

Soil Science

Issue: Volume 162(12), December 1997, pp 886-895

Copyright: © Williams & Wilkins 1997. All Rights Reserved.

Publication Type: [Article]

ISSN: 0038-075X

Accession: 00010694-199712000-00004

[Article]

ARSENIC(III) AND ARSENIC(V) ADSORPTION ON THREE CALIFORNIA SOILS

Manning, Bruce A.; Goldberg, Sabine

Author Information

Contribution from the U.S. Salinity Laboratory, Riverside, CA.

Address correspondence to Dr. Bruce A. Manning, USDA-ARS, U.S. Salinity Laboratory, 450 West Big Springs Road, Riverside, CA 92507. E-mail: bmanning@ussl.ars.usda.gov

Received Feb. 17, 1997; accepted July 16, 1997.

Abstract

Inorganic arsenite (As(III)) and arsenate (As(V)) are toxic pollutants that are transported in surface and ground waters and can adsorb on soil and sediment mineral surfaces. Because of the importance of adsorption reactions in determining the overall mobility of arsenic, we investigated the adsorption of As(III) and As(V) on three soils at varying As concentration, pH, and ionic strength. The objectives were to characterize and compare As(III) and As(V) adsorption on three arid-zone soils from California (Wasco, Fallbrook, and Wyo) and to determine the relationship between soil properties and adsorption. Chromatographic speciation of As(III)/(V) revealed that the three soils contained low levels of background As(V). Oxidation of added As(III) to As(V) was not detected below pH 8 in soil suspensions during 16-h adsorption experiments; however, As(III) oxidation was detected at higher adjusted pH. The soil with the highest citrate-dithionite extractable Fe and %clay (Wyo) had the highest affinity for As(III) and As(V) and displayed adsorption behavior similar to pure ferric oxide. Adsorption isotherms indicated that As(V) species adsorbed more strongly than As(III) under most conditions. However, a pH-dependent reversal in the relative affinity of As(III) and As(V) for the soils was observed at low As surface coverage.

Arsenic(As) is a toxic trace element that is an environmental concern because of leaching of mine wastes (Bowell 1994), coal fly ash disposal (Davidson et al. 1974), arsenical pesticide use (Peryea and Creger 1994), and accumulation in shallow ground waters associated with arid-zone soils derived from marine sedimentary rocks (Fujii and Swain 1995). Establishing the reactivity and deposition of As in soils and sediments is complicated by redox transformation reactions, precipitation and dissolution reactions, biological uptake and cycling, and adsorption on mineral surfaces. A comprehensive understanding of the relevant reactions of As in soils requires detailed knowledge of the magnitudes and rates of individual processes affecting As in whole soils.

A variety of As forms or species have been identified in soil and water. These include inorganic As solid phases that occur in iron ores and magmatic sulfides such as arsenopyrite (FeAsS), realgar (AsS), and orpiment (As₂S₃) (Huang 1994; Tanaka 1988). The two major soluble inorganic As species are arsenite (As(III)) and arsenate (As(V)) (Aurilio et al. 1994; Masscheleyn et al. 1991a), which exist at neutral pH as H₃AsO₃ and H₂AsO₄/HAsO₄²⁻, respectively. The As(V) species predominates under oxidizing conditions in soils (Sadiq et al. 1983) and converts to As(III) and under mildly reduced redox potential (E_h) conditions (E_h < + 100 mV, pH7) (Masscheleyn et al. 1991b; Ferguson and Gavis 1972; Sadiq et al. 1983).

Water soluble organic arsenical defoliant such as DMAA [(CH₃)₂AsO₂H] and herbicides such as DSMA [(CH₃)₂AsO₂H], MSMA[CH₃AsO₃HNa], and MAA [CH₃AsO₃H₂] can also be present in agricultural soils (Abernathy 1983) and tend to mineralize to As(V) (Huang 1994). The reduction of inorganic As to methylated arsine gases such as di- and trimethylarsine [(CH₃)₂HAs and (CH₃)₃As] under anaerobic conditions has been demonstrated (McBride et al. 1978). Though the genesis, disposition, and stability of methylarsine molecules in aerobic soil is poorly understood, it is likely that mineralization to inorganic As(III) and/or As(V), followed by adsorption, is their ultimate fate.

Adsorption of inorganic As(III) and As(V) on soil mineral surfaces is an extremely important process that affects the fate and mobility of As in soil. Though the overall rate of adsorption depends on several factors, such as ion diffusion to the particle surface, the adsorption reactions of oxyanions on soil mineral surfaces are considered to be rapid (Zhang and Sparks 1989; Sparks 1989).

Ferric oxides and hydroxides (hereafter, Fe(III) oxides) have a high affinity for both As(III) and As(V) (Wilkie and Hering 1996; Pierce and Moore 1982). The HAsO₄²⁻ anion adsorbs on Fe(III) oxide surfaces by formation of inner-sphere bidentate binuclear complexes (Sun and Doner 1996; Waychunas et al. 1993; Lumsdon et al. 1984) analogous to the HPO₄²⁻ anion (Parfitt et al. 1976). Inner-sphere complexes are defined as covalent linkages between the adsorbed ion and the reactive surface, with no water of hydration between the adsorbed ion and the surface functional group (Sposito 1984). Because adsorbed As is generally unavailable for biological cycling (Tamaki and Frankenburger 1992; Holm et al. 1980), adsorption reactions on soil minerals regulate As(III)/(V) redox transformation reactions by removing these species from solution and making them less available as dissolved electron donor/acceptor substrates for microorganisms.

Several studies have investigated As adsorption in soils (Elkhatib et al. 1984; Livesey and Huang 1981; Jacobs et al. 1970; Wauchope 1975; McGeehan and Naylor 1994; Goldberg and Glaubig 1988). The adsorption of As(V) in soils is correlated significantly with ammonium oxalate-extractable Al and Fe (Jacobs et al. 1970; Livesey and Huang 1981). Elkhatib et al. (1984) investigated adsorption of As(III) on soils in batch experiments and concluded that Fe(III) oxide content controlled the magnitude of As(III) adsorption. Fordham and Norrish (1974 and 1979) combined autoradiography, electron microscopy, and microprobe analysis, and found a high association of added ⁷³As(V) activity with goethite ([α]-FeOOH) in soil. Their study also concluded that aluminosilicates contribute to the total uptake of As(V) in soils, but to a lesser degree than goethite.

Because of the importance of critical soil properties (%Fe, %clay, surface area) in determining the magnitude of As(III) and As(V) adsorption and the lack of information on the disposition of As(III) in soil, the objectives of this study were (i) to compare As(III) and As(V) adsorption on three well characterized California soils and (ii) to investigate the effects of pH and ionic strength on As(III) and As(V) adsorption.

MATERIALS AND METHODS

Soils

The three arid-zone soils from California used in this study were the <2-mm fractions of Fallbrook (fine-loamy, mixed, thermic Typic Haploxeralf), Wasco (coarse-loamy, mixed, nonacidic, thermic Typic Torriorthent), and Wyo (fine-loamy, mixed, thermic Mollic Haploxeralf). Electrical conductivity (EC), pH, and *E_h* determinations were made in 1:10 soil:Deionized (DI) water suspensions that were shaken 16h, centrifuged (14,500 g), and filtered with 0.1 μm Whatman cellulose nitrate membranes. The *E_h* was measured with an Orion model 96-78 platinum redox combination electrode (Ag/AgCl reference). Cation exchange capacity (CEC) was analyzed using the method of Rhoades (1982). Inorganic carbon (IOC) and organic carbon (OC) were determined using the method of Nelson and Sommers (1982), and surface area (SA) was measured by the ethylene glycol monoethyl ether (EGME) adsorption method (Cihacek and Bremner 1979). The pH buffering capacities of the three soils were determined by batch titrations of suspensions containing 2 g of soil in 20 mL of varying HCl/NaOH solution at a constant ionic strength (*I*) of 2.5 × 10⁻⁵M NaCl. Important chemical and physical properties of the three soils are included in Table 1. Certain measurements (CEC, surface area, %clay, IOC, and OC) were reported in a previous paper (Goldberg et al. 1988).

Measurement	Soil		
	Wasco	Fallbrook	Wyo
EC (ds m ⁻¹) [‡]	0.065	0.045	0.082
pH	5.80	7.10	6.77
E _h (mV)	+96	+64	+88
CEC (mmol kg ⁻¹)	71	78	155
Surface area (m ² g ⁻¹)	55.9	28.5	78.2
Clay (%)	14.6	9.2	15.7
Inorganic carbon (mg kg ⁻¹)	10.0	240	15.0
Organic carbon (mg kg ⁻¹)	400	310	1370
Selective Dissolution by:			
Ammonium oxalate (pH 3.0) [‡]	mg kg ⁻¹		
Al	292 [§]	277	492
Fe	364	345	2660
Citrate-dithionite			
Al	648	540	989
Fe	2260	4090	8160

[‡]Measurement of EC, pH, and E_h were in 1:10 soil:solution suspensions.
[‡]See Materials and Methods for extraction procedures.
[§]Values are the average of duplicate extractions.

