

Adsorption, Sequestration, and Bioaccessibility of As(V) in Soils

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The influence of various soil physical and chemical properties (Fe and Mn oxides, pH, cation exchange capacity, total inorganic and organic carbon, and particle size) on As(V) adsorption, sequestration, and relative bioaccessibility (as a surrogate for oral bioavailability) was investigated in a wide range of well-characterized soils over a 6-month period. Arsenic(V) bioaccessibility was measured using a streamlined version of a physiologically based extraction test (PBET), designed to replicate the solubility-limiting conditions in a child's digestive tract. The soil's dithionite-citrate-bicarbonate (DCB) extractable Fe oxide content was the most important (and only statistically significant) soil property controlling the initial degree of adsorption. Sequestration, as measured by the reduction in bioaccessibility over time, occurred to a significant extent in 17 of 36 (47.2%) soils over the first 3 months. In contrast, only 4 of 36 (11.1%) soils exhibited a significant reduction in bioaccessibility from 3 to 6 months. Soil pH was the most important (and only statistically significant) soil property affecting the decrease in bioaccessibility upon aging for 6 months. Soils with pH < 6 generally sequestered As(V) more strongly over time, whereas those with pH > 6 generally did not. The Fe oxide content and pH were the most important soil properties governing the steady-state bioaccessibility of As(V) in soil. Two multivariable linear regression models of steady-state As(V) bioaccessibility were developed using soil properties as independent variables. Generally, soils having higher Fe oxide content and lower soil pH exhibited lower bioaccessibility. These models were able to account for ~75–80% of the variability in steady-state bioaccessibility and independently predict bioaccessibility in five soils within a root-mean-square error (RMSE) of 8.2–10.9%. One of these models was also able to predict within an RMSE of 9.5% the *in vivo* bioavailability of As in nine contaminated soils previously used in swine dosing trials. These results indicate the bioaccessibility, and thus, potentially the bioavailability of

otherwise soluble As(V) added to soils (i.e., the worst-case bioavailability scenario) is significantly reduced in some soils over time, particularly those with lower pH and higher Fe oxide content. These results also provide a means of estimating As(V) bioaccessibility and bioavailability on the basis of soil properties.

Introduction

Arsenic is the second most frequently encountered inorganic contaminant (behind lead) at contaminated U.S. Superfund sites (1). Arsenic contamination in soils originates from various anthropogenic sources, such as mining, milling, and agricultural applications, as well as natural geochemical processes that can be exacerbated by degradable organic contaminants at contaminated sites (2). The factors affecting As(V) adsorption to minerals and soils have been relatively well studied (3). However, the effect of As(V)–soil interactions on the cleanup of As-contaminated sites has been less well investigated (1). The ingestion of As-contaminated soils by children, which would have to be considered in addition to the risk from the intake of natural background As (e.g., in drinking water), is typically the risk driver at As-contaminated sites (4). Inorganic As is commonly present in two oxidation states in soil: +III and +V. As(III) is the thermodynamically stable oxidation state in reducing environments, whereas As(V) is the thermodynamically stable oxidation state in oxic surface soils where children typically contact contaminated soil. The risk of ingesting As (and other metals) in soil is often estimated by assuming that soil-bound As is completely absorbed through the human gastrointestinal tract upon ingestion (i.e., 100% bioavailable). This assumption potentially overestimates the risk and the associated cleanup requirements at contaminated sites (5), since soils are known to strongly sequester certain metals. Therefore, As bioavailability should be considered as a potential tool for better decision making in risk assessments and for remediation purposes (1).

The acceptable regulatory inorganic As dose was originally determined on the basis of an epidemiological study of the effects of As in drinking water in Taiwan (6). However, As in drinking water is potentially much more bioavailable than As in soil, because water-soluble inorganic As is rapidly and completely absorbed by humans, whereas As in soil is almost completely eliminated in the feces without being absorbed (7). Compared to drinking water, As in mining soils or aggregates generally exhibits low bioavailability because of the presence of residual metal sulfides, authigenesis, insoluble mineral rinds, etc. (8–10). However, even in nonmining areas, soil itself may lower the bioavailability of otherwise soluble metals due to adsorption to the solid phase and the formation of secondary solid phases.

