Environ. Sci. Technol. **2005**, *39,* 7102−7110

Adsorption, Oxidation, and Bioaccessibility of As(III) in Soils

JAE-KYU YANG,[†] MARK O. BARNETT,[*,†]
JINLING ZHUANG,[†]
SCOTT E. FENDORF,[‡] AND
PHILIP M. JARDINE[§]

Department of Civil Engineering, 238 Harbert Engineering Center, Auburn University, Auburn, Alabama 36849, Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305, and Environmental Sciences Division, Oak Ridge National Laboratory, Post Office Box 2008, Oak Ridge, Tennessee 37831

At As-contaminated sites, where the ingestion of soil by children is typically the critical human-health exposure pathway, information on the bioavailability of soil-bound As is often limited. The influence of various soil physical and chemical properties (iron and manganese oxides, pH, cation exchange capacity, total inorganic and organic carbon, and particle size) on As(III) adsorption, sequestration, bioaccessibility (as a surrogate for oral bioavailability), and oxidation was investigated in 36 well-characterized soils by use of a physiologically based extraction test (PBET). These results were compared to an earlier published study with As(V) on the same set of soils. The properties of the soils were able to explain >80% of the variability in the adsorption and sequestration (as measured by the reduction in bioaccessibility over time) of As(III) in these soils. The initial bioaccessibility of As(III) was significantly higher than the initial bioaccessibility of As(V) on the same set of soils. However, over a 6-month period of aerobic aging, a significant portion of the solid-phase As(III) on these soils was oxidized to As(V), decreasing its bioaccessibility markedly. A multivariable linear regression model previously developed to predict the steady-state bioaccessibility of As(V) in soils was able to predict the bioaccessibility in As(III)-spiked soils within a root-mean-square error (RMSE) of 16.8%. Generally, soils having a higher iron oxide content and lower soil pH exhibited lower bioaccessibility. This model was also able to predict the in vivo bioavailability of As in contaminated soils previously used in an independent juvenile swine dosing trial within an RMSE of 15.5%, providing a greatly improved yet conservative estimate of bioavailability relative to the typical default assumption of 100%. However, the model was not able to accurately predict the bioavailability of As in a different set of contaminated soils previously used in an independent *Cebus* monkey dosing trial, consistently overpredicting the bioavailability, resulting in an RMSE of 42.7%. This model can be used to provide an initial estimate of As bioavailability in soil to aid in screening sites and justifying expensive site-specific animal feeding studies. Further, as the model is based on major soil properties, the resulting estimates are valid as long as the major soil properties do not change, thus providing some confidence in the long-term applicability of the estimates.

Introduction

Arsenic contamination in soils results from various anthropogenic sources such as mining activities, the discharges of industrial wastes, and agricultural application as well as from geochemical reactions (*1*−*4*). Although As has multiple oxidation states (+5, +3, 0, and −3), arsenite As(III) and arsenate As(V) are the most common in natural environments (*5*, *6*). Generally, As(III) is favored in sediments or in the aqueous phase under anaerobic conditions, while the reverse order of species occurs under aerobic conditions. The speciation and solubility of inorganic As is sensitive to redox conditions and the pH of the environment, which affects the bioavailability, toxicity, and mobility of As in soils (*7*, *8*). Since As(III) is much more toxic and mobile than As(V) (*9*), the oxidation of As(III) to As(V) is important in reducing the risk of As-contaminated soils.

Children are often exposed to soils contaminated with toxic metals such as As through hand-to-mouth activity. Therefore, the ingestion of soils contaminated with toxic metals is of great concern because of their toxicity and threat to human health. The ingestion of As-contaminated soils by children is typically the risk driver at As-contaminated sites (*10*). This risk has often been estimated by assuming that soil-bound metals were completely absorbed (100% bioavailable) through the human gastrointestinal tract upon ingestion, although <100% of toxic metals have been known to dissolve from soils (*11*−*14*). Controlling factors in the bioavailability of As(V) from soil include the pH of both the gastrointestinal fluid and soil, the soil metal concentration, the soil-to-solution ratio, mineral form, and particle size (*15*−*17*).

In the study described in this paper, soluble As(III) was spiked into a wide range of well-characterized soils representing seven major soil orders within the United States. The resulting bioaccessibility (a surrogate for oral bioavailability) of As in these 36 soils was measured over 6 months with an in vitro extraction test. Oral bioaccessibility is defined as the fraction of a contaminant that is soluble and available for systemic absorption in the gastrointestinal environment (*16*). The benefits of using labile As(III) are to ascertain the ability of soils themselves to limit As bioaccessibility, without regard to any unique site-specific speciation, which is difficult to measure and which is subject to change over time. The speciation of As in the extraction fluid was monitored by wet chemical techniques, while the solid-phase speciation was monitored by synchrotron X-ray absorption near-edge structure (XANES) spectroscopy. To determine the macroscopic factors affecting adsorption and the oxidation of As(III), the effect of soil properties were evaluated with multivariable linear regression. The bioaccessibility results for these As(III)-spiked soils were compared to our earlier results by use of As(V)-spiked soils (*18*). A model previously developed to predict the bioaccessibility of As(V)-spiked soils was used to predict the bioaccessibility of these As(III)-spiked soils, and this model was also used to predict the in vivo bioavailability of As to juvenile swine (*19*) and *Cebus* monkeys (*20*) determined in independent studies.

Experimental Section

Materials. All chemicals employed in this research were analytical grade or above, and solutions were prepared with

---

[*] Corresponding author phone: +1 (334) 844-6291; fax: +1 (334) 844-6290; e-mail: barnettm@eng.auburn.edu.
[†] Auburn University.
[‡] Stanford University.
[§] Oak Ridge National Laboratory.