TABLE 1 Selected properties of three California soils

Selective Dissolution Analyses

Amorphous or "active" Fe and Al oxides were extracted by shaking duplicate 250-mL polycarbonate centrifuge bottles containing 4 g of soil in 120 mL of acidified ammonium oxalate buffer (0.175 M (NH₄)₂C₂O₄ + 0.1 M H₂C₂O₄, pH 3.0) for 2 h on a reciprocating shaker (140 oscillations min⁻¹) (Loeppert and Inskeep 1996). The 1.0 M ammonium acetate (pH 5.5) pretreatment step to remove CaCO₃ was not employed because of the low levels of IOC in these samples (Table 1). Citrate-dithionite (CD) extractable Fe was determined by a modification of the Holmgren (1967) procedure, which involved shaking duplicate 250-mL polycarbonate bottles containing 4 g soil in 120 mL of 0.57 M sodium citrate (Na₃C₆H₅O₇·5H₂O) and 0.1M sodium dithionite (Na₂S₂O₄) for 16 h (140 oscillations min⁻¹). After shaking, the suspensions (oxalate and CD) were centrifuged (4100 g, 10 min), and 15-mL aliquots were removed and filtered (0.1 μm). All sample analyses were run in duplicate, and the extracts were diluted with 1% high purity HNO₃ followed by analysis of Al and Fe by inductively coupled plasma atomic emission spectrometry (ICP-AES).

As(III) and As(V) Adsorption Experiments

Stock solutions containing 1000 mg L⁻¹ As(III) or As(V) were made by dissolving 0.860 g NaAsO₂ or 2.080 g Na₂HAsO₄·7H₂O in 500 mL of 0.1 M NaCl. These solutions were used to make standards and starting solutions for As adsorption isotherm and envelope experiments. The As(III)/(V) speciation of native soluble As in the soils as a function of suspension pH was first determined without added As to determine background levels. All As(III) and As(V) adsorption experiments employed 1:10 soil:solution batch suspensions containing 2 g of soil in 20 mL of solution. Adsorption isotherms were generated by varying the As(III) and As(V) starting concentrations from 0.27 to 13.3 μM As in suspensions. The isotherm suspensions were allowed to equilibrate at the native pH of each soil, which remained constant (despite increasing the As concentration from 0.27 to 13.3 μM) at 5.80, 7.10, and 6.77 for Wasco, Fallbrook, and Wyo, respectively.

Theoretical adsorption isotherms were fitted to experimental As(III) and As(V) adsorption isotherm data using the ISOTHERM nonlinear least squares optimization computer program (Kinniburgh 1987). The ISOTHERM program fitted the Langmuir adsorption isotherm equation Equation (1) and the Freundlich equation Equation (2) to experimental data where *n* is the amount of As adsorbed (μmol kg⁻¹), *c* is the equilibrium As concentration (μM), *K* and [beta] are adjustable parameters, and *M* is the adjustable adsorption maximum (μmol kg⁻¹) (See Table 2).

$$n = KcM / (1 + Kc)$$

Equation 1

$$n = (Kc)^{\beta}$$

Equation 2

Soil	As species	Langmuire			Freundlich		
		K	M ^l	R ²	K	β	R ²
Wasco	As(III)	0.183	37.4	0.992*	19.0	0.612	0.964*
	As(V)	0.043	235	0.989*	14.4	0.867	0.990*
Fallbrook	As(III)	0.200	142	0.992*	85.1	0.707	0.988*
	As(V)	0.182	272	0.996*	112	0.786	0.995*
Wyo	As(III)	0.300	279	0.989*	209	0.772	0.995*
	As(V)	0.554	298	0.996*	355	0.794	0.991*

†Units are μmol kg⁻¹.
*Significant at P < 0.01.

TABLE 2 Langmuir and Freundlich parameters calculated using ISOTHERM for As(III) and As(V) adsorption isotherms on Fallbrook, Wasco, and Wyo soils

The As(III) and As(V) adsorption envelope suspensions contained a constant initial As concentration (2 μM As(III) or As(V)) with pH adjustment between 3 and 11 with 0.1M NaOH or HCl. Ionic strength was adjusted by using background electrolyte concentrations of 0.001, 0.01, and 0.1 M NaCl in adsorption experiments. In all adsorption experiments, suspensions were shaken on a reciprocating shaker for 16 h at room temperature (22 ± 1°C), followed by centrifuging at 12,500 g for 10 min. Based on preliminary work, and previous studies by [Pierce and Moore \(1982\)](#), who found 99% of both As(III) and As(V) adsorption on soils taking place within 4 h, the 16-h reaction time was selected to allow adequate equilibration while also avoiding the potential for significant microbial activity. Supernatant pH was measured with a ROSS glass combination pH electrode and a Corning Ion Analyzer 150 potentiometer, followed by filtering through 0.45-μm pore size Whatman cellulose nitrate membrane filters. Sample solutions were then refrigerated (4°C) until As analysis, which was carried out within 24 h.

A parallel adsorption envelope experiment using a synthetic [alpha]-FeOOH sample determined the relative affinities of As(III) and As(V) for the pure Fe(III) oxide surface. The [alpha]-FeOOH sample had been characterized previously by X-ray diffraction and had a surface area of 45 m² g⁻¹ ([Manning and Goldberg 1996](#)). Fifty milligrams of [alpha]-FeOOH were equilibrated with 20 mL of either 107 μM As(III) or As(V) in 0.1 M NaCl for 16 h (pH adjusted with 0.1 M NaOH or HCl), followed by pH measurement, filtration, and As analysis.

Total As analyses were performed by continuous hydride generation atomic absorption spectrophotometry (HGAAS). Selected sample solutions were also analyzed for As(III)/As(V) speciation by a method that separates As(III) and As(V) by high performance liquid chromatography (HPLC) using a Dionex AS-11 IonPac anion exchange column coupled with detection by HGAAS ([Manning and Martens 1997](#)). Both applications of HGAAS used a Varian VGA 76 continuous flow-through hydride generator that mixed sample solutions 6 M HCl and 0.16 M NaBH₄ in 0.12 M NaOH. In all experiments, the amount of As(III) or As(V) adsorbed was calculated as the difference between the concentration before and after reaction with the solids.

RESULTS AND DISCUSSION

Soil Characterization

The EC, surface area, % clay, OC, and CD-extractable Al varied regularly from low to high in the Fallbrook, Wasco, and Wyo soils, respectively ([Table 1](#)). The E_h of 1:10 soil:DI water suspensions were similar, varying +64 to +96 mV, and represent moderately reduced systems ([Patrick et al. 1996](#)). Selective dissolution of the soils resulted in CD-extractable Fe levels of 2260, 4090, and 8160 mg kg⁻¹ in the Wasco, Fallbrook, and Wyo soils, respectively ([Table 1](#)). The Wasco and Fallbrook soils contained very similar levels of oxalate extractable Fe and Al, whereas the Wyo soil contained the highest levels of extractable Fe and Al. Based on the assumption that oxalate dissolves predominantly amorphous or short-range order Fe and Al oxides, the differences between CD and oxalate extracts indicate that approximately 50% of the extractable Al and between 10 and 25% of extractable Fe in the soils is amorphous.

The Wyo soil, which had a native pH of 6.7 and contained the highest OC, CD-extractable Fe and Al, % clay, and surface area, buffered pH changes more effectively than the other soils (Fig. 1). Fallbrook and Wasco soils, which had native pH values of 7.1 and 5.8, respectively, had similar buffering curves (Fig. 1). Native, soluble arsenic in 1:10 soil suspensions as a function of adjusted pH (Fig. 2) showed that alkalinization released up to 0.11 μM As(V) from Wasco and Wyo soil after 16 h. HPLC-HGAAS speciation analysis of alkaline (pH 8.5) extract solutions indicated that released As was predominantly As(V) with detectable As(III) in the Wyo soil extract (Fig. 3). Though the level of extractable As(III) in the Wyo soil is extremely low ($\sim 0.2 \mu\text{mol kg}^{-1}$), its occurrence in air-dried soil suggests that As(III) remains in metastable equilibrium under oxidizing conditions in certain soils. Calculations of As(III) or As(V) adsorption in all subsequent experiments included corrections for the released native As from the soils.