Much less research has focused on potentially more labile (e.g., adsorbed) forms of As in soil, although such information could be critical for several reasons. First, even in mine tailings, potentially soluble forms of As can be important (11). Second, As in sulfides in surface soils may weather to more labile forms over time (12). Finally, an understanding of the bioavailability of potentially more labile forms of As in soil is important in assessing the risk of As-contaminated soils that originate from processes other than mining. Controlling factors governing the health risk due to ingestion of soils contaminated with As(V) are the pH of both the gastrointestinal fluid and soil, soil metal concentration, soil-to-solution ratio, mineralogy, and particle

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

soil	soil type	series	pH	CEC (cmol _c /kg)	organic carbon (%)	inorganic carbon (%)	Particle size (%)			Fe (g/kg)	Mn (g/kg)
							clay	silt	sand		
1	alfisol	Angola-A	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-A	6.57	5.60	0.55	0.39	22.5	75.8	1.7	13.34	0.72
4		Crider-B	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-B	4.35	5.50	0.36	0.25	64.7	29.5	5.8	15.69	0.12
7		Lawrence-A	4.97	5.80	0.91	0.59	19.5	48.5	32.0	11.17	1.35
8	aridisol	Doakum-A	6.94	6.90	0.28	0.08	10.8	24.8	64.4	4.74	0.19
9		Doakum-B	6.84	7.00	0.39	0.18	29.3	15.0	55.7	6.86	0.16
10		Kzin-A	7.74	13.30	3.27	1.35	22.2	44.2	33.6	4.07	0.29
11		Kzin-B	7.8	10.00	3.4	1.88	27.0	38.5	34.5	3.26	0.18
12		Oricto-A	8.72	13.70	0.09	0.94	10.2	34.7	55.1	2.92	0.34
13		Oricto-B	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-B	6.8	7.80	0.66	0.32	21.4	23.2	55.4	2.2	0.2	
16	entisol	Wakeland-A	5.86	6.10	0.92	0	23.8	64.7	11.5	8.82	0.71
17		Wakeland-B	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		Melton-A	6.91	8.00	3.55	0.62	6.0	69.0	25	10.68	1.42
20		Melton-B	4.23	14.00	0.42	0.26	19.0	42.2	38.8	22.07	0.17
21		Rockaway-A	3.86	10.60	3.54	1.49	12.4	34.8	52.8	14.03	0.52
22		Rockaway-B	4.1	3.70	0.21	0.18	12.6	32.1	55.3	17.34	0.16
23		Weikert-A	4.44	13.30	3.97	2.37	24.4	56.2	19.4	21.41	6.47
24		Weikert-B	4.28	8.00	2.01	1.15	23.9	54.3	21.8	28.98	5.42
25	mollisol	Dennis-A	5.82	8.70	1.32	0.89	15.9	66.1	18	15.11	0.6
26		Dennis-B	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-B	6.36	6.80	0.72	0.52	26.9	68.0	5.1	9.11	0.59	
29	spodosol ultisol	Charlton-A	3.15	11.90	2.3	0.4	2.9	28.7	68.4	1.33	0
30		Allen-A	4.59	7.70	1.55	0.56	8.7	29.5	61.8	6.95	0.31
31		Allen-B	4.3	1.30	0.19	0.09	14.9	28.4	56.7	18.96	0.1
32		Cecil-A	4.04	5.80	1.64	0.39	10.2	23	66.8	6.01	0.06
33		Cecil-B	4.44	1.60	0.29	0.21	44.8	15.5	39.7	32.56	0.11
34		Lawrence-B	4.28	3.70	0.11	0.1	25.8	38.3	35.9	17.53	0.29
35		Walker-A	6.01	6.00	1.89	0.99	6.1	58.9	34.9	7.71	1.51
36		Walker-B	4.3	4.00	0.1	0.07	23.6	44.2	32.2	19.55	0.16
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
mean			5.6	7.4	1.3	0.6	21.0	42.5	36.9	11.9	0.8
SD			1.5	3.2	1.3	0.5	16.9	21.8	8.0	8.0	1.3

size of soils (5, 13, 14). However, the influence of soil properties on As(V) bioavailability has not been systematically investigated.

