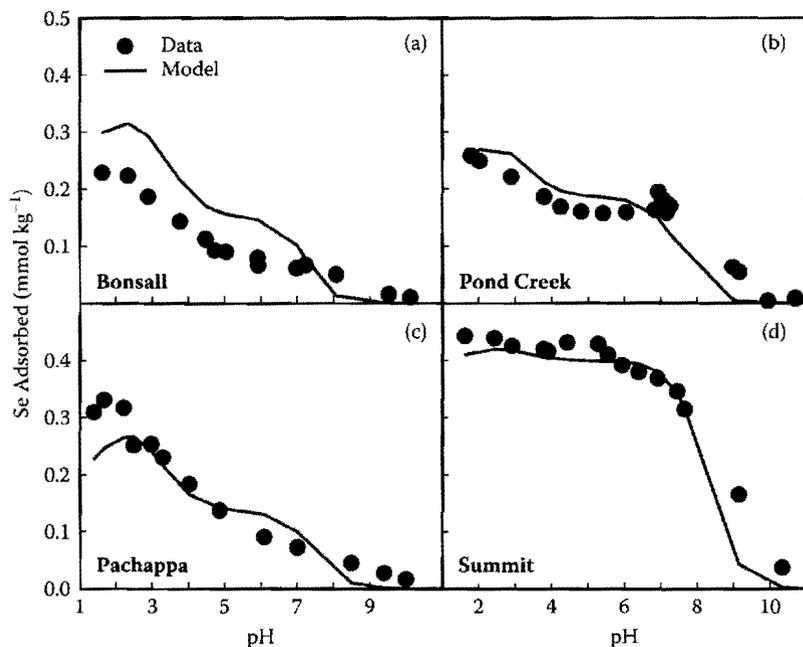


FIGURE 3.5 Constant capacitance model prediction of Se(IV) adsorption by southwestern soils (a, c) and midwestern soils (b, d): (a) Bonsall soil, (b) Pond Creek soil, (c) Pachappa soil, and (d) Summit soil. Experimental data are represented by circles. Model predictions are represented by solid lines. (Source: Adapted from Goldberg, S., S.M. Lesch, and D.L. Suarez. 2007. *Geochim. Cosmochim. Acta* 71: 5750–5762.)

states differing in toxicity and reactivity. Methylation and volatilization reactions occur in soils and can act as detoxification pathways. Precipitation-dissolution reactions control As and Se concentrations only in highly contaminated situations. Oxidation-reduction reactions determine which redox state is thermodynamically stable, although more than one redox state may be present in soils. Adsorption-desorption reactions most often control the dissolved As and Se concentrations. Empirical and chemical models of adsorption were discussed. The constant capacitance model, a chemical surface complexation model, has been used to predict As and Se adsorption under changing conditions of solution pH and equilibrium ion concentration.

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