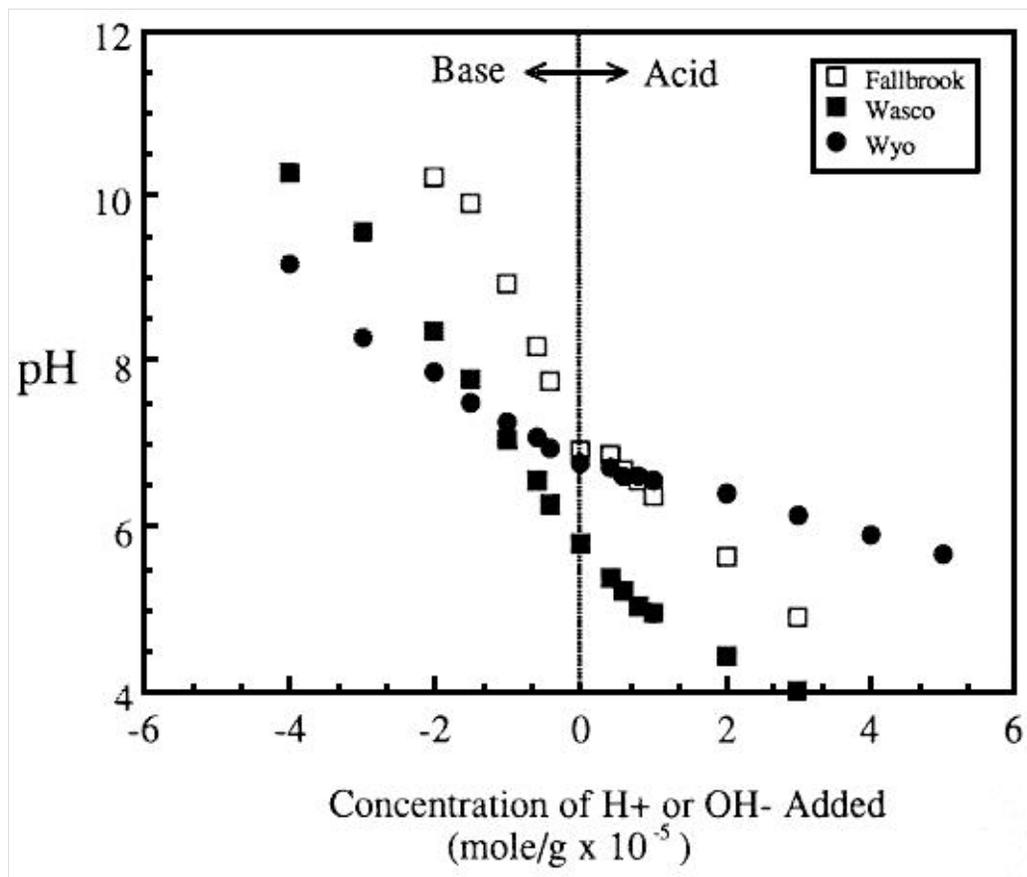


Fig. 1. Acid-base titration of 1:10 soil:DIwater suspensions.

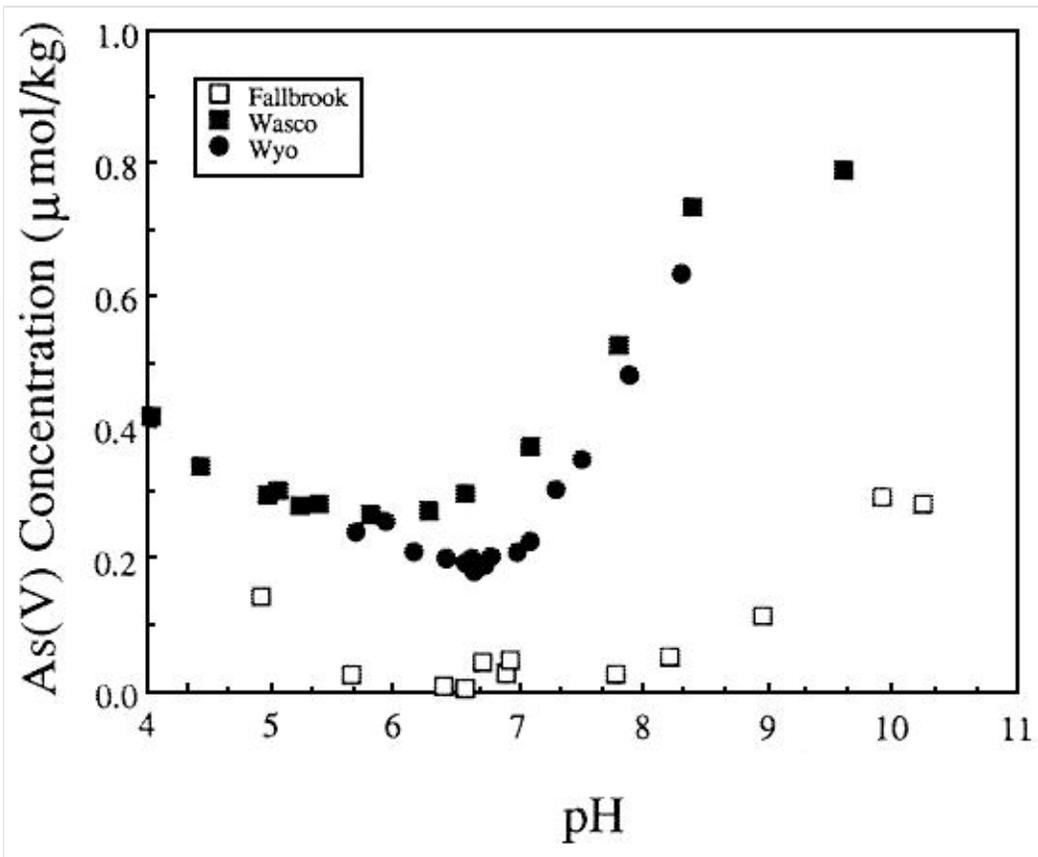


Fig. 2. Effect of suspension pH on the release of soluble As from Fallbrook, Wasco, and Wyo soils.

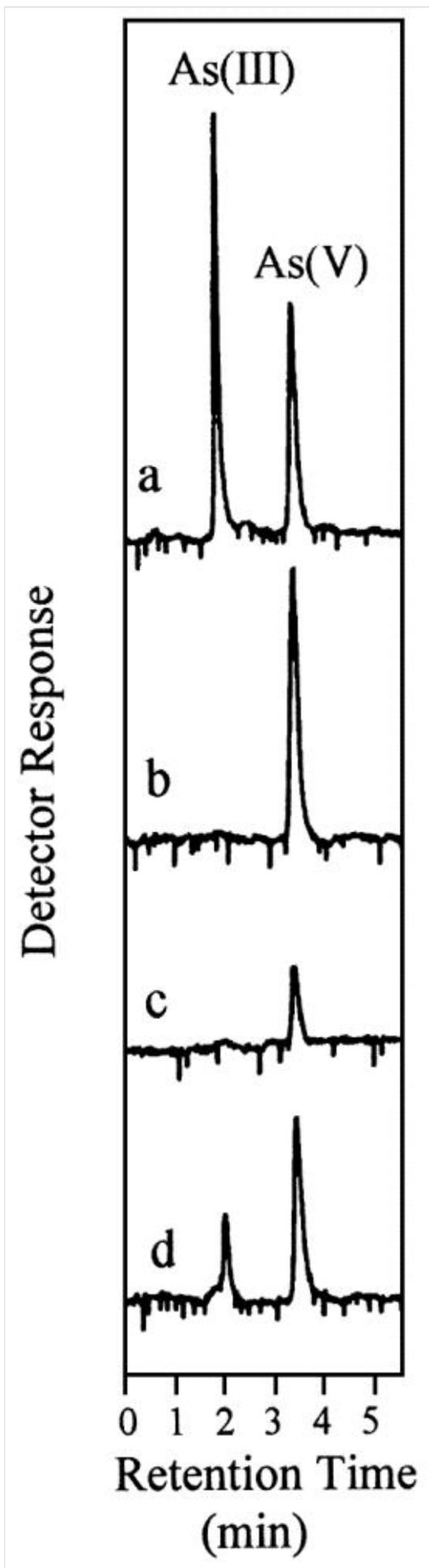


Fig. 3. Representative HPLC-HGAAS chromatograms of a standard solution containing $0.07 \mu\text{M}$ As(III) plus $0.07 \mu\text{M}$ As(V) (a), <http://ovidsp.tx.ovid.com/sp-3.27.2b/ovidweb.cgi>

and alkaline (pH 8.5) extracts of Wasco (b), Fallbrook (c), and Wyo (d) soils. HPLC Retention times for As(III) and As(V) are 2.0 and 3.6 min, respectively.

As(III) and As(V) Adsorption on Soils

Varying the amount of added As(III) or As(V), while holding temperature, pH, *I*, and suspension density constant, resulted in the set of adsorption isotherms presented in [Fig. 4](#). The soil isotherm suspensions were equilibrated at the native pH values of the 1:10 soil suspensions (see [Fig. 4](#)). The As(V) species was adsorbed more strongly than As(III) over the 0.27 to 13.3 μM As concentration range in all soils. Langmuir and Freundlich adsorption isotherms calculated using ISOTHERM gave comparable, highly significant ($P < 0.01$) fits to As(III) and As(V) experimental data on all soils ([Table 2](#)). For clarity, only the Langmuir isotherms are plotted in [Fig. 4](#). Neither As(III) or As(V) adsorption isotherms reached the adsorption maxima under our experimental conditions, and, thus, they reflect higher energy binding sites and low surface coverage. Calculated Langmuir adsorption maxima (M , $\mu\text{mol kg}^{-1}$) plotted as a function of CD-extractable Fe content ([Fig. 5](#)) indicate that, for the 16-h reaction period, these soils that contain more than 10 g kg^{-1} CD-extractable Fe adsorb more As(V) than As(III). The Wyo soil, which contained the highest surface area, %clay, and levels of CD-extractable Fe and Al, had the greatest As adsorption capacity. Based on previous investigations, which have emphasized the importance of free Fe(III) oxides in establishing the As adsorption capacity of soils ([Elkhatib et al. 1984](#); [Livesey and Huang 1981](#); [Fordham and Norrish 1979](#); [Jacobs et al. 1970](#)), the variations in Fe(III) oxide content of the three soils probably explain the different slopes observed in the adsorption isotherms.