In the study described in this paper, soluble As(V) was added to 36 well-characterized soils with a wide range of soil properties representing seven major soil orders within the U. S. The soils were aged at 30% moisture content for 6 months, with bioaccessibility (a surrogate for oral bioavailability) measured periodically with a physiologically based extraction test (PBET) that was designed to mimic the solubility-limiting conditions in a child's digestive tract. Oral bioaccessibility is defined as the fraction of a contaminant that is soluble and available for systemic absorption in the gastrointestinal environment (5). The soils were spiked with soluble As(V) to elucidate the ability of soil-metal interactions to limit bioaccessibility without reference to any preexisting site-specific solid-phase speciation (e.g., presence in sulfides) that is subject to change over time. Multivariable linear regression was used to identify and quantify the macroscopic soil properties (e.g., Fe and Mn oxide content, pH, cation exchange capacity (CEC), total organic and inorganic carbon (TOC and TIC), and particle size) controlling As(V) adsorption, sequestration, and bioaccessibility. For the purposes of this paper, adsorption was defined as the fraction of As(V) adsorbed to the soil over the initial 48 h contact period and sequestration was defined as the relative change in bioaccessibility over 6 months.

Experimental Section

Materials. All chemicals employed in this research were analytical grade or above, and solutions were prepared with 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 U.S. soil orders were collected from 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 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 (15). The soil's cation exchange capacity (CEC) and particle size distribution were measured using standard methodologies and reported by the NRCS. The soil pH was measured in a 2:1 solution-to-solid ratio in 5 mM CaCl₂ using a combination pH electrode and meter. Extractable Fe and Mn oxides were measured by extraction with dithionite-citrate-bicarbonate (DCB) (16), and total organic and inorganic carbon (TOC and TIC) was measured by combustion on a total carbon analyzer. The physicochemical properties of the soils are shown in Table 1.

Soil Spiking. Soluble As(V) was added to the soils (2 g) from a small volume of a concentrated As(V) stock solution to a 1:10 g/mL soil suspension of 10⁻³ M CaCl₂ with a target

soil As(V) concentration of 100 mg/kg (previous research indicated no significant difference in As(V) bioaccessibility over the concentration range of 10–100 mg/kg (14)). To neutralize the NaOH added from the As(V) stock solution, HNO₃ was also immediately added to the soil slurry to maintain the original soil pH (Table 1). After 48 h mixing, the soil suspensions were centrifuged, and the supernatant was decanted. The remaining soil was washed twice with a small volume (~2–3 mL) of distilled water to remove any remaining soluble traces of the original As(V) spike. Negligible As(V) desorption occurred while rinsing the soil with distilled water. The decanted supernatant and rinse water were then combined and filtered through a 0.45- μ m membrane filter, and the concentration of As in the filtrate was analyzed using an atomic absorption spectrophotometer (AAS) equipped with an electrodeless discharge lamp (EDL). The detection limit for the AAS was ~3 μ g/L with a relative precision of \pm 5%. The difference between the amount of As(V) added and the amount of As(V) remaining in the supernatant was used to calculate the adsorbed As(V) concentration. After air-drying, the soils were homogenized by mixing, and a subsample of each soil was taken, which marked the beginning of the aging experiment (i.e., $t=0$). The remaining soil was placed in a weighing dish and brought to 30% moisture content with deionized water. The soils were then aged in a larger container through 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%. Periodically, subsamples were removed and analyzed as described below.

Extractions. Bioaccessibility was measured on duplicate soil subsamples over time using a streamlined version of the original PBET (17). This method has been shown to correlate well with in vivo bioavailability for Pb and is currently being validated for As. 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. 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). The extraction solution consisted of 30 g/L glycine (0.4 M), pH-adjusted to 1.5 with HCl. 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 to be immersed into 100 mL of PBET solution. However, the procedure was modified for 0.1 g of soil and 10 mL PBET solution to conserve soil samples while maintaining the same soil-to-solution ratio. Replicate analyses using 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. After extraction for 1 h, a portion of the supernatant was filtered with a 0.45- μ m filter. The dissolved As concentration in the filtrate was measured as described previously, with the fraction of metal dissolved representing the absolute bioaccessibility. The remaining soil sample was analyzed for As using acid digestion as described below to verify mass balance within \pm 10%. As described previously (14), the absolute bioaccessibility of a soluble As solution measured in the same manner was $96.1 \pm 0.1\%$. Therefore, in this study, the absolute and relative (to soluble As) bioaccessibility were the same. Ruby et al. provide formal definitions of relative and absolute bioavailability and bioaccessibility (5). To verify the mass balance, the residual soil As was determined using a strong acid extraction method (EPA 3050B) after each PBET extraction. After digestion, the samples were filtered using a Whatman filter paper, and the filtrate was measured with AAS to obtain the total As remaining on the soil. Analysis of the soil residues from the

procedure yielded a mass recovery of $100 \pm 10\%$. For all soils, blanks were used to correct all data obtained from PBET extractions.