10.1021/es0481474 CCC: $30.25

TABLE 1. Some Physical and Chemical Properties of Soils Used in Study

soil	soil type	series	pH	CEC ($\mathrm{cmol_c/kg}$)	organic carbon (%)	inorganic carbon (%)	particle size (%)			Fe (g/kg)	Mn (g/kg)
							clay	silt	sand		
1	Alfisol	Angola-Ap	5.29	6.70	3.72	0.96	32.1	56.1	11.8	23.28	1.23
2		Angola-B	7.86	4.50	0.09	0.25	25.6	52.9	21.5	5.83	0.19
3		Crider-Ap	6.57	5.60	0.55	0.39	22.5	75.8	1.7	13.34	0.72
4		Crider-B2lt	5.26	5.40	0.21	0.13	30.9	67.2	1.9	13.38	0.3
5		Lenberg-A	5.92	7.90	3.41	1.01	49.1	44.5	6.4	12.94	1.37
6		Lenberg-Btl	4.35	5.50	0.36	0.25	64.7	29.5	5.8	15.69	0.12
7		Lawrence-Apl	4.97	5.80	0.91	0.59	19.5	48.5	32.0	11.17	1.35
34		Lawrence-Btl	4.28	3.70	0.11	0.1	25.8	38.3	35.9	17.53	0.29
8	Aridisol	Doakum-Ab	6.94	6.90	0.28	0.08	10.8	24.8	64.4	4.74	0.19
9		Doakum-Bt	6.84	7.00	0.39	0.18	29.3	15.0	55.7	6.86	0.16
10		Kzin-A2	7.74	13.30	3.27	1.35	22.2	44.2	33.6	4.07	0.29
11		Kzin-Bk	7.8	10.00	3.4	1.88	27.0	38.5	34.5	3.26	0.18
12		Oricto-A2	8.72	13.70	0.09	0.94	10.2	34.7	55.1	2.92	0.34
13		Oricto-Bt	9.01	8.60	0.16	1.1	23.2	27.5	49.3	3.16	0.29
14		Stoneham-A	6.42	10.10	1.45	0.71	16.2	41.4	42.4	3.4	0.26
15		Stoneham-Bt1	6.8	7.80	0.66	0.32	21.4	23.2	55.4	2.2	0.2
16	Entisol	Wakeland-Ap	5.86	6.10	0.92	0	23.8	64.7	11.5	8.82	0.71
17		Wakeland-Cg1	5.77	5.70	0.56	0.25	21.1	66.4	12.5	9.18	0.8
18	Inceptisol	Berks-A	3.65	9.10	2.72	1.01	15.7	46.6	37.7	13.18	0.15
19		Montevello-A	6.91	8.00	3.55	0.62	6.0	69.0	25	10.68	1.42
20		Montevello-B	4.23	14.00	0.42	0.26	19.0	42.2	38.8	22.07	0.17
21		Rockaway-A1	3.86	10.60	3.54	1.49	12.4	34.8	52.8	14.03	0.52
22		Rockaway-B2t	4.1	3.70	0.21	0.18	12.6	32.1	55.3	17.34	0.16
23		Weikert-Ap	4.44	13.30	3.97	2.37	24.4	56.2	19.4	21.41	6.47
24		Weikert-Be	4.28	8.00	2.01	1.15	23.9	54.3	21.8	28.98	5.42
25	Mollisol	Dennis-Ap	5.82	8.70	1.32	0.89	15.9	66.1	18	15.11	0.6
26		Dennis-Ba	4.77	4.40	0.38	0.41	29.7	57.5	12.8	24.29	0.59
27		Sibley-A	6.36	7.10	1.06	0.49	23.5	69.7	6.8	8.23	0.67
28		Sibley-B1	6.36	6.80	0.72	0.52	26.9	68.0	5.1	9.11	0.59
29	Spodosol	Charlton-A2	3.15	11.90	2.3	0.4	2.9	28.7	68.4	1.33	0
30	Ultisol	Allen-A	4.59	7.70	1.55	0.56	8.7	29.5	61.8	6.95	0.31
31		Allen-Ba	4.3	1.30	0.19	0.09	14.9	28.4	56.7	18.96	0.1
32		Cecil-Ap	4.04	5.80	1.64	0.39	10.2	23	66.8	6.01	0.06
33		Cecil-Bt1	4.44	1.60	0.29	0.21	44.8	15.5	39.7	32.56	0.11
35		Minvale-Ap	6.01	6.00	1.89	0.99	6.1	58.9	34.9	7.71	1.51
36		Minvale-Bt1	4.3	4.00	0.1	0.07	23.6	44.2	32.2	19.55	0.16
		mean	5.6	7.4	1.3	0.6	21.0	42.5	36.9	11.9	0.8
		min	3.2	1.3	0.1	0.0	0.4	15.0	1.7	1.3	0.0
		max	9.0	14.0	4.0	2.4	64.7	75.8	70.6	32.6	6.5
		std deviation	1.5	3.2	1.3	0.5	16.9	21.8	8.0	8.0	1.3

deionized water (18 MΩ·cm) from a reverse osmosis/ion exchange apparatus (Milli-Q water system). The A- and upper B-horizons of soils from seven major United States soil orders were supplied by the U.S. Department of Agriculture National Resources Conservation Service (NRCS). The A- and upper B-horizons from two well-characterized soils from the U.S. Department of Energy Oak Ridge Reservation in East Tennessee were also included for a total of 36 soils. The soil's cation exchange capacity (CEC) and particle size distribution were measured by standard methodologies and reported by the NRCS (*21*). The soil pH was measured in a 2:1 solution-to-solid ratio in 5 mM $CaCl_2$ by use of a combination pH electrode and meter. Extractable iron and manganese oxides were measured by extraction with dithionite–citrate–bicarbonate (DCB) (*22*) and total organic and inorganic carbon (TOC and TIC) were measured by combustion on a total carbon analyzer. The physicochemical properties of the soils are shown in Table 1. Because we had limited amounts of these diverse, well-characterized soils, some analytical procedures discussed below were modified by using a smaller soil sample size than usual. Before use, these modifications were tested on a select number of samples/replicates as explicitly described below. The consistent verification of As mass balances from hundreds of soil and solution analyses within ±10% and coefficient of variations for duplicate bioaccessibility extractions of <10% during the study further confirms the validity of these modifications.

Soil Spiking. The soils were gently ground with a mortar and pestle and sieved to <250 μm, representing the soil particles that are more adherent to children's hands and thus more likely to be ingested (*23*). As(III) was added to the soils (2 g) with a target concentration of ~100 mg/kg from a small volume of concentrated As(III) stock solution to a 1:10 g/mL soil solution of 10^{-3} M $CaCl_2$. The As(III) stock solution was prepared by dissolving As_2O_3(s) in 1 M NaOH. Dilute HNO_3 solution was added to the soil slurry at the same time as the As(III) spike to neutralize the NaOH added with the As(III) in order to maintain the original soil pH (Table 1). In this manner, the pH of the <250 μm fraction, measured as described above, remained essentially constant before and after spiking. After 48 h of mixing, the soil suspension was centrifuged and the supernatant was decanted. The oxidation state of As in the supernatant was not measured during this 48 h period. However, As(III) blanks in homogeneous solution (no soil) remained stable during this time period. Thus any significant As(III) oxidation that occurred during this time period was due to the presence of the soil. The remaining soil was washed twice with a small volume (~2–3 mL) of deionized water to remove any traces of the original soluble As(III) spike. Analysis of a few ($n = 4$) of the rinsates indicated negligible As(III) desorption occurred while the soil was rinsed with deionized water. The decanted supernatant and rinse water were filtered through a 0.45-μm membrane filter, and the concentration of As(III) in the filtrate was analyzed on an atomic absorption spectrophotometer (AAS) equipped with an electrodeless discharge lamp (EDL). The detection limit for the AAS was approximately 3 μg/L with a relative precision of ±5%. The difference between the amount of As added and that remaining in the supernatant was used to calculate the initial spiked soil As concentration, the percent As(III) adsorbed, and the partition coefficient (K_D). The As remaining on the soils was analyzed by EPA method 3050B (*24*) to verify a mass balance of ±10%. EPA method 3050B was modified by using 0.1 versus 1.0 g of dry soil. Replicate ($n > 4$) analyses with both sample sizes indicated there was no significant difference ($P < 0.05$) between the 0.1 and 1.0 g extractions and that good repeatability could be obtained. Although not measured specifically, the initial As concentrations in the <250 μm soil fractions were negligible compared to the As concentrations after spiking as verified by an As mass balance of ±10% for all soils.

After air-drying of the soil and homogenizing by mixing, a sample was taken representing the beginning of the aging experiment (i.e., $t = 0$); the remaining soil was placed in a weighing dish and deionized water was added to achieve 30% moisture. The soils were then aged in a larger container in which a steady flow of 100% relative humidity air was passed. The moisture content of the soils was monitored periodically by weight, with deionized water added as necessary to maintain a constant moisture content of 30%. Over the next 6 months, subsamples were periodically removed and analyzed as described below.