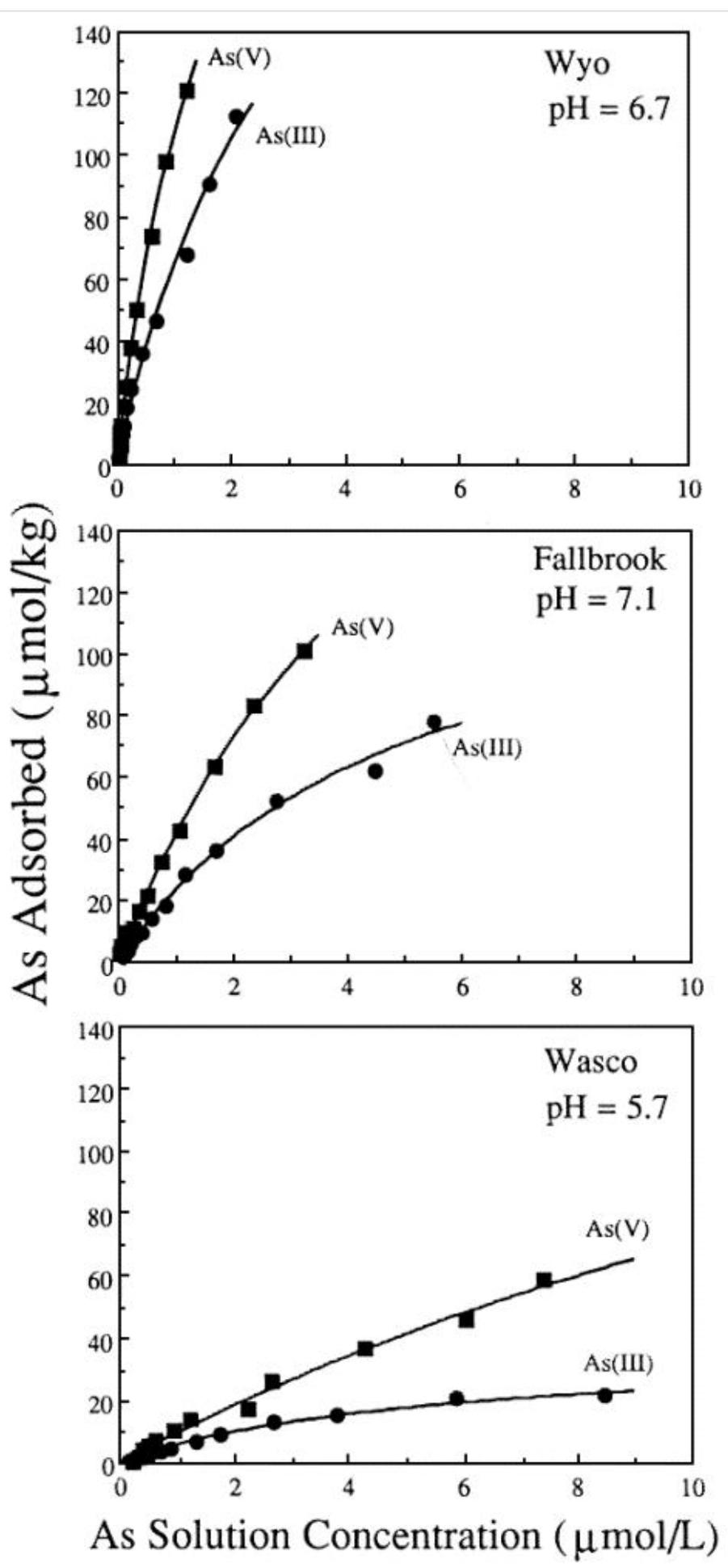


Fig. 4. Experimental As(III) and As(V) adsorption isotherms for Wyo, Fallbrook, and Wasco soils (points). Lines are Langmuir isotherms fitted to experimental data using the ISOTHERM computer program.

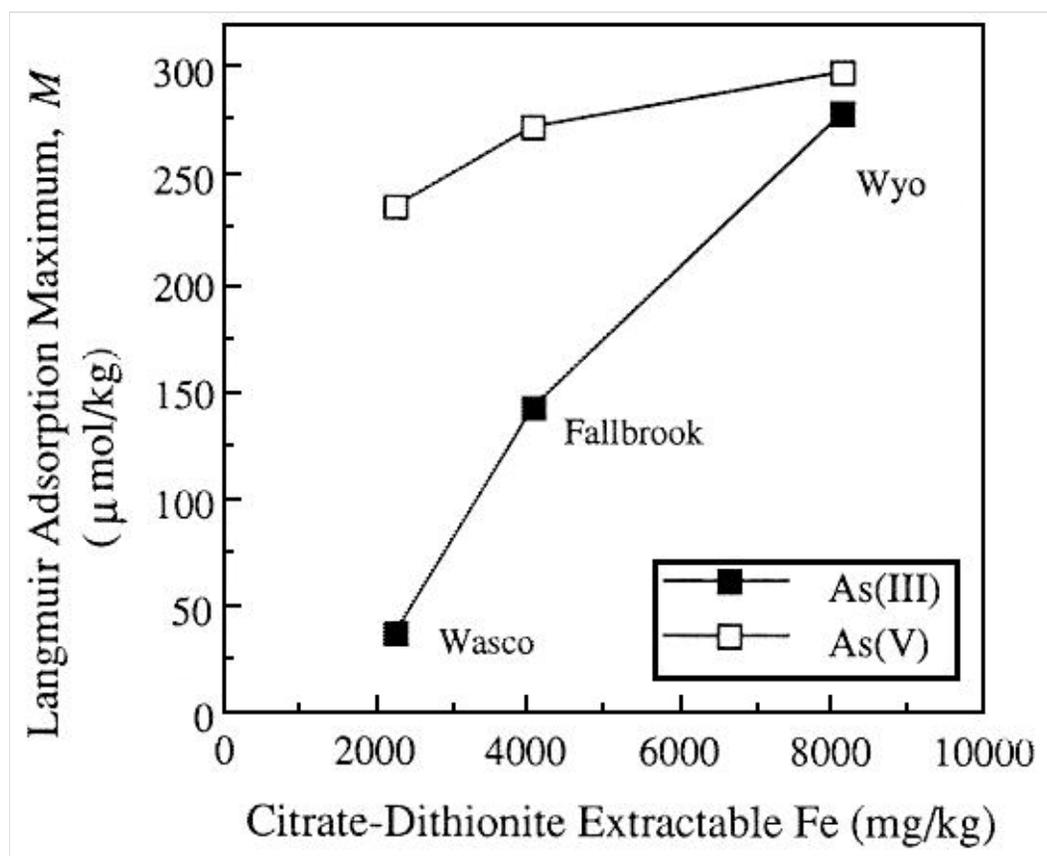
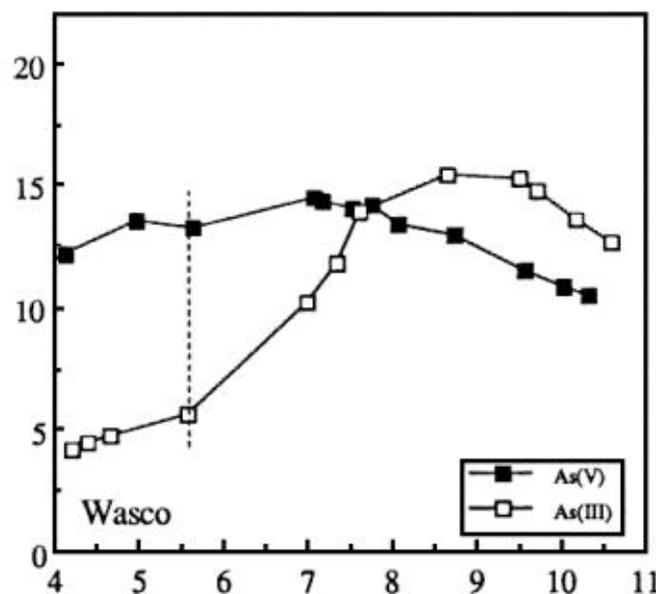
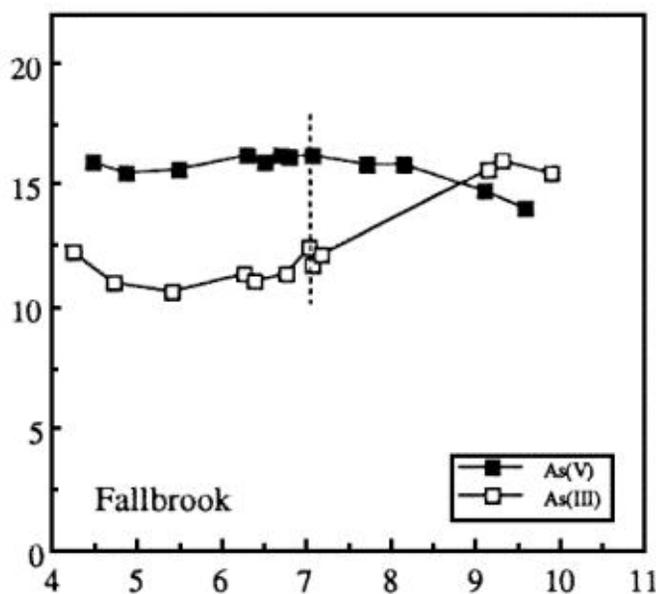
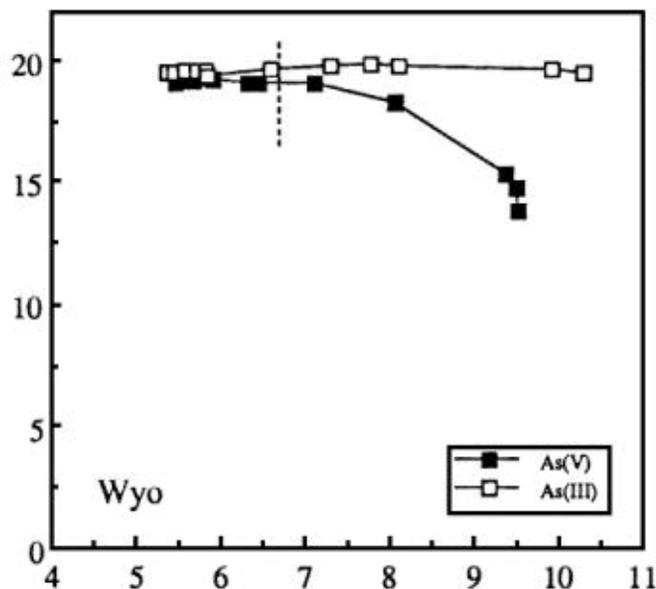


