Anion Sorption on a Calcareous, Montmorillonitic Soil—Arsenic

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ABSTRACT

Arsenic sorption on a calcareous, montmorillonitic soil was investigated as a function of solution pH (2–11) at two initial As concentrations (2.0 and 20 mmol m⁻³). Arsenite sorption could not be determined because oxidation of arsenite occurred during the experiment. Arsenate sorption increased with increasing pH, exhibited a maximum near pH 10.5, and decreased at higher pH. Arsenate sorption as a function of pH was studied on reference minerals representative of the dominant inorganic constituents of the soil: montmorillonite, kaolinite, and calcite. Arsenate sorption on the two clay minerals increased at low pH, exhibited a peak near pH 5, and decreased at higher pH. Arsenate sorption on the calcite increased from pH 6 to 10, peaked between pH 10 and 12, and decreased above pH 12. The constant capacitance model was able to describe arsenate sorption on kaolinite over the entire pH range studied and on montmorillonite and soil below pH 9. The soil sorption maximum near pH 10.5 was much reduced after removal of carbonates, indicating that carbonates play a major role in arsenate sorption above pH 9. Arsenate sorption on soil and calcite was unaffected by the presence of equimolar selenite concentrations.

A RSENIC IS TOXIC to animals and has accumulated to phytotoxic levels in some soils through the use of arsenical pesticides (Walsh and Keeney, 1975). Arsenic sorption in soils has been investigated previously by various researchers (Misra and Tiwari, 1963; Jacobs et al., 1970; Wauchope, 1975; Livesey and Huang, 1981; Elkhatib et al., 1984a,b). Jacobs et al. (1970) suggested that As sorption was related to the amorphous Al and Fe oxide content of 24 Wisconsin soils. The sorption behavior of As is dependent on its oxidation state. Gulens et al. (1979) found that the mobility of arsenite through sand columns was greater than that of arsenate. Arsenite sorption rate was significantly correlated with Fe oxide content of five West Virginia soils (Elkhatib et al., 1984a,b) and with dithionite extractable Fe content of 15 Japanese soils (Sakata, 1987). Amount of sorbed arsenate in soils was significantly correlated with oxalate extractable Al and Fe and with clay (Wauchope, 1975; Livesey and Huang, 1981). Fordham and Norrish (1979) added radioactive arsenate to acid soils and found, using au-

toradiography, that it was retained mainly by Fe oxides.

The As sorbing inorganic constituents of soils include Al and Fe oxides, clay minerals, and calcite. Sorption of arsenate on amorphous Fe hydroxide (Pierce and Moore, 1982), goethite, gibbsite (Hingston et al., 1971), amorphous Al hydroxide (Anderson et al., 1976), and activated alumina (Gupta and Chen, 1978) exhibited maxima in the pH range 3 to 7 followed by a decline with increasing pH. Sorption of arsenite on amorphous Fe hydroxide (Pierce and Moore, 1980, 1982) and activated alumina (Gupta and Chen, 1978) increased at low pH, peaked between pH 7 and 8, and decreased at high pH. Arsenite sorption was less than arsenate sorption on activated alumina (Gupta and Chen, 1978) and amorphous Fe hydroxide (Pierce and Moore, 1982).

Arsenate sorption on goethite (Lumsdon et al., 1984) and hydrous Fe oxide (Harrison and Berkheiser, 1982) occurred via a ligand exchange mechanism with reactive surface hydroxyl ions, as observed directly using infrared spectroscopy. Ligand exchange is a mechanism by which anions become specifically adsorbed. Arsenate sorption on amorphous Al hydroxide (Anderson et al., 1976) and arsenite sorption on amorphous Fe hydroxide (Pierce and Moore, 1980) produced shifts in the zero points of charge of the solids providing evidence for specific adsorption of As in both oxidation states.