Extractions. The bioaccessibility of As(III) was measured on duplicate soil subsamples over time with a sreamlined version (*25*) of the physiologically based extraction test (PBET) (*3*). This method has been shown to correlate well with in vivo bioavailability for Pb and is currently being validated for As. This method (*25*) is a modification of the original PBET method (*26*) in that the $NaHCO_3$ extraction step (mimicking the small intestine) has been eliminated, reflecting recent research that has shown an acidic gastriclike extraction is predictive of As bioavailability to juvenile swine (*16*, *23*). The streamlined PBET consisted of a sample holder that held 16 wide-mouth, high-density polyethylene bottles (125 mL) and a motor that rotated the sample holder at 30 ± 2 rpm (<1 rcf). The sample holder was located in a temperature-controlled water bath. During the 1-h extraction, the water temperature in the bath was maintained at body temperature (37 ± 2 °C). These conditions were designed to replicate the solubility-limiting conditions in a fasting child's stomach. The streamlined procedure was originally designed for 1 g of each soil immersed into 100 mL of PBET solution. However, the procedure was modified for 0.1 g of soil and 10 mL of PBET solution to conserve soil samples while maintaining the same soil-to-solution ratio. Replicate ($n > 4$) analyses with both sample sizes indicated there was no significant difference ($P < 0.05$) between the 0.1 and 1.0 g extractions. Over the length of the study, several hundred bioaccessibility measurements were conducted and the average coefficient of variation for duplicate samples was <10%, indicating that good repeatability could be obtained with this reduced sample size. The extraction solution consisted of 30 g/L glycine (0.4 M) with the pH adjusted to 1.5 with HNO_3. Although HCl is generally used to make PBET solution, HNO_3 was used as substitute due to the interference of Cl^- in the speciation of As(III) and As(V) by ion exchange. However, no significant ($n = 4$, $P < 0.05$) difference in bioaccessibility was observed when the two different types of PBET solution (HCl-based versus HNO_3-based) were compared. After a 1 h extraction at 30 ± 2 rpm, a portion of the supernatant was filtered with a 0.45 μm filter. Then the dissolved As concentration in the filtrate was measured with an AAS, with the fraction of As dissolved representing the bioaccessibility. The remaining soil sample was analyzed for As by EPA method 3050B to verify mass balance within ±10%. Soluble As(III) was recovered from the PBET quantitatively (94.7% ± 7.3%, errors represent standard deviation, $n = 3$). The soil pH was measured over time for approximately 5% of the soil samples, with the pH of those soils remaining well within ±0.05 unit over the length of the experiment.

Separation of As(III) and As(V). To quantify As(V) and As(III) in the PBET solution, an anion-exchange method (*27*) was used. The chloride form of the anion-exchange resin (Dowex 1 × 8−100) was converted to the acetate form in a glass column ($d = 0.8$ cm, 1.5 mL of resin). Prior to separation of As(III) and As(V), each PBET sample was diluted 10 times and then adjusted by the addition of HNO_3 to a measured pH of ~3.5. In this condition, fully protonated As(III) passes through the column while partly deprotonated As(V) is retained. Before analysis of the sample, the column performance was tested with known amounts of both As(V) and As(III) dissolved in PBET solution. As(III) recovery was >87% and complete As(V) retention was observed. The total dissolved As concentration before the column separation and the As(III) concentration from the column effluent were measured with AAS, and the As(V) concentration was then calculated by difference.

XANES Spectroscopy. At the end of the aging experiment, the remaining samples of the As(III)-spiked soils were shipped to the Stanford Synchrotron Radiation Laboratory (SSRL) where several were analyzed for As oxidation state via XANES spectroscopy as beam time became available. XANES analyses were conducted within 10 months of the end of the aging experiment on beamlines 4-1 and 4-3 (8 pole wiggler) running under dedicated conditions. The ring operated at 3 GeV with a current ranging from ≈100 to ≈50 mA. Energy selection was accomplished by use of a Si(220) monochromator with an unfocused beam. XANES spectra were recorded by fluorescent X-ray production with a wide-angle ionization chamber for all samples. A 3-μx filter (Z-1) and Soller slits were used to minimize the effects of scattered primary radiation. Incident and transmitted intensities were measured with in-line ionization chambers. XANES spectra were recorded over the energy range of −200 to +500 eV about the K-edge of arsenic (11 867 eV). Each scan was calibrated internally by placing either a sodium arsenate or iron foil standard between the second and third in-line ionization chambers, with the first inflection point of arsenate at 11 874 eV. Between 3 and 7 individual spectra were averaged for each sample.

Arsenic XANES spectra were analyzed with the computer code WinXAS (*28*) and compared to standard spectra for mineralogical estimation. Averaged XANES spectra of model compounds and samples were background-subtracted by use of a low-order polynomial function and normalized by setting the total atomic cross-sectional absorption to unity. The first derivative of each spectrum was obtained by use of a Savitzky−Golay algorithm. Arsenic(V) and As(III) species, as well as sulfide and organic complexes of arsenic, are unique in their peak energy as noted within the first-derivative spectra (*29*, *30*). Using a set of reference standards for As that included orpiment (As_2S_3), sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), sodium arsenite ($Na_2AsO_2 \cdot 4H_2O$), scorodite ($FeAsO_4 \cdot 2H_2O$), As(V) adsorbed to goethite, and As(III) adsorbed to goethite, we examined the first-derivative intensities (*31*). The various forms of As(III) and As(V) gave equivalent main peak intensities and energies in the first-derivative spectrum, and thus we calibrated to the intensity of the sodium salts. By use of Lorentzian−Gaussian peaks, the unknown spectra were deconvoluted and the main peak intensity was resolved and related to the species fraction.

Modeling. Multivariable linear regression was used to identify the significant soil properties affecting adsorption

TABLE 2. As(III) Bioaccessibility of 36 Soils over 6 Months[1]