Fig. 5. Calculated Langmuir adsorption maxima (M , $\mu\text{mol kg}^{-1}$) as a function of citrate-dithionite extractable Fe content of Wyo, Fallbrook, and Wasco soils.

Adsorption envelopes for both As(III) and As(V) are shown in Fig. 6. Characterization of the As(III) and As(V) adsorption as a function of pH was carried out at low As starting concentration ($2 \mu\text{M}$), which resulted in low As loading on soils ($\leq 20 \mu\text{mol kg}^{-1}$ soil). At the ambient pH of the Fallbrook and Wasco soils (dashed lines, Fig. 6), As(V) was bound more strongly than As(III). The Wyo soil had a higher affinity for As(III), regardless of pH, with nearly 100% As(III) adsorption. This result is in contrast to the As(III) and As(V) adsorption isotherm data in Fig. 4, which suggested that the Wyo soil had a higher affinity for As(V) than As(III). However, a likely explanation is that adsorption site heterogeneity in the Wyo soil resulted in preferential adsorption of As(III) to higher energy binding sites at lower As surface loadings (e.g., $20 \mu\text{mol/kg}$).

As Adsorbed ($\mu\text{mol/kg}$)



pH

Fig. 6. As(III) and As(V) adsorption envelopes for Wyo, Fallbrook, and Wasco soils. Dashed lines indicate the ambient pH (zero acid or base addition) for the soil suspensions.

A small, pH-dependent amount of As(III) oxidation to As(V) was detectable in soil suspensions. Recoveries of As(V) from As(III)-treated soils attributable to oxidation of added As(III) were low (<4% As(III) added) when the suspension pH was less than 8.5. However, oxidation of As(III) to As(V) increased with increasing soil suspension pH. Previous work (Manning and Goldberg 1997) has shown that homogeneous oxidation of As(III) occurs in alkaline solutions (pH > 9), whereas As(III) oxidation at pH less than 9 is caused by heterogeneous reactions at the soil mineral-water interface.

The As(III) and As(V) adsorption envelopes in Fig. 6 display features that are remarkably similar to systems containing individual mineral components (Manning and Goldberg, unpublished data). For example, As(III) and As(V) adsorption on the Wyo soil as a function of pH is analogous to $[\alpha\text{-FeOOH}]$, where As(III) adsorption is consistently higher than As(V) above pH 7 (Fig. 7). The general shape of the As(III) adsorption envelopes on the Fallbrook and Wasco soils reflect the lesser importance of Fe(III) oxide soil components and are similar to As(III) adsorption envelopes reported for amorphous Al hydroxide and phyllosilicate minerals that display As(III) adsorption maxima at alkaline pH (pH > 8) (Manning and Goldberg 1997). The As(V) adsorption envelope on the Wyo soil (Fig. 6) is also reflected by the As(V) adsorption behavior on $[\alpha\text{-FeOOH}]$ (Fig. 7). This general interpretation is supported by the investigations of Fordham and Norrish (1974 and 1979), who concluded that Fe(III) oxides such as $[\alpha\text{-FeOOH}]$ preferentially adsorb As(V) in soil, and by others (Jacobs et al. 1970; Livesey and Huang 1981; Elkhatib et al. 1984), who found that the magnitude of As(V) adsorption in soil is in proportion to Fe(III) oxide content.

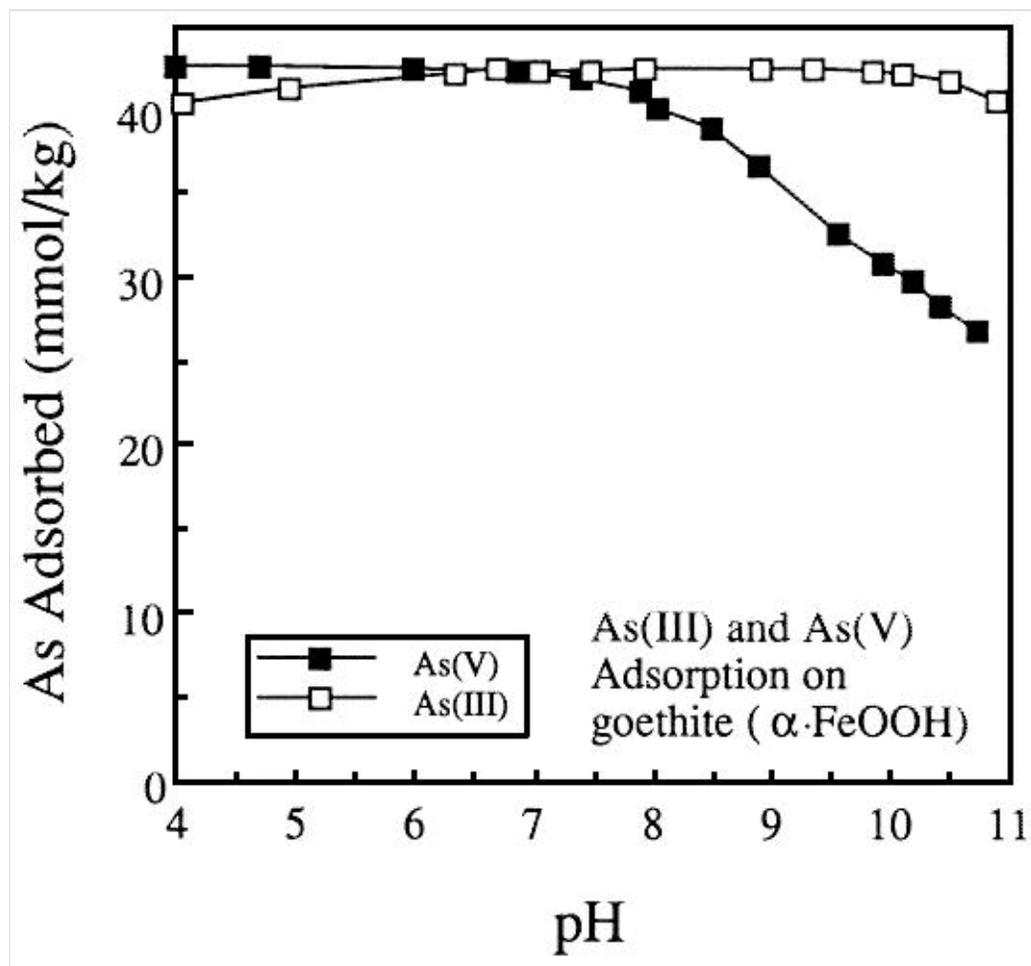


Fig. 7. As(III) and As(V) adsorption envelopes on goethite($[\alpha\text{-FeOOH}]$).

The effects of I on As(V) and As(III) adsorption over the pH range 6.5 to 8.5 and $[As]_0 = 2 \mu M$ are shown in [Figs 8 and 9](#), respectively. The greater adsorption of both As(III) and As(V) at higher ionic strength demonstrates that both As(III) and As(V) exhibit I -dependent adsorption behavior on the Wasco soil, perhaps due to weaker adsorption on aluminosilicate mineral surfaces. In contrast, the Wyo soil adsorbs both As(III) and As(V) species strongly, with only a minor detectable effect of I . The experimental conditions resulted in nearly 100% adsorption of both As(III) and As(V) on the Wyo soil, possibly confounding the conclusion that As(III) and As(V) adsorption behavior on this soil is " I -independent." Higher As(III) or As(V) concentrations (higher surface coverages) on Wyo soil are probably necessary for I -dependent adsorption behavior to be displayed. The Fallbrook soil has an overall affinity and I -dependent adsorption behavior, which is intermediate to the Wasco and Wyo soils.