Arsenate sorption on the clay minerals kaolinite and montmorillonite increased below pH 4, exhibited a peak between pH 4 and 6, and decreased above pH 6; arsenite sorption on montmorillonite peaked near pH 7, while arsenite sorption on kaolinite increased steadily from pH 4 to 9 (Frost and Griffin, 1977). These researchers found that montmorillonite sorbed both arsenate and arsenite more strongly than kaolinite and that arsenite was sorbed much less then arsenate by both clay minerals. While the sorption of As on synthetic calcite was below the detection limit of the spectrophotometric method used by Oscarson et al. (1983), Misra and Tiwari (1963) observed an increase in arsenite sorption on soil in the presence of calcium carbonate. Brannon and Patrick (1987) found a significant correlation between As release and calcium carbonate equivalent of sediments. It is possible that the carbonates might have been coated with hydrous Al or Fe oxides.

The constant capacitance model is an appropriate

surface complexation model for specific adsorption (Sposito, 1984). This model successfully described arsenate sorption on Al and Fe oxides (Goldberg, 1986a), as well as phosphate and B sorption on soils (Goldberg, 1986b).

In the present study, the sorption behavior of As on a calcareous, montmorillonitic soil from the Imperial Valley of California was investigated. We also studied the sorption behavior of arsenate onto reference minerals representative of the dominant inorganic constituents in the above soil: montmorillonite, kaolinite, and calcite. The ability of the constant capacitance model to describe these sorption reactions was evaluated.

MATERIALS AND METHODS

Arsenate and arsenite sorption was studied using the < 2-mm fraction of a surface (0–7.6 cm) sample belonging to the Imperial soil series [fine, montmorillonitic (calcareous), hyperthermic Vertic Torrifluvent]. The procedures used to determine physical and chemical characteristics of the sample are listed in Goldberg and Glaubig (1988). The soil contained 44% clay, 0.83% organic carbon, 0.67% free Fe, 0.043% free Al, and had 14.7% calcium carbonate equivalent. X-ray diffraction analysis showed that montmorillonite and kaolinite constituted about two-thirds of the clay fraction. Minor amounts of illite, chlorite, vermiculite, and quartz were also present. Arsenate sorption was studied on SAz-1 Ca-montmorillonite "Cheto" and KGa-2 poorly crystallized kaolinite obtained from the Clay Mineral Society's Source Clay Repository, on Purecal U $CaCO_3$ from the Wyandotte Chemical Co. (Wyandotte, MI), and on samples of the above soil before and after treatment to remove carbonates using the procedure described by Kunze and Dixon (1986). Specific surface areas using N_2 gas adsorption were 36.1, 36.4, 18.6, 20.5, and 12.1 m² g⁻¹ for the soil, treated soil, montmorillonite, kaolinite, and calcite, respectively. This method measures only the external specific surface area of expanding minerals. The removal of carbonates did not significantly change the specific surface area of the soil, suggesting that the carbonates were present as coatings on soil minerals.

Arsenic sorption experiments were carried out in batch systems using the procedure outlined by Goldberg and Glaubig (1988). The equilibrating solutions contained 2.0 or 20 mmol As m⁻³ in a background electrolyte of 0.1 M NaCl and had been adjusted in pH using 4 M HCl or 4 M NaOH. Sodium m-arsenite and sodium arsenate were obtained from Sigma Chemical Co., St. Louis, MO. Suspension densities were 40 and 10 g l⁻¹ for the soil and calcite, respectively. After 2 h of shaking, the decantates were analyzed for pH and Eh, filtered, acidified, and analyzed for As concentration. Arsenic(III plus V) and arsenic(III) were determined using a Perkin-Elmer Model 3030B atomic absorption spectrophotometer with an electrodeless discharge lamp (Perkin-Elmer Corp., Norwalk, CT), a Varian VGA-76 hydride generator (Varian Associates, Inc., Palo Alto, CA), and the method described by Glaubig and Goldberg (1988). Release of native As from the soil into 0.1 M NaCl, arsenate sorption on soil treated for carbonate removal, and arsenate sorption on soil and on calcite in the presence of 19 mmol m⁻³ selenite were studied using the above procedure described in more detail by Goldberg and Glaubig (1988).