								significant aging?	
soil	initial % adsorbed	log K_D (mL/g)	0 mo.	1 mo.	2 mo.	3 mo.	6 mo.	over 6 months[b]	between 3 and 6 months[c]
1	83.0	1.75	40.0 ± 0.5	19.6 ± 0.2	18.6 ± 2.2	17.6 ± 0.2	17.9 ± 1.1	yes	no
2	61.3	1.26	63.0 ± 5.0	47.0 ± 0.6	32.0 ± 3.1	46.0 ± 3.6	41.8 ± 0.8	yes	no
3	70.6	1.44	59.8 ± 7.4	19.0 ± 1.2	16.9 ± 1.6	16.6 ± 0.1	16.2 ± 0.8	yes	no
4	86.1	1.85	61.6 ± 1.8	30.2 ± 6.2	9.3 ± 0.3	3.8 ± 1.1	4.2 ± 1.5	yes	no
5	68.1	1.23	48.8 ± 4.7	31.4 ± 7.1	26.6 ± 1.0	35.0 ± 2.8	30.6 ± 1.2	yes	no
6	51.2	1.08	49.4 ± 3.1	21.0 ± 0.4	23.8 ± 12.2	15.8 ± 0.5	18.4 ± 2.2	yes	no
7	74.6	1.53	38.0 ± 0.6	19.2 ± 1.8	15.0 ± 4.3	13.7 ± 0.4	13.0 ± 2.8	yes	no
8	29.9	0.69	66.6 ± 3.4	66.3 ± 8.6	50.6 ± 1.5	64.2 ± 1.9	58.1 ± 1.1	no	no
9	50.8	1.07	60.9 ± 1.3	47.2 ± 3.0	34.4 ± 0.6	36.8 ± 1.9	38.7 ± 2.4	yes	no
10	36.8	0.84	62.6 ± 0.6	58.8 ± 3.2	63.7 ± 4.8	59.4 ± 0.0	48.7 ± 0.4	yes	yes
11	29.9	0.70	66.4 ± 2.8	67.0 ± 4.0	63.7 ± 7.5	67.8 ± 0.2	57.7 ± 1.8	no	no
12	28.9	0.68	59.4 ± 10.5	47.8 ± 4.7	37.0 ± 11.4	47.6 ± 1.0	37.0 ± 1.1	yes	yes
13	30.2	0.70	55.8 ± 0.2	53.0 ± 2.8	44.8 ± 8.3	50.3 ± 3.1	42.3 ± 0.5	yes	no
14	27.5	0.64	100.0 ± 0.0	81.7 ± 16.4	58.6 ± 19.4	83.4 ± 2.6	81.4 ± 12.3	no	no
15	31.5	0.72	100.0 ± 0.0	88.0 ± 5.3	75.3 ± 2.3	92.5 ± 4.7	92.3 ± 10.3	no	no
16	58.1	1.20	60.0 ± 3.2	30.9 ± 2.8	32.3 ± 2.8	31.4 ± 1.1	31.6 ± 1.8	yes	no
17	71.5	1.46	45.6 ± 1.8	22.7 ± 0.4	24.2 ± 1.3	20.4 ± 0.4	21.6 ± 1.3	yes	no
18	30.8	0.72	45.2 ± 1.3	22.0 ± 4.7	20.3 ± 1.0	19.8 ± 1.8	20.6 ± 1.7	yes	no
19	72.6	1.48	65.6 ± 6.6	49.9 ± 4.5	49.8 ± 4.1	51.3 ± 2.1	43.9 ± 1.2	yes	yes
20	24.5	0.66	59.1 ± 4.2	36.6 ± 3.4	31.7 ± 4.7	29.2 ± 1.8	20.4 ± 1.7	yes	yes
21	31.2	0.74	60.8 ± 1.2	34.0 ± 1.1	32.2 ± 6.9	27.6 ± 1.8	23.2 ± 4.2	yes	no
22	49.5	1.07	60.6 ± 3.8	33.4	28.9 ± 1.8	22.6 ± 1.7	10.0 ± 0.5	yes	yes
23	93.5	2.22	28.8 ± 0.6	22.8 ± 2.8	18.3 ± 1.1	20.4 ± 1.0	16.8 ± 1.8	yes	no
24	96.5	2.52	28.0 ± 0.2	13.4 ± 3.7	12.2 ± 3.1	14.7 ± 1.2	13.1 ± 0.3	yes	no
25	70.3	1.43	52.5 ± 1.8	21.2 ± 0.1	20.2 ± 2.0	19.9 ± 0.8	18.2 ± 1.7	yes	no
26	87.6	1.91	45.1 ± 4.0	7.2 ± 0.4	4.8 ± 0.9	4.3 ± 0.1	4.7 ± 0.1	yes	no
27	52.4	1.10	59.0 ± 1.6	29.0 ± 8.6	35.4 ± 1.5	33.2 ± 0.6	32.9 ± 0.4	yes	no
28	68.8	1.40	49.4 ± 5.4	23.6 ± 3.7	24.6 ± 5.6	25.9 ± 1.4	26.6 ± 0.6	yes	no
29	19.0	0.44	25.6 ± 4.3	15.9 ± 1.3	13.4 ± 8.6	13.5 ± 0.5	12.7 ± 1.1	no	no
30	46.7	1.02	72.8 ± 7.1	33.2 ± 4.7	24.6 ± 5.7	29.0 ± 2.0	27.6 ± 0.2	yes	no
31	50.7	1.07	53.6 ± 0.8	13.4 ± 0.2	11.2 ± 2.0	8.7 ± 1.6	13.8 ± 2.5	yes	no
32	20.7	0.50	67.8 ± 3.4	47.1 ± 21.6	29.2 ± 1.3	29.0 ± 1.3	22.5 ± 4.0	yes	no
33	86.1	1.86	49.2 ± 5.1	19.4 ± 3.7	4.8 ± 1.5	4.0 ± 0.4	3.7 ± 1.3	yes	no
34	70.2	1.45	57.9 ± 4.2	27.2 ± 6.1	17.2 ± 2.3	9.6 ± 0.5	7.8 ± 0.1	yes	yes
35	67.1	1.37	52.5 ± 4.5	34.4 ± 3.8	30.9 ± 2.1	30.9 ± 0.6	26.2 ± 0.6	yes	yes
36	81.7	1.70	62.2 ± 4.3	22.4 ± 4.5	14.6 ± 1.6	6.8 ± 1.4	3.1 ± 0.8	yes	yes
mean	55.8	1.21	56.5	34.9	29.2	30.6	27.8		
min	19.0	0.44	25.6	7.2	4.8	3.8	3.1		
max	96.5	2.52	100	88	75.3	92.5	92.3		
std dev	23.2	0.50	15.6	19.3	17.2	22.0	20.6		

[a] Errors represent standard deviation ($n = 2$). Some data shown without errors were obtained by single measurements. [b] As measured by paired *t*-test results with 0 and 6 months bioaccessibility data. [c] As measured by paired *t*-test results with 3 and 6 months bioaccessibility data.

and sequestration (the relative change in bioaccessibility over 6 months) by backward elimination (*32*) by employing the general equation

$$Y = \beta_0 + \sum_{i=1}^{N} \beta_i X_i \tag{1}$$

where i is an index, β_0 and β_i are coefficients, X_i is an independent variable (soil properties), and Y is the dependent variable (adsorption or sequestration). Multivariable regression was employed with the eight independent variables shown in Table 1 (only two of the three particle size variables are independent). The least significant variables (as measured by the largest P value), including the intercept (β_0) if warranted, were removed one at a time until all the remaining variables were significant at the 95% confidence level ($P < 0.05$). The agreement between the measured and model-predicted values were quantified with the root-mean-square error (RMSE):

$$\mathrm{RMSE} = \left[\frac{1}{n_\mathrm{d} - n_\mathrm{p}} \sum_{i=1}^{n_\mathrm{d}} (Y_i - \hat{Y}_i)^2 \right]^{1/2} \tag{2}$$

where nd is the numbers of data points, n_d is the number of adjustable parameters (zero when used in a purely predictive manner), i is an index, and Y_i and $\hat{Y}_i$ are the measured and predicted values, respectively. The RMSE, the square root of the mean squared difference between measured and predicted values, is a measure of the average error between the predicted and measured values.

Results and Discussion

Adsorption. The fate of As in soils is influenced by interactions with the solid phase, which govern the mobility of As in the aqueous phase (*33*). The percentage of the spiked As(III) adsorbed in the initial 48 h period varied from 19% to near 100% with a mean and median of 55.8% and 55.3%, respectively (Table 2). By use of a paired *t*-test, As(III) adsorption to these 36 soils was significantly ($P < 0.0001$) less than As(V) adsorption to this same set of soils published earlier (18). The only two soils (12 and 13) that adsorbed more As(III) than As(V) were also the only two soils with a pH >8, which is consistent with favorable As(V) adsorption on iron oxides at low pH and favorable As(III) adsorption at high pH values (*33*−*35*). The log partition coefficient (K_D) for these soils ranged over 2 orders of magnitude, from 0.44 to 2.52 mL/g. With multivariable linear regression by backward elimination, five soil properties (iron and manganese oxide concentrations, CEC, pH, and silt content) significantly ($P < 0.05$) influenced the adsorption of As(III) to these soils as measured by log K_D. These five soil properties were able to explain 86% ($r^2 = 0.861$) of the variability in log K_D, and remarkably, the resulting regression model was able to fit K_D within half an order of magnitude (log $K_D \pm 0.5$) for all of the soils (Figure 1).

The importance of most of these variables in As(III) adsorption to these soils can be rationalized on the basis of a knowledge of As and soil chemistry. The adsorption of As(III) to these soils is directly proportional to the pH, Fe, Mn, and silt content and inversely proportional to the CEC. The importance of iron oxides in adsorbing As(III) and As(V) is well-known, and the adsorption of As(III) to iron oxides generally increases with pH (*34*, *35*). Similarly, the CEC is typically directly related to the permanent negative charge induced by cation substitution in aluminosilicates, which would be expected to decrease the adsorption of (oxy)anions such as As(III). Manganese oxides have been shown to be important in oxidizing As(III) to As(V) in the environment, and As(V) generally adsorbs to soils more strongly than As(III), particularly at lower pH (*34*, *35*). Additional evidence indicating the importance of As(III) oxidation is discussed below. The importance of the silt content in influencing As(III) adsorption to these soils is less clear, except as perhaps the size fraction containing natural Fe- and Mn-coated minerals that are so important in controlling the adsorption of trace metals to natural materials (*36*, *37*). These results also indicate the potential complexity of As(III) adsorption to these same soils in comparison to As(V), where the (log) Fe concentration was the only statistically significant ($P < 0.05$) soil property that governed the adsorption of As(V) to these same set of soils (*18*).