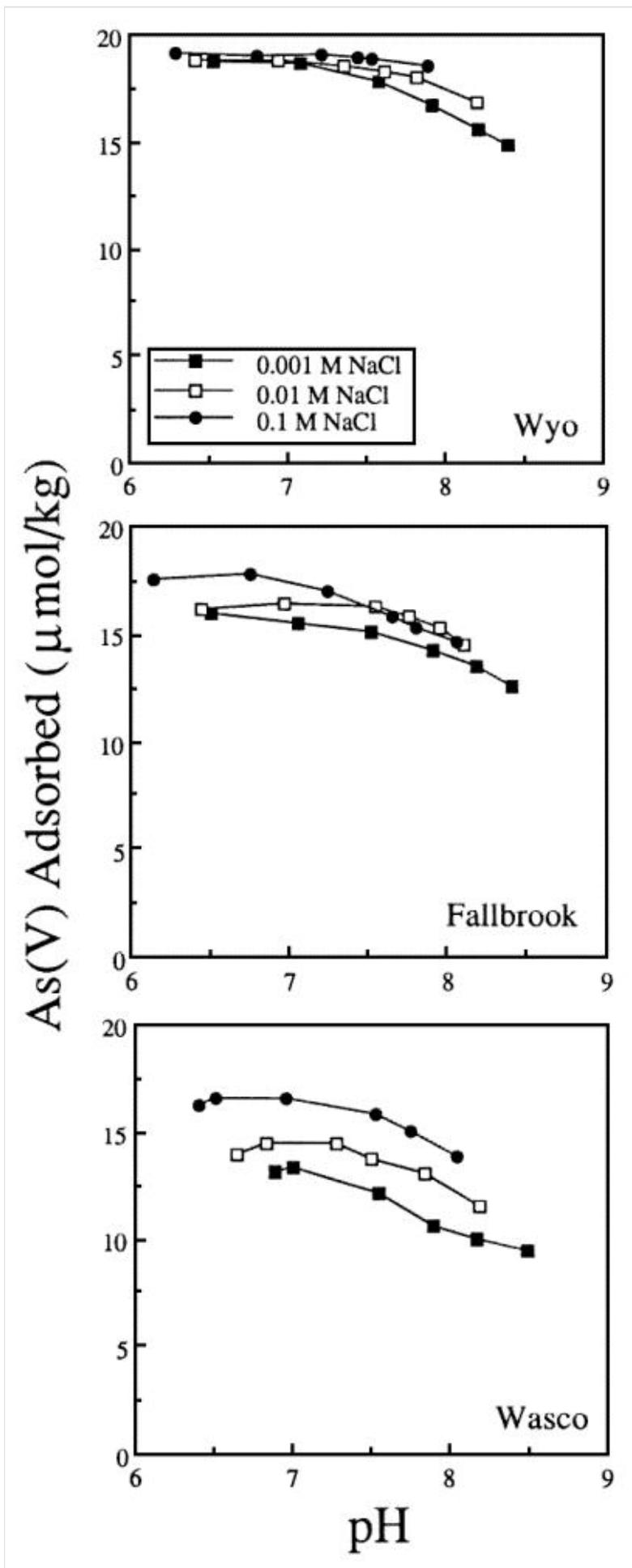


Fig. 8. Effects of pH and ionic strength (*I*) on As(V) adsorption on Wyo, Fallbrook, and Wasco soils.

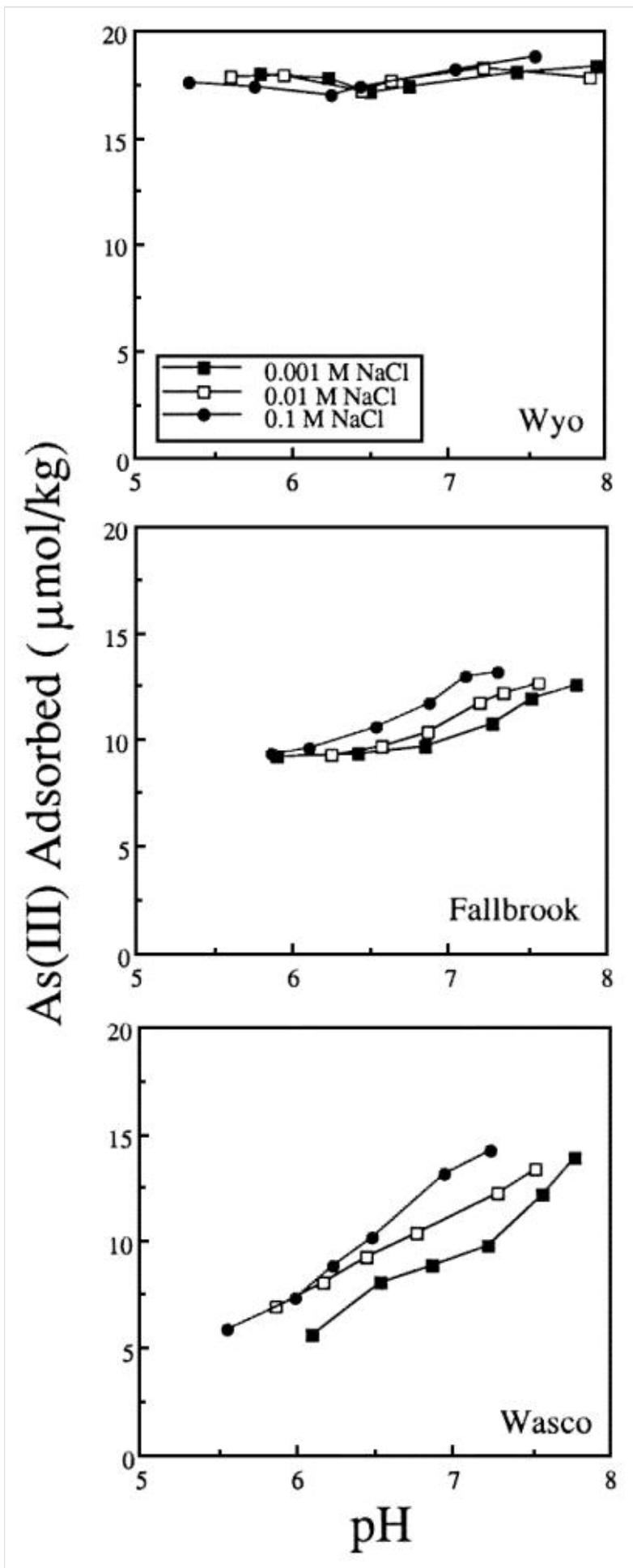


Fig. 9. Effects of pH and ionic strength (*I*) on As(III) adsorption on Wyo, Fallbrook, and Wasco soils.

Investigations of selenite and phosphate anion adsorption on metal oxides have concluded that adsorption behavior that is indifferent to variations in I is macroscopic evidence for an inner-sphere adsorption mechanism (Hayes et al. 1988; Hingston et al. 1968). Both EXAFS (Waychunas et al. 1993) and attenuated total reflectance-FTIR spectroscopies (Sun and Doner 1996) suggest that As(III) and As(V) oxyanions form inner-sphere surface complexes on the $[\alpha]$ -FeOOH surface. However, in whole soils, the adsorption behaviors of As(III) and As(V) appear to be affected by I , which is likely caused by the variety of mineral surfaces other than Fe(III) oxides that contribute to the total adsorption.

CONCLUSIONS

The As(V) species was found to have a higher overall affinity for soil than As(III) based on adsorption isotherms at the native pH (5.7 to 7.1) of the individual soil. However, this generalization was not always true, especially at the low As surface coverages achieved in adsorption envelope studies, where As(III) displayed a higher affinity for the soil with the highest Fe(III) oxide content (Wyo) than As(V). Alkaline pH conditions (pH > 8) appeared to cause As(III) oxidation and increased As(III) uptake by the soils. The overall As adsorption capacities of the soils in this study were related to the amount of CD-extractable Fe. Based on our results, and the growing evidence for the importance of Fe(III) oxides, measurements of the free Fe(III) oxide content of soil samples is critical for characterizing the anion adsorption capacity of soils. It may then be possible to develop models for anion retention and mobility in whole soil that include soil properties (%Fe and Al oxides, %clay) and solution parameters (pH, I , anion concentration). Molecular-level information derived from spectroscopy that describes the bonding configuration of adsorbed anions will also be critical for a complete understanding of the reactivity of As(III) and As(V) in soils.

ACKNOWLEDGMENTS

Gratitude is expressed to Ms. N. Gill for technical assistance and to Dr. J. D. Rhoades of the U.S. Salinity Laboratory for providing the soil samples.