The constant capacitance model (Stumm et al., 1980) was used to describe As sorption. The computer program FITEQL containing this model (Westall, 1982) was used to fit intrinsic conditional equilibrium constants to the experimental data as described in Goldberg (1986b) using the same capacitance density and protonation-dissociation constants

as Goldberg and Glaubig (1988). The arsenic surface complexation reactions are defined as:

$$AlOH(s) + H_3AsO_4(aq) = AlH_{(3-i)}AsO_4^{(1-i)}(s)$$
$$+ H_2O + (i-1)H^+(aq) \quad [1]$$
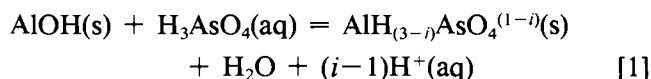
where AlOH represents 1 mol of reactive surface hydroxyls (aluminols) bound to an Al^{3+} ion in the clay mineral and $1 \leq i \leq 3$.

RESULTS AND DISCUSSION

Release of native As from the soil was studied. Arsenite release was low, while release of arsenate was substantial (up to 1.5 mmol m⁻³ at pH 1). Oxidation of arsenite to arsenate occurred in the arsenite sorption experiment. The Eh-pH values (e.g., Eh = 590 mV at pH 4.3; Eh = 390 mV at pH 9.9) also corroborate arsenate as the stable oxidation state under the experimental conditions used. Oxidation of arsenite has been found to occur within 5 h in unfiltered soil pore waters (Haswell et al., 1985) and within 3 h in a soil extract (Glaubig and Goldberg, 1988) when present at the milligrams per cubic meter level. Manganese oxides have the ability to oxidize arsenite to arsenate (Oscarson et al., 1983). Arsenate sorption as a function of pH is shown in Fig. 1. Arsenate sorption increases with increasing pH, exhibits a peak near pH 10.5, and decreases at higher pH. Using the computer program GEOCHEM (Sposito and Mattigod, 1979), we calculated that our systems were several orders of magnitude undersaturated with respect to $FeAsO_4$, $AlAsO_4$, and $Ca_3(AsO_4)_2$.

Figure 2a,b,c shows arsenate sorption as a function of pH for the reference minerals. The sorption curves for the clay minerals (Fig. 2a,b) increase at low pH, exhibit a peak near pH 5, and decrease at higher pH. The shapes of the sorption curves for montmorillonite and kaolinite agree well with those found by Frost and Griffin (1977). However, the lowest As addition studied by these researchers was almost seven times greater than the concentration used in our study. In addition, different types of reference clays were used and were found to be much less reactive toward As than our materials. Arsenate sorption on montmorillonite exhibits another rise at pH values > 9, whereas sorption on kaolinite continues to decrease steadily at high pH. The magnitude of the arsenate sorption maxima are similar for both clays. In contrast, Frost and Griffin (1977) found greater As sorption on their montmorillonite than their kaolinite clay. Arsenate sorption on the calcite increases from pH 6 to 10, peaks between pH 10 and 12, and decreases above pH 12. The magnitude of the sorption maximum for calcite is four times that for kaolinite and montmorillonite.

Table 1 lists the As surface complexation constants obtained from the application of the constant capacitance model to the experimental sorption data using the computer program FITEQL. For the montmorillonite, these values were obtained by optimizing all five surface complexation constants simultaneously. Optimization of solely the As surface complexation constants gave very poor fits. This behavior had been observed previously in the modeling of B sorption on montmorillonites (Goldberg and Glaubig, 1986). The intrinsic protonation-dissociation constants were fixed
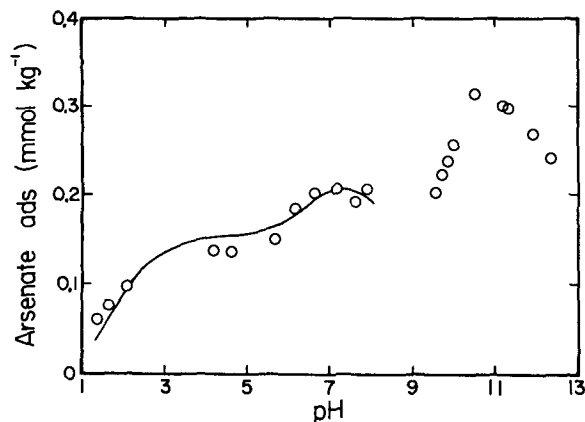
Fig. 1. Arsenate sorption on Imperial soil. $As_T = 20$ mmol m^{-3}. Circles represent experimental data points. Model results are represented by a solid line.

at log K_+(int) $= 7.38$, log K_-(int) $= -9.09$ for kaolinite, and at log K_+(int) $= 7.35$, log K_-(int) $= -8.95$ for soil, as done previously for B sorption on kaolinite and soil (Goldberg, 1986b).