Multivariable Regression. Multivariable linear regression was used to identify the significant soil properties affecting adsorption and sequestration (the relative change in bioaccessibility over 6 months) and to derive a model to predict the steady-state bioaccessibility of As(V) in the soils using backward elimination (18) by employing the general equation

$$Y = \beta_0 + \sum_{i=1}^N \beta_i X_i \quad (1)$$

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 (bioaccessibility). Multivariable regression was employed using 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 percentile confidence level ($P < 0.05$). Five soils (one soil chosen at random from each of the five soil orders with more than two samples) were not used in the regression in order to independently validate the resulting model. In addition, the resulting model was used to predict the in vivo bioavailability of As in nine contaminated soils previously used in swine dosing trials (15). The agreement between the measured and model predicted steady-state bioaccessibility/bioavailability were quantified with the root-mean-square error (RMSE),

$$\text{RMSE} = \left[\frac{1}{n_d - n_p} \sum_{i=1}^{n_d} (B_i - \hat{B}_i)^2 \right]^{1/2} \quad (2)$$

where n_d is the numbers of data points, n_p is the number of adjustable parameters (zero when used in a purely predictive manner), i is an index, and B_i and \hat{B}_i are the measured and predicted bioaccessibility at 6 months, 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. Arsenic concentrations in groundwater at contaminated (e.g., U.S. "Superfund") sites are frequently high (2), and the risk of exposure to As from drinking shallow groundwater can be significant (1). Since interactions with the solid phase will govern the transport of As from soil to shallow groundwater at contaminated sites, the soil properties influencing the adsorption of As(V) to these soils over the initial 48 h contact period were examined. There was a wide range in the relative amount of As(V) adsorbed to these soils, ranging from 13 to ~100% with a mean of 81.4% (Table 2). The soil's Fe oxide content was the major factor governing the initial adsorption of As(V) to the soils (Figure 1a). The percentage of As(V) adsorbed increased sharply as the soil's Fe oxide content reached ~5 g/kg, indicating the important role of Fe oxide as binding sites of As(V). Of the eight soils with <5 g/kg of Fe oxides, none adsorbed more than 60% of the added As(V). Above 5 g/kg Fe oxide, 27 of the other 28 soils (96.4%) adsorbed >80% of the dissolved As. An Fe oxide concentration of 5 g/kg and 100 mg/kg of As corresponds to an Fe/As molar ratio of 67 and to a log surface excess (Γ , mole As(V) per mole Fe, calculated from the concentration of each in the soil) of -1.8. This surface excess also closely corresponds to the number of preferred reactions sites (singly coordinated surface hydroxyl groups) on goethite (19, 20).