REFERENCES

- Abernathy, J. R. 1983. Role of arsenical chemicals in agriculture. *In* Arsenic. Van Nostrand Reinhold Company, New York, pp. 57-62. [\[Context Link\]](#)
- Aurilio, A. C., R. P. Mason, and H. F. Hemond. 1994. Speciation and fate of arsenic in three lakes of the Aberjona Watershed. *Environ. Sci. Technol.* 28:577-585. [\[Context Link\]](#)
- Bowell, R. J. 1994. Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem.* 9:279-286. [\[Context Link\]](#)
- Cihacek, L. J., and J. M. Bremner. 1979. A simplified ethylene glycol monoethyl ether procedure for assessing soil surface area. *Soil Sci. Soc. Am. J.* 43:821-822. [\[Context Link\]](#)
- Davidson, R. L., D. S. Natusch, J. R. Wallace, and C. A. Evans. 1974. Trace elements in fly ash. Dependence of concentration on particle size. *Environ. Sci. Technol.* 8:1107-1112. [\[Context Link\]](#)
- Elkhatib, E. A., O. L. Bennett, and R. J. Wright. 1984. Arsenite sorption and desorption in soils. *Soil Sci. Soc. Am. J.* 48:1025-1030. [\[Context Link\]](#)
- Ferguson, J. F., and J. Gavis. 1972. A review of the arsenic cycle in natural waters. *Water. Res.* 6:1259-1274. [\[Context Link\]](#)
- Fordham, A. W., and K. Norrish. 1979. Arsenate-73 uptake by components of several acid soils and its implications for phosphate retention. *Aust. J. Soil Res.* 17:307-316. [\[Context Link\]](#)
- Fordham, A. W., and K. Norrish. 1974. Direct measurement of the composition of soil components which retain added arsenate. *Aust. J. Soil Res.* 12:165-172. [\[Context Link\]](#)

Fujii, R., and W. C. Swain. 1995. Areal distribution of selected trace elements, salinity, and major ions in shallow groundwater, Tulare Basin, Southern San Joaquin Valley, California. U.S. Geological Survey, Water Resources Investigations Report, 95-4048. [\[Context Link\]](#)

Goldberg, S., D. L. Suarez, and R. A. Glaubig. 1988. Factors affecting clay dispersion and aggregate stability of arid-zone soils. *Soil Sci.* 146:317-325. [Buy Now](#) | [\[Context Link\]](#)

Goldberg, S., and R. A. Glaubig. 1988. Anion sorption on a calcareous, montmorillonitic soil-Arsenic. *Soil Sci. Soc. Am. J.* 52:1297-1300. [\[Context Link\]](#)

Hayes, K. F., C. Papelis, and J. Leckie. 1988. Modeling ionic strength effects on anion adsorption at hydrous oxide/solution interfaces. *J. Colloid. Interface Sci.* 125:717-726. [\[Context Link\]](#)

Hingston, F. J., A. M. Posner, and J. P. Quirk. 1968. Adsorption of selenite by goethite. *Adv. Chem. Ser.* 79:82-90. [\[Context Link\]](#)

Holm, T. R., M. A. Anderson, R. S. Stanforth, and D. G. Iverson. 1980. The influence of adsorption on the rates of microbial degradation of arsenic species in sediments. *Limnol. Oceanogr.* 25:23-30. [\[Context Link\]](#)

Holmgren, G.G.S. 1967. A rapid citrate-dithionite extractable iron procedure. *Soil Sci. Soc. Am. Proc.* 31:210-211. [\[Context Link\]](#)

Huang, Y.-C. 1994. Arsenic distribution in soils. *In* Arsenic in the environment, part I: Cycling and characterization. J. O. Nriagu (ed.). Wiley-Interscience, New York, pp. 17-49. [\[Context Link\]](#)

Jacobs L. W., J. K. Syers, and D. R. Keeney. 1970. Arsenic sorption by soils. *Soil Sci. Soc. Am. Proc.* 34:750-754. [\[Context Link\]](#)

Kinniburgh, D. G. 1987. ISOTHERM: A computer program for analyzing adsorption data. Version 2.2. British Geological Survey, Wallingford, Oxon, UK. [\[Context Link\]](#)

Livesey N. T., and P. M. Huang. 1981. Adsorption of arsenate by soils and its relation to selected chemical properties and anions. *Soil. Sci.* 131:88-94. [Buy Now](#) | [\[Context Link\]](#)

Loeppert, R. L., and W. P. Inskeep. 1996. Iron. *In* Methods of soil analysis, part 3: Chemical methods. D. L. Sparks et al. (eds.) Soil Science Society of America, Inc. Madison, WI, pp. 639-664. [\[Context Link\]](#)

Lumsdon, D. G., A. R. Fraser, J. D. Russell, and N. T. Livesey. 1984. New infrared band assignments for the arsenate ion adsorbed on synthetic goethite(α)-FeOOH). *J. Soil Sci.* 35:381-386. [\[Context Link\]](#)

Manning, B. A., and S. Goldberg. 1997. Adsorption and stability of arsenic(III) at the clay mineral-water interface. *Environ. Sci. Technol.* 31:2005-2011. [\[Context Link\]](#)

Manning, B. A., and D. A. Martens. 1997. Speciation of arsenic(III) and arsenic(V) in sediment extracts by high performance liquid chromatography-hydride generation atomic absorption spectrophotometry. *Environ. Sci. Technol.* 31:171-177. [\[Context Link\]](#)

Manning, B. A., and S. Goldberg, 1996. Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. *Soil Sci. Soc. Am. J.* 60:121-131. [\[Context Link\]](#)

Masscheleyn, P. H., R. D. Delaune, and W. H. Patrick, Jr. 1991a. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ. Sci. Technol.* 25:1414-1419. [\[Context Link\]](#)

Masscheleyn P. H., R. D. Delaune, and W. H. Patrick Jr. 1991b. Arsenic and selenium chemistry as affected by sediment redox potential and pH. *J. Environ. Qual.* 20:522-527. [\[Context Link\]](#)

McBride, B. C., H. Merilees, W. R. Cullen, and W. Pickett. 1978. Anaerobic and aerobic alkylation of arsenic. *In Organometals and organometalloids: Occurrence and fate in the environment.* F. E. Brickman and J.M. Bellama (eds.). *Am. Chem. Soc. Symp. Ser.* 82:94-115. [\[Context Link\]](#)

McGeehan, S. L., and D. V. Naylor. 1994. Sorption and redox transformation of arsenite and arsenate in two flooded soils. *Soil Sci. Soc. Am. J.* 58:337-342. [\[Context Link\]](#)

Nelson, D. W., and L. E. Sommers. 1982. Total carbon, organic carbon, and organic matter. *In Methods of soil analysis, part 2, 2nd Ed.* A. L. Page et al. (eds.). ASA-SSSA, Madison, WI, pp. 539-579. [\[Context Link\]](#)

Parfitt, R. L., J. D. Russell, and V. C. Farmer. 1976. Confirmation of the surface structures of goethite ($[\alpha]\text{-FeOOH}$) and phosphated goethite by infrared spectroscopy. *J. Chem. Soc. Faraday Trans. I.* 72:1082-1087. [\[Context Link\]](#)

Patrick, W. H., R. P. Gambrell, and S. P. Faulkner. 1996. Redox measurements of soils. *In Methods of Soil Analysis, part 3: Chemical Methods.* D. L. Sparks et al. (eds.) Soil Science Society of America, Inc. Madison, WI, pp. 1255-1273. [\[Context Link\]](#)

Peryea, F. J., and T. L. Creger. 1994. Vertical distribution of lead and arsenic in soils contaminated with lead arsenate pesticide residues. *Water Air Soil Pollut.* 78:297-306. [\[Context Link\]](#)

Pierce, M. L., and C. B. Moore. 1982. Adsorption of arsenite and arsenate on amorphous iron oxyhydroxide. *Water Res.* 16:1247-1253. [\[Context Link\]](#)

Rhoades, J. D. 1982. Cation exchange capacity. *In Methods of soil analysis, part 2, 2nd Ed.* A. L. Page et al. (eds.). ASA-SSSA, Madison, WI, pp. 149-157. [\[Context Link\]](#)

Sadiq, M., T. H. Zaida, and A. A. Mian. 1983. Environmental behavior of arsenic in soils: Theoretical. *Water Air Soil Pollut.* 20:369-377. [\[Context Link\]](#)

Sparks, D. L. 1989. Kinetics of soil chemical processes. Academic Press, New York, Chapter 4. pp. 61-98. [\[Context Link\]](#)

Sposito, G. 1984. The surface chemistry of soils. Oxford Univ. Press, Oxford, England. [\[Context Link\]](#)

Sun, X., and H. E. Doner. 1996. An investigation of arsenate and arsenite bonding structures on goethite by FTIR. *Soil Sci.* 161:865-872. [Ovid Full Text](#) | [\[Context Link\]](#)

Tamaki S, and W. T. Frankenburger, Jr. 1992. Environmental biochemistry of arsenic. *Rev. Environ. Contam. Toxicol.* 124:79-110. [\[Context Link\]](#)

Tanaka, T. 1988. Distribution of arsenic in the natural environment with emphasis on rocks and soil. *Appl. Organomet. Chem.* 2:283-295. [\[Context Link\]](#)

Wauchope, R. D. 1975. Fixation of arsenical herbicides, phosphate, and arsenate in alluvial soils. *J. Environ. Qual.* 4:355-358. [\[Context Link\]](#)

Waychunas, G. A., B. A. Rea, C. C. Fuller, and J. A. Davis. 1993. Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochim. Cosmochim. Acta* 57:2251-2269. [\[Context Link\]](#)

Wilkie, J. A., and J. G. Hering. 1996. Adsorption of arsenic onto hydrous ferric oxide. Effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloids Surf. A: Phys. Chem. Eng. Aspects* 107:97-110. [\[Context Link\]](#)