The constant capacitance model is able to describe arsenate sorption on the soil up to pH 9, but is unable to fit the sorption peak occurring in the pH range 9 to 12 (Fig. 1). The As surface complexation constants were the only constants optimized by the model. The inability of the model to describe sorption over the entire pH range, suggests that arsenate sorption may be occurring on more than one set of competing sites.

The constant capacitance model describes arsenate sorption on kaolinite with some deviations above pH 8 (Fig. 2b). The model describes sorption on kaolinite using three adjustable parameters, the As surface complexation constants. The constant capacitance model assumes that inorganic anion sorption on clays occurs via ligand exchange with reactive surface aluminol groups at the edges of the particles. This mechanism was previously suggested by Sposito (1984) for oxyanion sorption by clay minerals. The reasonable fit of the model to the experimental data, suggests that this mechanism may be appropriate for arsenate sorption on kaolinite. As was the case for the soil, the model is able to describe arsenate sorption on montmorillonite up to pH 9, but is unable to describe the rise in sorption occurring at higher pH values (Fig. 2a). This montmorillonite has a small amount of calcite impurity. It is possible that this material is responsible for the sorption at high pH. The optimized value for log K_-(int) was insignificantly small. This result would imply that the constant is unnecessary and that the surface aluminol group, AlOH, does not dissociate. This chemically unrealistic situation, combined with the fact that five surface complexation constants were optimized, casts doubt on the chemical significance of the model application to arsenate sorption on montmorillonite. Additional studies on additional montmorillonites are needed to determine whether the constant capacitance model application to arsenate sorption on these clays is purely a curve fitting procedure.

The constant capacitance model was not applied to arsenate sorption on calcite because no surface complexation constants are available for the potential de-
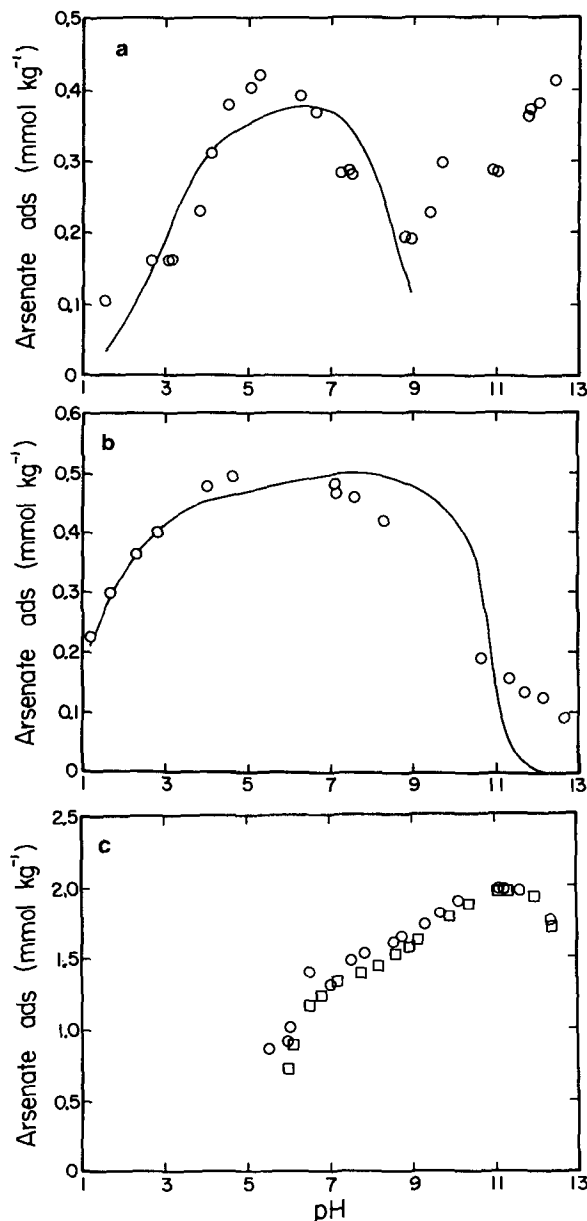