TABLE 2. As(V) Adsorption and Bioaccessibility^a

soil	init As(V) adsorption (%)	0 month	1 month	2 month	3 month	6 month	significant aging	
							over 6 months? ^b	between 3 and 6 months? ^c
1	94.8	28.2 ± 3.9	23.3 ± 1.9	26.3 ± 2.2	21.8 ± 1.0	16.6 ± 3.5	yes	no
2	86	45.8 ± 5.8	40.9 ± 0.2	47.7 ± 0.7	44.7 ± 0.1	47.0 ± 2.2	no	no
3	96.5	25.3 ± 0.2	23.2 ± 1.9	23.6 ± 0.4	20.5 ± 0.9	19.4 ± 4.2	no	no
4	98.6	5.4 ± 2.0	15.0 ± 7.7	6.4 ± 1.2	5.8 ± 0.4	4.6 ± 2.0	no	no
5	87.6	50.4 ± 8.4	42.0 ± 4.0	33.6 ± 0.8	31.9 ± 1.0	32.5 ± 2.7	no	no
6	98.6	32.5 ± 0.4	25.7 ± 2.1	24.9 ± 1.3	20.0 ± 0.1	17.0 ± 0.1	yes	yes
7	78.9	60.6 ± 2.3	65.0 ± 4.8	57.3 ± 0.7	52.2 ± 2.6	46.7 ± 2.3	yes	no
8	57.8	57.7 ± 8.9	54.0 ± 5.5	46.8 ± 3.2	49.0 ± 0.9	42.5 ± 7.5	no	no
9	94.4	45.6 ± 17.2	39.9 ± 1.0	26.3 ± 0.5	37.2 ± 4.4	37.5 ± 3.5	no	no
10	37.1	93.0 ± 10.0	98.7 ± 1.3	97.6 ± 2.4	98.8 ± 1.2	100 ± 0.0	no	no
11	43.8	82.2 ± 1.1	90.4 ± 3.2	92.5 ± 4.1	100 ± 0.0	95.8 ± 5.9	no	no
12	13.0	94.0 ± 8.4	100.0 ± 0.0	94.8 ± 5.2	99.2 ± 0.8	100 ± 0.0	no	no
13	17.3	45.0 ± 2.1	75.6 ± 1.0	71.0 ± 3.9	75.3 ± 3.3	73.6 ± 0.6	no ^d	no
14	48.7	63.8 ± 9.4	71.2 ± 3.7	70.5 ± 1.6	71.5 ± 2.2	68.6 ± 8.8	no	no
15	57.5	72.5 ± 5.9	83	60.6 ± 3.2	86.5 ± 3.5	73.2 ± 12.8	no	no
16	93.4	42.6 ± 0.7	39.9 ± 2.0	39.6 ± 0.1	36.6 ± 2.2	37.3 ± 0.7	yes	no
17	97.2	29.2 ± 2.1	24.3 ± 3.7	27.2 ± 2.7	22.6 ± 0.8	23.3 ± 2.1	yes	no
18	92.7	49.1 ± 0.6	52	35.4 ± 1.6	35.9 ± 0.0	28.9 ± 1.1	yes	yes
19	93.8	62.8 ± 1.1	42.4	43.4	30.8 ± 3.1	31.3 ± 0.1	yes	no
20	97.4	51.8 ± 1.1	27.8	27.3	19.6 ± 0.5	16.6 ± 0.4	yes	yes
21	96.0	43.8 ± 4.3	39.0 ± 6.3	31.8 ± 0.5	33.9 ± 1.7	26.2 ± 2.5	yes	no
22	100	16.5 ± 0.9	14.2 ± 0.5	12.3 ± 0.7	12.0 ± 0.8	10.2 ± 0.7	yes	no
23	95.3	29.8 ± 4.1	28.8 ± 4.3	23.6 ± 1.9	19.8 ± 0.4	17.6 ± 0.6	no	no
24	99.2	19.4 ± 2.6	17.7 ± 3.9	14.6 ± 0.1	11.6 ± 0.7	9.4 ± 5.3	no	no
25	92.3	36.1 ± 3.8	25.8	28.0 ± 4.1	26.6 ± 1.2	24.9 ± 0.6	no	no
26	98.6	11.3 ± 0.3	7.6 ± 0.9	6.3 ± 0.6	4.9 ± 1.6	3.6 ± 1.2	yes	no
27	86.9	45.0 ± 0.7	38.8 ± 2.2	36.5 ± 2.7	39.4 ± 1.7	35.9 ± 6.6	no	no
28	96.1	31.4 ± 1.9	32.4 ± 1.2	30.6 ± 2.0	30.0 ± 0.6	26.1 ± 4.1	no	no
29	24.0	100 ± 0.0	51	29.2 ± 9.0	21.4 ± 0.8	14.3 ± 0.7	yes	yes
30	83.0	45.5 ± 3.9	32.4	38.5 ± 2.0	37.1 ± 2.0	34.0 ± 3.7	yes	no
31	97.6	25.3 ± 3.5	22.8 ± 5.5	16.4 ± 0.1	13.8 ± 0.8	11.8 ± 1.5	no	no
32	87.2	54.3 ± 10.1	48.8	38.1 ± 2.4	36.4 ± 0.2	26.6 ± 6.8	yes	no
33	98.2	6.5 ± 3.7	4.0 ± 1.4	6.9 ± 0.8	2.7 ± 1.5	3.4 ± 0.6	no	no
34	99.7	13.6 ± 2.5	9.8	8.6 ± 1.3	8.0 ± 0.1	5.0 ± 1.6	yes	no
35	93.0	47.1 ± 1.6	31.5	33.6	23.9 ± 0.7	24.1 ± 0.7	yes	no
36	99.9	6.6 ± 0.3	5.9	7.8	1.7 ± 0.8	2.6 ± 0.5	yes	no
mean	13.0	43.6	40.1	36.5	35.6	33.0		
min	100.0	5.4	4.0	6.3	1.7	2.6		
max	81.4	100	100	97.6	100	100		
SD	25.6	24.6	25.7	24.3	27.5	27.1		

^a Errors represent standard deviation ($n = 2$). Some data without errors obtained by single measurement. ^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. ^d For this soil only, there was a significant increase in bioaccessibility between 0 and 6 months.