Reduction in Bioaccessibility with Aging. Table 2 shows the bioaccessibility values of As(III) in these 36 soils as a function of time. A wide range of initial bioaccessibility was observed, with values ranging from 25.6% to 100%. Most soils exhibited a significant decrease in bioaccessibility over time (i.e., aging). From a paired *t*-test, 31 of the 36 soils (86.1%) showed a significantly ($P < 0.05$) reduced bioaccessibility over 6 months, while only eight soils (22.2%) further exhibited a significantly ($P < 0.05$) reduced bioaccessibility from 3 to 6 months, indicating aging was typically completed after 3 months. The number of soils exhibiting a significant ($P < 0.05$) reduction in As(III) bioaccessibility over 6 months (86.1%) was greater than that of As(V) (47.2%) in the same set of soils (*18*).

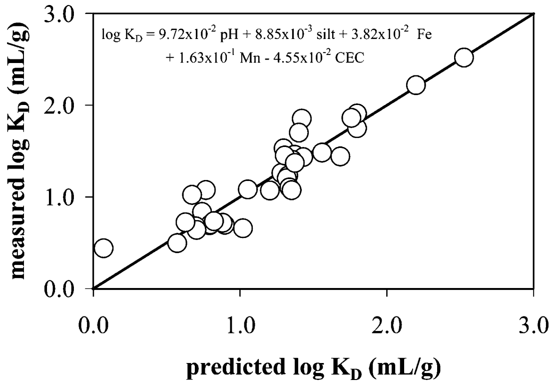

FIGURE 1. Measured log K_D versus log K_D calculated from multivariable linear regression.

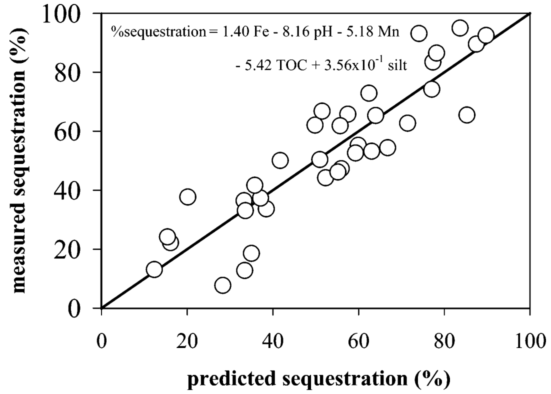

FIGURE 2. Measured sequestration versus sequestration calculated from multivariable linear regression.

To quantify the reduction in As(III) bioaccessibility over time, the relative change in bioaccessibility over the 6-month period was calculated as the percent sequestration:

$$\%\ \text{sequestration} = \frac{B_0 - B_6}{B_0} \cdot 100\% \qquad (3)$$

where B_0 and B_6 represent the initial and 6-month bioaccessibility, respectively. Thirty-two of the 36 soils (88.9%) showed greater sequestration of As(III) than As(V), indicating a greater aging effect for As(III) than As(V). From multivariable regression with backward elimination, five soil properties significantly influenced the sequestration of As(III) in these soils: pH ($P < 0.0001$), silt content ($P < 0.01$), and Fe ($P < 0.001$), Mn ($P < 0.01$), and TOC ($P < 0.01$) concentrations. The sequestration of As(III) was proportional to the Fe concentration and silt content and inversely proportional to pH and the Mn and TOC concentration. These results indicate the complexity of As(III) sequestration compared to As(V) sequestration in these same soils, where only pH significantly ($P < 0.05$) influenced As(V) sequestration. Although a relatively large number of soil properties (five of the eight independent properties measured) influenced As(III) sequestration, they were able to explain 81% ($r^2 = 0.806$) of the variability in sequestration in these soils (Figure 2). Sequestration was not significantly ($P > 0.05$) influenced by the CEC of the soils.

As(III) Oxidation to As(V). As the soils aged, the bioaccessibility in the As(III)-spiked soils decreased to levels closer to the bioaccessibility of the As(V)-spiked soils (*18*). Initially, the average bioaccessibility in the As(III)-spiked soils (56.5%) was higher than the initial average bioaccessibility (43.6%) in the As(V)-spiked soils. The initial bioaccessibility in the As(III)-spiked soils was also greater than the initial bioaccessibility in the As(V)-spiked soils in 28 of the 36 soils (77.8%), and by use of a paired *t*-test the initial bioaccessibility was statistically ($P < 0.05$) greater in the As(III)-spiked soils than in the As(V)-spiked soils. In contrast, after 6 months of aging, the average bioaccessibility in the As(III)-spiked soils (27.8%) was actually less than the average bioaccessibility in the As(V)-spiked soils (33.0%). Only 16 of the 36 (44.4%) As(III)-spiked soils had a higher bioaccessibility than the As(V)-spiked soils after 6 months of aging, and there was no longer a significant ($P > 0.05$ by a paired *t*-test) difference between the bioaccessibility in the As(III)-spiked soils and the As(V)-spiked soils.

The reduction in bioaccessibility in the As(III)-spiked soils was accompanied by the heterogeneous oxidation of As(III) to As(V). All of the soils in this study were initially spiked with As(III). However, after just the initial 48 h contact period, well over half (62.6%) of the As leached from the soils in the PBET solution was As(V) (Table 3). As discussed above, As(III) in blanks without soil was not oxidized, indicating any oxidation during this time period was due to the presence of the soil. Figure 3 shows the variation of As(III) (this study) and As(V) (previous study) bioaccessibility with aging for two example soils along with the percentage of As(III) in the