Zhang, P. C., and D. L. Sparks. 1989. Kinetics and mechanisms of molybdate adsorption/desorption at the goethite/water interface using pressure-jump relaxation. *Soil Sci. Soc. Am. J.* 53:1028-1034. [\[Context Link\]](#)

IMAGE GALLERY

Select All

Export Selected to PowerPoint

Measurement	Fullbrook	Wasco	Wyo
EC (dS/m)	0.669	0.684	0.661
pH	5.80	7.29	4.22
CEC (meq/100g)	176	118	161
CEC (meq/kg)	71	78	100
NaOH-saturated p _H	99.8	28.6	79.2
As(III) (mg/kg)	216	32	18.7
As(V) (mg/kg)	39.9	287	10.8
Organic carbon (mg/kg)	887	243	1079

Adsorption Isotherm by	Langmuir	Freundlich
As(III)	26.0	275
As(V)	84.1	141
Cation exchange	148	141
As	238	830

$$n = KcM / (1 + Kc) \quad \text{Equation 1}$$

$$n = (Kc)^{\beta} \quad \text{Equation 2}$$

Equation 1

Table 1

Soil	As	Langmuir			Freundlich		
		K _L	Q _{max}	b	K _F	n	R ²
Wasco	As(III)	0.183	27.4	0.902	19.0	0.613	0.994
	As(V)	0.033	275	0.997	18.4	0.607	0.997
Fullbrook	As(III)	0.200	142	0.982	65.1	0.767	0.989
	As(V)	0.183	172	0.999	115	0.786	0.999
Wyo	As(III)	0.388	278	0.989	308	0.723	0.989
	As(V)	0.014	896	0.999	388	0.794	0.999

Table 2

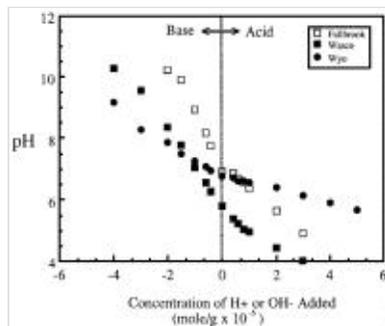


Fig. 1

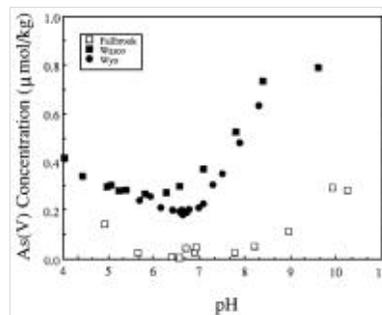


Fig. 2

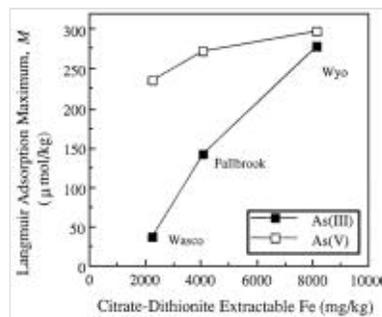


Fig. 5

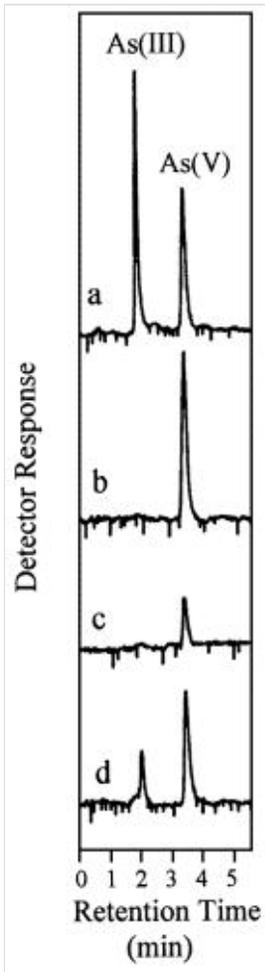


Fig. 3

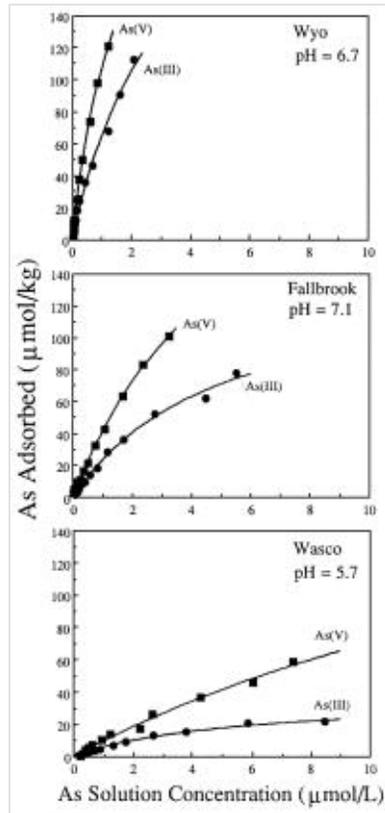


Fig. 4

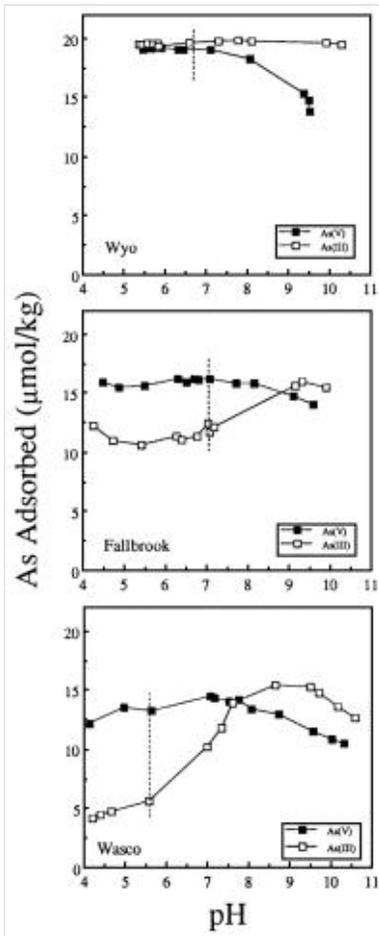


Fig. 7

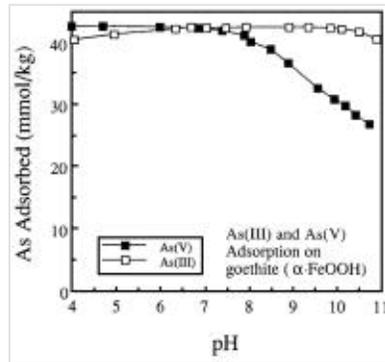


Fig. 6

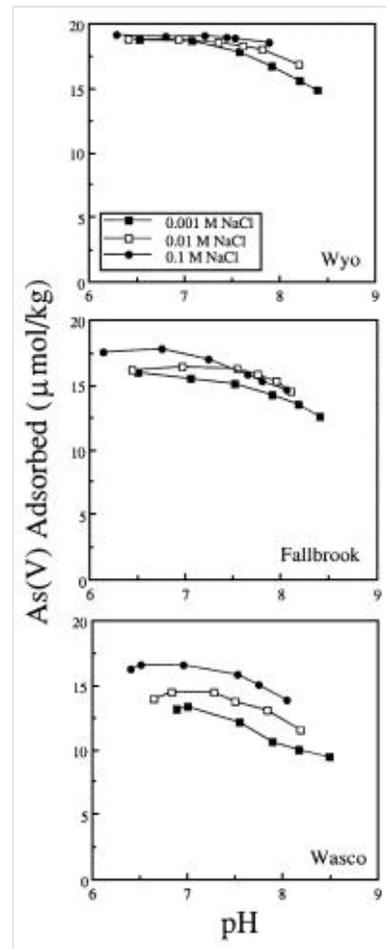


Fig. 8

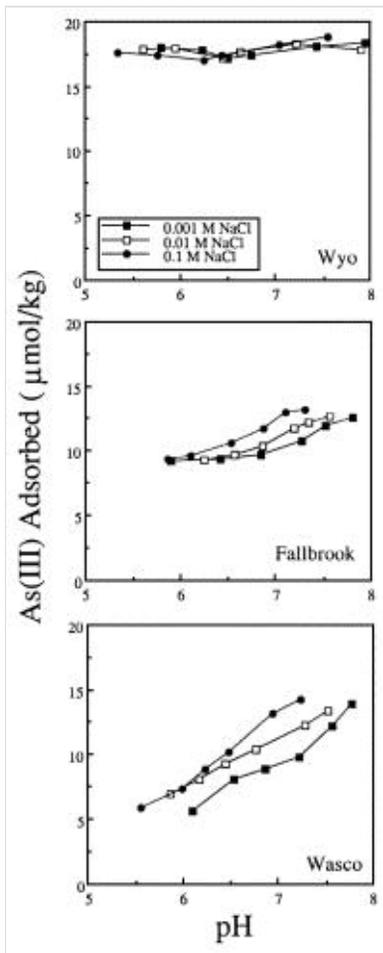


Fig. 9

[Back to Top](#)