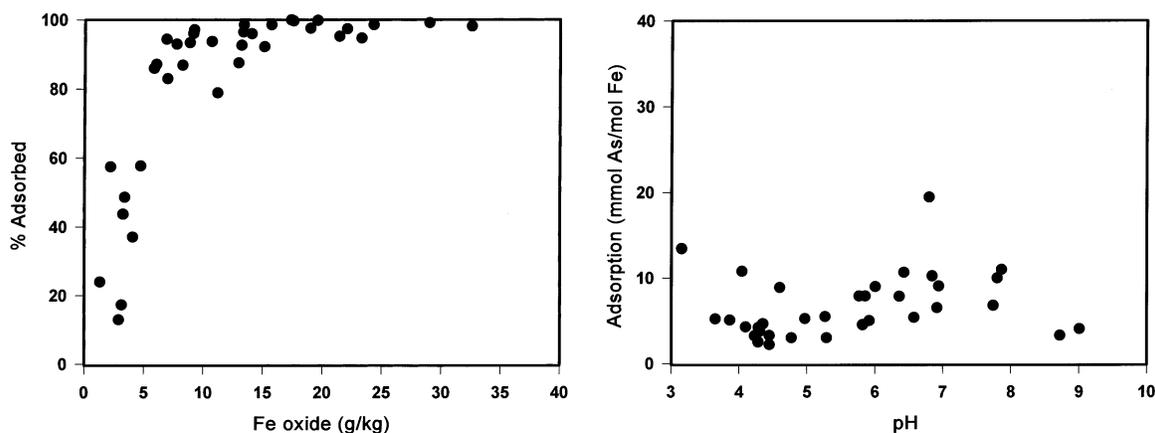


FIGURE 1. (A) Percentage of As adsorbed versus the Fe oxide content. (B) As(V) adsorbed per mole of Fe versus pH.

There were no other readily discernible relationships between As(V) adsorption and the other soil properties. Although As(V) typically exhibits pH-dependent adsorption onto Fe oxides (21), when normalized to the Fe oxide concentration (Figure 1b), there was no evidence of pH-dependent adsorp-

tion. Multivariable regression using backward elimination confirmed that only one variable, log Fe oxide content, significantly ($P < 0.001$) influenced As(V) adsorption over the initial 48 h contact period. The Fe oxide data was logarithmically transformed because of the obvious nonlinearity of

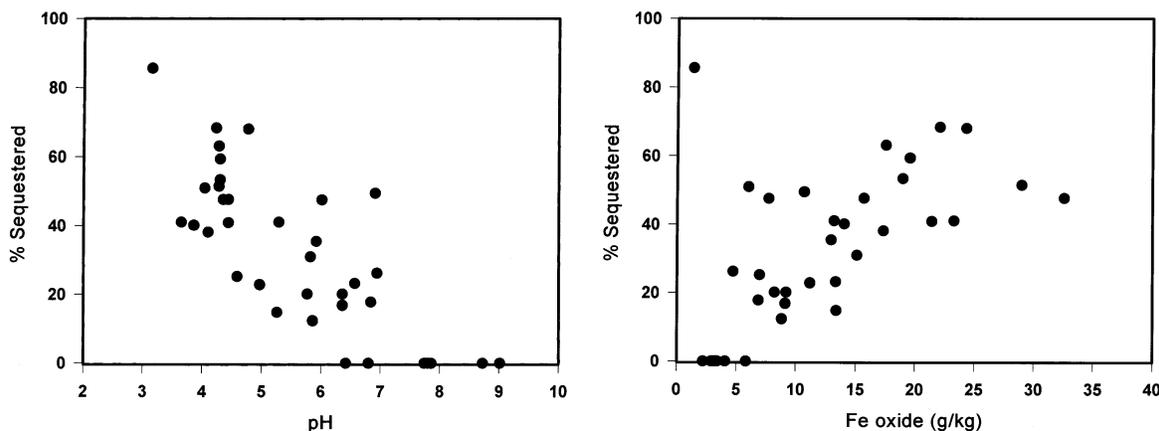


FIGURE 2. (A) Percentage of As(V) sequestered (eq 3) versus pH. (B) Percentage of As(V) sequestered (eq 3) versus the Fe oxide content.