TABLE 3. As(V) as a Percentage of Total As in PBET Leachate with Aging Time

soil	soil type	series	initial	7 days	14 days	1 mo.	2 mo.	3 mo.	6 mo.
1	Alfisol	Angola-Ap	55.8	47.9	53	100	100	100	100
2		Angola-B	88.2	83.2	82.9	100	100	100	100
3		Crider-Ap	52.8	56.1	56	100	100	100	100
4		Crider-B2lt	N/A	41.3	43.3	70.2	100	100	100
5		Lenberg-A	86.6	N/A	68.1	100	100	100	100
6		Lenberg-Btl	31.8	N/A	51.2	68.1	74.4	N/A	79.3
7		Lawrence-Apl	62.4	N/A	81	79.7	66.7	N/A	50.8
34		Lawrence-Btl	52.3	65.8	42	62.5	50.6	100	100
8	Aridisol	Doakum-Ab	73.3	79.2	75.7	N/A	81.8	100	100
9		Doakum-Bt	53	88.4	N/A	90.2	N/A	84.8	83.2
10		Kzin-A2	68	88	100	100	100	100	100
11		Kzin-Bk	53.8	88.8	100	92.7	100	100	89.2
12		Oricto-A2	70.2	89.1	99.3	92.7	100	100	100
13		Oricto-Bt	63.8	87.8	100	100	100	100	100
14		Stoneham-A	91.1	100	92.9	100	100	100	100
15		Stoneham-Bt1	76.9	75.2	98.1	100	100	100	100
16	Entisol	Wakeland-Ap	N/A	62	62.3	100	100	100	100
17		Wakeland-Cg1	67.8	88	76	100	100	100	100
18	Inceptisol	Berks-A	43.8	72.2	62.4	51.8	61.6	67.2	65.6
19		Montevello-A	94.8	93.8	90.4	100	100	100	100
20		Montevello-B	41.3	33.7	37.7	51.4	57.4	74.7	100
21		Rockaway-A1	79.1	66.7	57.1	78.5	N/A	100	100
22		Rockaway-B2t	N/A	24.6	42.2	58.7	46	65.5	100
23		Weikert-Ap	100	100	100	100	100	100	100
24		Weikert-Be	100	100	100	100	100	100	100
25	Mollisol	Dennis-Ap	46.3	70.8	76.6	79.2	79.2	N/A	78.6
26		Dennis-Ba	32.2	N/A	57.5	100	100	100	100
27		Sibley-A	70.7	67.4	72.2	100	100	100	100
28		Sibley-B1	63.2	68.7	76.8	100	100	100	100
29	Spodosol	Charlton-A2	29.3	47.7	N/A	42.1	73.1	85.2	N/A
30	Ultisol	Allen-A	77.5	56	65.6	88.2	100	100	100
31		Allen-Ba	37.3	47.9	58.3	68.7	68.8	55.2	71
32		Cecil-Ap	66.5	75	47.9	67.3	N/A	100	100
33		Cecil-Bt1	30.3	N/A	44	41.2	100	100	100
35		Minvale-Ap	79.8	89.3	100	100	100	100	100
36		Minvale-Bt1	27.2	32.7	33.3	36.2	34.9	100	100
		<chgrow;lp;4q>mean	62.6	70.6	70.7	83.4	87.7	94.9	94.8
		min	27.2	24.6	33.3	36.2	34.9	55.2	50.8
		max	100.0	100.0	100.0	100.0	100.0	100.0	100.0
		std dev	21.4	21.2	21.8	20.8	19.5	11.9	11.9

TABLE 4. As(III) and As(V) as a Percentage of Total As on Selected Soils

soil	soil series	% As(V)	% As(III)
1	Angola (A)	62	38
5	Lenberg (A)	100	0
6	Lenberg (Btl)	38	62
7	Lawrence (Apl)	38	62
17	Wakeland (Cg1)	39	61
18	Berks (A)	38	62
23	Weikert (Ap)	37	63
24	Weikert (BE)	36	65
26	Dennis (BA)	39	61
28	Sibley (B1)	36	64
29	Charlton (A)	39	61
30	Allen (A)	100	0
31	Allen (BA)	40	60
32	Cecil (Ap)	100	0
33	Cecil (Bt1)	100	0

PBET leachate. In soil 35 (Figure 3a), the As(III) was oxidized to As(V) almost completely over the initial 48 h contact period and the resulting bioaccessibility mirrored the change in bioaccessibility observed in As(V)-spiked soils. In soil 36 (Figure 3b), much less of the As(III) was oxidized over the initial 48 h contact period, and the initial bioaccessibility of the As(III)-spiked soil was considerably higher than the bioaccessibility of the same soil spiked with As(V). However, as the As(III) was oxidized to As(V) over time, the bioaccessibility in the As(III)-spiked soil decreased to approximately the same value as the As(V)-spiked soil. Similar to these two selected soils, rapid As(III) oxidation was observed for all soils, and little As(III) (<20% of total As on average) was identified in the PBET solution after 1 month. After 6 months, only seven soils had detectable As(III) in the PBET solution.

The oxidation of As(III) to As(V) occurred on the solid phase, as indicated by the differences in the oxidation rate among the soils and the stability of As(III) in homogeneous solutions. Synchrotron-XANES spectroscopy was used to monitor the oxidation state of As directly on several of these soils (Table 4), and the results indicated that indeed the As(III) was being oxidized to As(V) on the soils. The rates of oxidation among the soils as indicated by both the aqueous-phase (PBET) and solid-phase (XANES) speciation were different. Several factors are known to affect the oxidation of As(III) to As(V) such as pH, mineralogy, manganese oxides, and ferric iron (*38*). Manning and Goldberg (*39*) suggested that As(III) oxidation might be enhanced by heterogeneous oxidation on kaolinite and illite surfaces. There is controversy surrounding the role of iron(III) (hydro)oxides in As(III) oxidation. Although DeVitre et al. (*40*) reported As(III) oxidation within 2 days irrespective of pH by iron(III) (hydro)oxides, Oscarson et al. (*41*) and Hug et al. (*42*) reported no oxidation of As(III) by iron(III) (hydro)oxides. Perhaps reflecting this complexity, there was not a strong relationship (at least as measured by multivariable linear regression) between the oxidation rate of As(III) and any of the soil properties, including manganese oxides.

Steady-State Bioaccessibility. Previously, Yang et al. (*18*) developed a correlation between As bioaccessibility and a

TABLE 5. Predicted Bioaccessibility and Measured Bioavailability

soil[a]	pH	iron oxide (mg/kg)	predicted bioaccessibility[b] (%)	measured bioavailability[a] (%)
	Juvenile Swine			
Bingham Creek-Channel soil	7.02	17 000	41.8	39.3
Murray smelter–slag composite	7.43	23 100	42.7	55.1
Midvale-slag composite	7.54	51 100	33.1	22.9
California Gulch-FeMnPb oxide soil	5.92	24 900	24.3	56.6
Murray smelter–soil composite	7.86	12 100	55.8	33.0
California Gulch-Phase I Residential Soil Composite	6.68	31 900	29.6	8.35
VBI70-soil composite 1	5.92	7200	40.7	40.3
VBI70-soil composite 2	6.28	8650	42.4	42.2
VBI70-soil composite 3	5.96	7580	40.5	36.7
VBI70-soil composite 4	6.27	8220	42.9	23.8
VBI70-soil composite 5	4.83	6940	28.9	21.2
VBI70-soil + PAX	5.51	6800	36.9	23.5
	Monkey			
pesticide site 1	7.53	12 000	52.1	10.7
pesticide site 2	7.65	5410	64.1	17.0
wood treatment site	7.65	2070	76.8	16.3
cattle dip vat site	4.79	5880	30.7	24.7
electrical substation soil	7.65	12 300	53.2	14.6

[a] From reference (*19*) (juvenile swine) or reference (*20*) (monkey). [b] Predicted using eq 4.

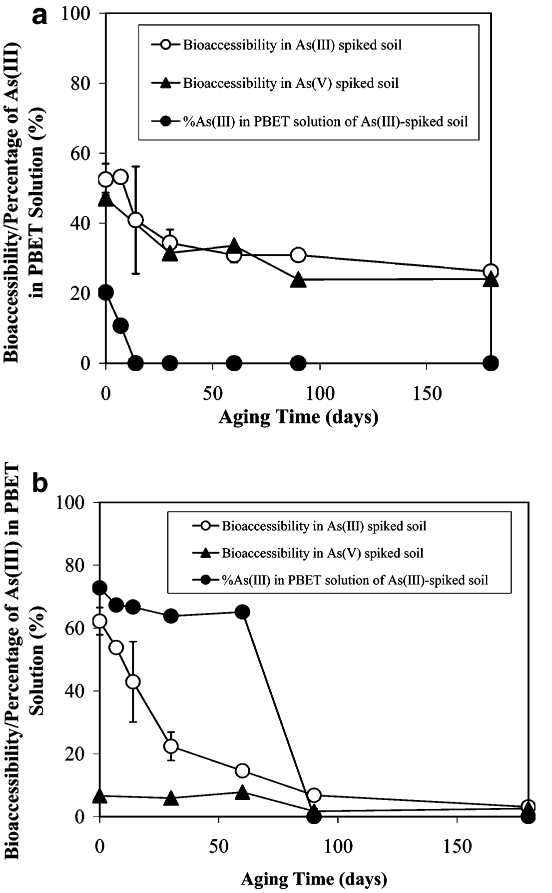

FIGURE 3. Bioaccessibility and speciation of As in PBET leachate versus time from (A) As(III)- and As(V)-spiked soil 35 and (B) As(III)- and As(V)-spiked soil 36.