Fig. 2 Arsenate sorption on reference minerals: (a) SAz-1, Ca-montmorillonite, (b) KGa-2, poorly crystallized kaolinite, (c) Purecal U calcite. $As_T = 20$ mmol m^{-3}. Squares represent sorption in the presence of 19 mmol Se m^{-3} and circles represent experimental data points. Model results are represented by solid lines.

termining carbonate and bicarbonate anions. The high magnitude and the pH of the sorption maximum suggest that carbonates may be responsible for the sorption peak occurring on soil near pH 10.5. Indeed, after

Table 1. Surface complexation constants obtained from FITEQL.[†]

Solid	Log K_+(int)	Log K_-(int)	Log K^i_{As}(int)[‡]	Log K^i_{As}(int)	Log K^i_{As}(int)
Soil[‡]	[§]	[§]	9.94	3.71	-4.18
Kaolinite	[§]	[§]	11.04	8.24	-3.21
Montmorillonite[‡]	4.83	[¶]	7.12	4.23	[¶]

[†] All surface complexation constants were obtained using concentrations in mol L^{-1}. Ionic strength $= 0.1$ M NaCl. Temperature $= 23 \pm 1$°C.
[‡] Optimization included only data points where pH ≤ 9.
[§] Log K^i_{As}(int) were optimized while holding log K_+(int) and log K_-(int) constant.
[¶] Indicates that this constant was insignificantly small (≤ -29).
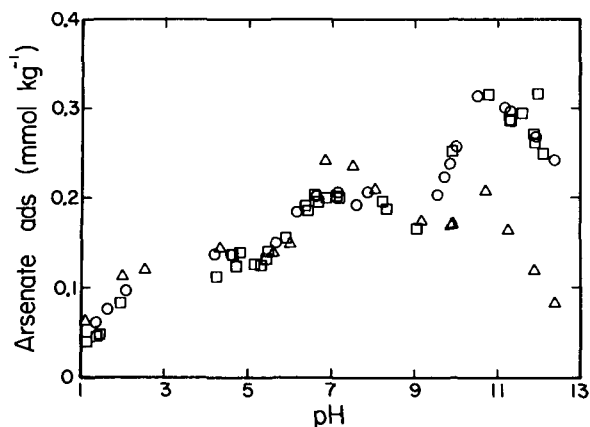
Fig. 3. Arsenate sorption on untreated soil (circles), on soil after treatment to remove carbonates (corrected for weight of calcium carbonate equivalent removed; triangles), and in the presence of selenite (squares). $As_T = 20$ mmol m^{-3}. $Se_T = 19$ mmol m^{-3}.

removal of carbonates, the magnitude of this sorption peak was much reduced (Fig. 3). These results indicate that carbonates play an important role in the arsenate sorption of calcareous soils in the pH range 9 to 12.

The competitive effect of selenite on arsenate sorption was studied using equilibrating solutions containing both anions in approximately equimolar amounts. In contrast to the effect of arsenate on selenite sorption (Goldberg and Glaubig, 1988), arsenate sorption was unaffected by the presence of selenite over the entire pH range (1–13 on soil, Fig. 3, and 6–12 on calcite, Fig. 2c) investigated. This result indicates that these two anions either sorb on separate sets of sites or that sorption sites are not limiting at the trace concentrations we investigated.

The mineralogy of the Imperial soil series is dominated by montmorillonite and kaolinite, and the free oxide content is low. Therefore, we suggest that the two clay minerals are responsible for the arsenate sorption on soil below pH 9. Our results indicate that above pH 9 arsenate sorption occurs primarily on soil carbonates. Additional clay minerals present in minor amounts could also play a role in As sorption. Sorption of arsenate on carbonates in field situations may not be very significant, however, since the mean pH of a calcareous soil in the field under a variety of moisture conditions has been found to be 7.41 ± 0.13 (Suarez, 1986). Our results indicate that the constant capacitance model can describe arsenate sorption on calcareous soils below pH 9 and thus suggest that arsenate sorption on noncalcareous soils can be described with this model. Experimental data are needed to test this hypothesis.

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