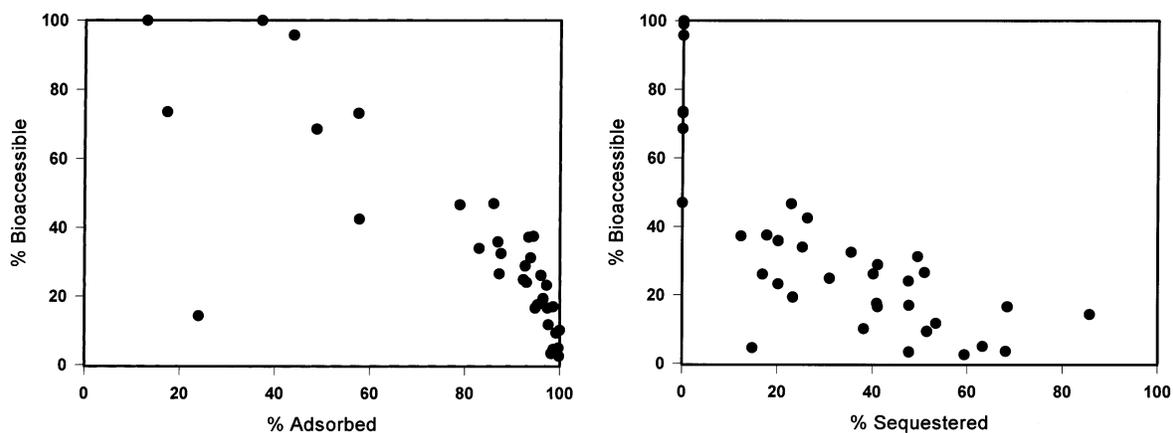


FIGURE 3. (A) Percentage of bioaccessible As(V) versus percent adsorbed. (B) Percentage of bioaccessible As(V) versus percentage sequestered (eq 3).

the relationship between the percentage of As(V) adsorbed and the Fe oxide content exhibited in Figure 1a. The log Fe oxide content explained 56% ($r^2 = 0.564$) of the variability in the relative adsorption of the soils, but all of the variables together explained only 66% ($r^2 = 0.660$) of the variability.

Reduction in Bioaccessibility with Aging. The bioaccessibility values as a function of time are shown in Table 2. There was a wide range in the initial bioaccessibility (5.4–100%) as well as the rate of change of bioaccessibility over time, with some soils exhibiting a significant aging effect and the bioaccessibility in the other soils remaining relatively constant. Using a paired *t*-test, 17 of the 36 soils (47.2%) exhibited a significant reduction ($P < 0.05$) in bioaccessibility over 6 months. In contrast, only four soils (nos. 6, 18, 20, and 29) exhibited a significant ($P < 0.05$) reduction in bioaccessibility from 3 to 6 months' aging. Thus, reductions in bioaccessibility were largely completed by 3 months. The pH was the major factor affecting the reduction in bioaccessibility over time, with a threshold pH of ~ 6 . Of the 22 soils with $\text{pH} < 6$, the bioaccessibility was significantly reduced in 15 (68.2%) of the soils over 6 months. In contrast, of the 14 soils with $\text{pH} > 6$, only 2 (14.3%) exhibited a significant reduction in bioaccessibility over 6 months.

The reduction in bioaccessibility was quantified by calculating the percent sequestration, which was defined as the relative change in bioaccessibility over the 6-month study period by the equation

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

where B_0 and B_6 represent the initial and 6-month bioac-

cessibility, respectively. Soils in which the bioaccessibility increased over time were assigned a sequestration of 0% (with one exception, no. 13, these increases were not significant ($P < 0.05$)). There was a clear relationship between sequestration and pH ($r^2 = 0.654$), with sequestration consistently increasing at lower pH (Figure 2a). However, the relationship between sequestration and Fe oxide content ($r^2 = 0.339$) was not as clear (Figure 2b). Multivariable linear regression confirmed that the pH was the only significant ($P < 0.001$) variable influencing sequestration. The variability in pH was able to explain 65% ($r^2 = 0.654$) of the variability in sequestration alone, but all the variables together explained only 71% ($r^2 = 0.715$) of the variability. The gradual increase in As(V) sequestration over time at lower pH may be related to changes in the bonding mechanism of As(V) onto the soils. However, because the log Fe oxide concentration was not statistically related to sequestration, the change in bonding at lower pH may involve species other than Fe oxides.