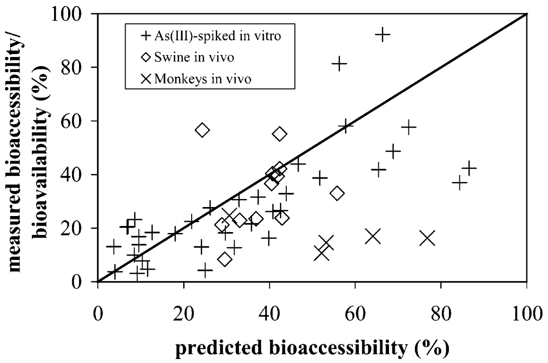

FIGURE 4. Measured bioaccessibility or bioavailability versus bioaccessibility predicted from eq 4.

soil's pH and iron oxide concentration:

$$\% \text{ bioaccessibility} = 11.3(\text{pH}) - 30.5(\log \text{Fe}) \quad (4)$$

This correlation was derived by measuring steady-state bioaccessibility in As(V)-spiked soils. However, eq 4 was able to independently predict the in vivo bioavailability of As in soil to juvenile swine in feeding studies within a root-mean-square error of 9.5% (*18*). The results above clearly indicate that, in As(III)-spiked soils, As(III) is oxidized to As(V) with a corresponding decrease in As bioaccessibility over time. Equation 4 was used to independently estimate the As bioaccessibility in the As(III)-spiked soils in this study, producing estimates within a RMSE of 16.8% (Figure 4). Additional As-contaminated soil samples that had been used in independent animal dosing studies were obtained, and after measurement of the pH and iron oxide concentration, the As bioavailability was estimated from eq 4 and compared to the results obtained in vivo. In 12 samples from an ongoing EPA region 8 bioavailability study (*19*), eq 4 was able to predict the relative bioavailability of As in these soils within a RMSE of 15.5% (Figure 4 and Table 5). The RMSE in using a default relative bioavailability of 100% for these 12 soils would have been 67.8%. In addition, 10 of the 12 (83.3%) bioavailability values estimated from eq 4 were greater than the measured bioavailability values. Thus eq 4 provided a greatly improved yet generally conservative bioavailability estimate relative to the default value. Recently, Roberts et al. (*20*) measured the oral bioavailability of As to *Cebus* monkeys in five samples from waste sites in Florida (Table 5). Equation 4 was not able to predict the bioavailability of As from these samples to the *Cebus* monkey as accurately as for the juvenile swine, consistently overpredicting the bioavailability, resulting in an RMSE of 42.7%. The original PBET also overpredicted the bioavailability of As to primates (*26*). Determining which animal (juvenile swine or *Cebus* monkey) is a better model for human children is currently an active area of toxicological research. Finally, these animal dosing trials were conducted prior to and independent of this study, and details regarding the animal model selected, experimental design, data interpretation, etc. may be found in the original references (*19*, *20*).

Environmental Implications. The results above demonstrate that As(III) added to aerobic soils with a wide range of properties oxidizes to As(V) over time, significantly reducing its bioaccessibility. A previous model developed from As(V)-spiked soils (eq 4) was able to estimate the bioaccessibility in 36 As(III)-spiked soils within an RMSE of 16.8%. In addition, this model was able to provide a greatly improved yet generally conservative estimate of soil As bioavailability to juvenile swine (RMSE = 15.5%) but was not able to provide as accurate of an estimate of soil As bioavailability to monkeys (RMSE = 42.7%). These results indicate the potential use of this model in providing better soil As bioavailability estimates than the 100% default value. This model can be used to provide rapid and inexpensive preliminary bioavailability estimates at contaminated sites. These preliminary estimates can then be used to screen and prioritize As-contaminated sites as well as to justify the use of relatively expensive site-specific animal feeding studies. Finally, as these estimates are based solely on major soil properties (as opposed to As speciation in soils, which is difficult to measure and subject to change over time), the estimates are valid as long as the major soil properties do not change. Major soil properties generally evolve as a result of interactions with their environment over a relatively long period of time (e.g., thousands to hundreds of thousands of years), and thus are unlikely to change over relatively short time spans (e.g., human lifetimes) unless conditions change dramatically (*43*). Thus these estimates of bioavailability are just as stable over the long term as the major soil properties, which are arguably the most stable aspect of soils.

Acknowledgments

This research was sponsored by the Strategic Environmental Research and Development Program (SERDP) under the direction of Dr. Andrea Leeson. We appreciate the efforts of Mr. Warren Lynn of the National Resource Conservation Service (NRCS), who provided us with the uncontaminated soils for this study. We also gratefully acknowledge Mike Ruby of Exponent and Bill Brattin and Angela Wahlquist of the Syracuse Research Corporation for supplying As-contaminated soils samples from the in vivo bioavailability studies. Finally, we acknowledge the comments of three anonymous reviewers that significantly improved the manuscript. Oak Ridge National Laboratory is managed by the University of Tennessee−Battelle LLC, under Contract DE-AC05-00OR22725 with the U.S. Department of Energy.

Literature Cited

(1) Davis, A.; Sherwin, D.; Ditmars, R.; Hoenke, K. A. An analysis of soil arsenic records of decision. *Environ. Sci. Technol.* **2001**, *35*, 2401−2406.

(2) Mariner, P. E.; Holzmer, F. J.; Jackson, R. E.; Meinardus, H. W.; Wolf, F. G. Effects of high pH on arsenic mobility in a shallow sandy aquifer and on aquifer permeability along the adjacent shoreline, Commencement Bay Superfund Site, Tacoma, Washington. *Environ. Sci. Technol.* **1996**, *30*, 1645−1651.

(3) Davis, A.; Ruby, M. V.; Bloom, M.; Schoof, R.; Freeman, G.; Bergstom, P. D. Mineralogic constraints on the bioavailability of arsenic in smelter-impacted soils. *Environ. Sci. Technol.* **1996**, *30*, 392−399.

(4) Welch, A. H.; Westjohn, D. B.; Helsel, D. R.; Wanty, R. B. Arsenic in ground water of the United States: Occurrence and geochemistry. *Ground Water* **2000**, *38*, 589−604.

(5) Sadiq, M. Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. *Water, Air, Soil Pollut.* **1997**, *93*, 117−136.

(6) Smith, E.; Naidu, R.; Alston, A. M. In *Advances in Agronomy*; Sparks, D. L., Ed.; Academic Press: New York, 1998; Vol. 64, pp 149−195.

(7) Bowell, R. J. Sorption of arsenic by iron-oxides and oxyhydroxides in soils. *Appl. Geochem.* **1994**, *9*, 279−286.

(8) McGeehan, S. L.; Naylor, D. V. Sorption and redox transformation of arsenite and arsenate in two flooded soils. *Soil Sci. Soc. Am. J.* **1994**, *58*, 337−342.

(9) Hrudey, S. E.; Chen, W.; Rousseaux, C. G. *Bioavailability in Environmental Risk Assessment*; Lewis Publishers: Boca Raton, FL, 1996.

(10) Dudka, S.; Miller, W. P. Permissible concentrations of arsenic and lead in soils based on risk assessment. *Water, Air, Soil Pollut.* **1999**, *113*, 127−132.

(11) Ruby, M. V.; Davis, A.; Kempton, J. H.; Drexler, J. W.; Bergstrom, P. D. Lead bioavailability − Dissolution kinetics under simulated gastric conditions. *Environ. Sci. Technol.* **1992**, *26*, 1242−1248.

(12) Davis, A.; Ruby, M. V.; Bergstrom, P. D. Bioavailability of arsenic and lead in soils from the Butte, Montana mining district. *Environ. Sci. Technol.* **1992**, *26*, 461−468.

(13) Freeman, G. B.; Johnson, J. D.; Liao, S. C.; Feder, P. I.; Davis, A. O.; Ruby, M. V.; Schoof, R. A.; Chaney, R. L.; Bergstrom, P. D. Absolute bioavailability of lead acetate and mining waste lead in rats. *Toxicology* **1994**, *91*, 151−163.

(14) Casteel, S. W.; Cowart, R. P.; Weis, C. P.; Henningsen, G. M.; Hoffman, E.; Brattin, W. J.; Guzman, R. E.; Starost, M. F.; Payne, J. T.; Stockham, S. L.; Becker, S. V.; Drexler, J. W.; Turk, J. R. Bioavailability of lead to juvenile swine dosed with soil from the Smuggler Mountain NPL site of Aspen, Colorado. *Fundam. Appl. Toxicol.* **1997**, *36*, 177−187.

(15) Hamel, S. C.; Buckley, B.; Lioy, P. J. Bioaccessibility of metals in soils for different liquid-to-solid ratios in synthetic gastric fluid. *Environ. Sci. Technol.* **1998**, *32*, 358−362.

(16) Ruby, M. V.; Schoof, R.; Brattin, W.; Goldade, M.; Post, G.; Harnois, M.; Mosby, D. E.; Casteel, S. W.; Berti, W.; Carpenter, M.; Edwards, D.; Cragin, D.; Chappell, W. Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environ. Sci. Technol.* **1999**, *33*, 3697−3705.

(17) Yang, J. K.; Barnett, M. O.; Jardine, P. M.; Brooks, S. C. Factors controlling the bioaccessibility of arsenic(V) and lead(II) in soil. *Soil Sediment Contam.* **2003**, *12*, 165−179.

(18) Yang, J. K.; Barnett, M. O.; Jardine, P. M.; Basta, N. T.; Casteel, S. W. Adsorption, sequestration, and bioaccessibility of As(V) in soils. *Environ. Sci. Technol.* **2002**, *36*, 4562−4569.

(19) Syracuse Research Corporation. Estimation of relative bioavailability of arsenic in soil and soil-like materials by in vivo and in vitro methods. Draft report prepared for the U.S. Environmental Protection Agency (currently undergoing Agency review), Denver, CO, 2003.

(20) Roberts, S. M.; Weimar, W. R.; Vinson, J. R. T.; Munson, J. W.; Bergeron, R. J. Measurement of arsenic bioavailability in soil using a primate model. *Toxicol. Sci.* **2002**, *67*, 303−310.

(21) Soil Survey Staff. *National Soil Survey Characterization Data*; Soil Survey Laboratory, National Soil Survey Center, U.S. Department of Agriculture National Resources Conservation Service: Lincoln, NE.

(22) Mehra, O. P.; Jackson, M. L. Iron oxide removed from soils and clays by a dithionite−citrate system buffered with sodium bicarbonate. *Clays Clay Miner.* **1960**, *7*, 317−327.

(23) Rodriguez, R. R.; Basta, N. T.; Casteel, S. W.; Pace, L. W. An in vitro gastrointestinal method to estimate bioavailable arsenic in contaminated soils and solid media. *Environ. Sci. Technol.* **1999**, *33*, 642−649.

(24) U.S. Environmental Protection Agency. *Acid Digestion of Sediments, Sludges, and Soils, Method 3050B, Revision 2*; U.S. EPA: Washington, DC, 1996.

(25) Kelley, M. E.; Brauning, S. E.; Schoof, R. A.; Ruby, M. V. *Assessing Oral Bioavailability of Metals in Soil*; Battelle Press: Columbus, OH, 2002.

(26) Ruby, M. V.; Davis, A.; Schoof, R.; Eberle, S.; Sellstone, C. M. Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environ. Sci. Technol.* **1996**, *30*, 422−430.

(27) Wilkie, J. A.; Hering, J. G. Rapid oxidation of geothermal arsenic(III) in seawaters of the Eastern Sierra Nevada. *Environ. Sci. Technol.* **1998**, *32*, 657−662.

(28) Ressler, T. *WinXAS 97*; Published by the author: Hamburg, Germany, 1997.

(29) Hansel, C. M.; La Force, M. J.; Fendorf, S.; Sutton, S. Spatial and temporal association of As and Fe species on aquatic plant roots. *Environ. Sci. Technol.* **2002**, *36*, 1988−1994.

(30) Rochette, E. A.; Li, G. C.; Fendorf, S. E. Stability of arsenate minerals in soil under biotically generated reducing conditions. *Soil Sci. Soc. Am. J.* **1998**, *62*, 1530−1537.

(31) La Force, M. J.; Hansel, C. M.; Fendorf, S. Arsenic speciation, seasonal transformations, and co-distribution with iron in a mine waste-influenced palustrine emergent wetland. *Environ. Sci. Technol.* **2000**, *34*, 3937−3943.

(32) Kleinbaum, D. G.; Kupper, L. L.; Muller, K. E.; Nizam, A. *Applied Regression Analysis and Other Multivariable Methods*, 3rd ed.; Duxbury Press: Pacific Grove, CA, 1998.

(33) Smith, E.; Naidu, R.; Alston, A. M. Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium, and calcium on arsenic sorption. *J. Environ. Qual.* **2002**, *31*, 557−563.

(34) Smith, E.; Naidu, R.; Alston, A. M. Chemistry of arsenic in soils: I. Sorption of arsenate and arsenite by four Australian soils. *J. Environ. Qual.* **1999**, *28*, 1719−1726.

(35) Dixit, S.; Hering, J. G. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.* **2003**, *37*, 4182−4189.

(36) Penn, R. L.; Zhu, C.; Xu, H.; Veblen, D. R. Iron oxide coatings on sand grains from the Atlantic coastal plain: High-resolution transmission electron microscopy characterization. *Geology* **2001**, *29*, 843−846.

(37) Coston, J. A.; Fuller, C. C.; Davis, J. A. Pb^{2+} and Zn^{2+} adsorption by a natural aluminum-bearing and iron-bearing surface coating on an aquifer sand. *Geochim. Cosmochim. Acta* **1995**, *59*, 3535−3547.

(38) Chiu, V. Q.; Hering, J. G. Arsenic adsorption and oxidation at manganite surfaces. 1. Method for simultaneous determination of adsorbed and dissolved arsenic species. *Environ. Sci. Technol.* **2000**, *34*, 2029−2034.

(39) Manning, B. A.; Goldberg, S. Adsorption and stability of arsenic-(III) at the clay mineral−water interface. *Environ. Sci. Technol.* **1997**, *31*, 2005−2011.

(40) DeVitre, R.; Belzile, N.; Tessier, A. Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides. *Limnol. Oceanogr.* **1991**, *36*, 1480−1485.

(41) Oscarson, D. W.; Huang, P. M.; Defosse, C.; Herbillon, A. Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature* **1981**, *291*, 50−51.

(42) Hug, S. J.; Canonica, L.; Wegelin, M.; Gechter, D.; Von Gunten, U. Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. *Environ. Sci. Technol.* **2001**, *35*, 2114−2121.

(43) Brady, N. C.; Weil, R. R. *Elements of the Nature and Properties of Soils*; Prentice-Hall: Upper Saddle River, NJ, 2000.

Received for review November 24, 2004. Revised manuscript received June 30, 2005. Accepted July 7, 2005.

ES0481474