Steady-State Bioaccessibility. With the exception of four soils, no further significant ($P < 0.05$) changes in bioaccessibility occurred after 3 months, indicating bioaccessibility had reached a near-steady-state condition. There was a large range in steady-state As(V) bioaccessibility (2.6–100%), with a mean bioaccessibility of 33.0%. There was not a strong linear relationship ($r^2 = 0.509$) between adsorption and bioaccessibility (Figure 3a). The lack of a relationship between adsorption and bioaccessibility is consistent with the generally poor correlation observed between measures of contaminant mobility (e.g., TCLP) and bioaccessibility/bioavailability (22) and reflects the significant differences between conditions in the environment and the human gastrointestinal tract. There was a slightly stronger relationship ($r^2 =$

TABLE 3. Multivariable Regression Models

variable	value	Model 1		VIF ^a
		std error	P value	
	$r^2 = 0.809$		$P < 0.001$	
pH	10.1	0.87	<0.001	1.49
TIC	13.1	4.2	0.004	1.07
log Fe	-32.7	4.5	<0.001	1.65
		Model 2		
	$r^2 = 0.743$		$P < 0.001$	
pH	11.3	0.89	<0.001	1.38
log Fe	-30.5	5.0	<0.001	1.65

^a The variance inflation factor (VIF) is a measure of collinearity. A VIF of 1 indicates the independent variables have no redundant information.

TABLE 4. Predicted Bioaccessibility and Measured Bioavailability

soil no. ^a	pH ^a	Fe Oxide (g/kg)	predicted bioaccessibility ^b (%)	measured bioavailability ^a (%)
1	2.6	125	0	8.62
2	2.6	110	0	4.07
3	3.1	108	0	7.88
4	3.1	88.2	0	19.7
6	7.4	30.4	38.4	38.7
7	7.7	20.2	47.2	42.9
8	7.1	12.9	46.4	39.1
9	7.4	33.4	37.1	42.4
10	7.4	39.5	34.9	21.9

^a From refs 15 and 28. ^b Predicted using model 2 (Table 3). Predicted values <0% were assigned a value of 0%.

0.590) between sequestration and bioaccessibility (Figure 3b). Sequestration and bioaccessibility are not necessarily related, since sequestration is defined as the relative change in bioaccessibility over 6 months (eq 3). For example, some soils initially exhibited a relatively high bioaccessibility that decreased significantly over time (i.e., a low steady-state bioaccessibility and a high degree of sequestration), whereas other soils initially exhibited a relatively low bioaccessibility that remained relatively constant over time (i.e., low steady-state bioaccessibility and low sequestration).

Using multivariable linear regression, models were developed to describe the steady-state bioaccessibility as a function of soil properties (Table 3). Three variables were shown to significantly ($P < 0.05$) influence steady-state bioaccessibility: log Fe oxide (Figure 4a), pH (Figure 4b), and TIC. These three variables (model 1) were able to describe over 80% of the variability in the measured steady-state

bioaccessibility ($r^2 = 0.809$). Previous molecular-scale observations can be used to interpret the influence of these variables on bioaccessibility. The inverse relationship between bioaccessibility and Fe oxide content may be attributed to the transformation of labile As(V) species to less-soluble mineral phases by complexing with Fe oxyhydroxides. Recent spectroscopic information has revealed that As(V) forms a variety of inner sphere surface complexes with Fe oxides (e.g., mono- and bidentate and mono- and binuclear) (19, 20, 23–26). Soil pH was another important factor governing As(V) bioaccessibility, yielding generally lower bioaccessibility at lower pH. The adsorption of anions such as As(V) is favored at low pH values, where variably charged Fe oxides are generally positively charged (21, 27). However, pH was not a significant variable affecting the initial adsorption of As(V) to the soils, and the Fe oxide concentration was not a significant variable affecting the reduction in As(V) bioaccessibility over time. Values of pH < 6 yielded lower steady-state bioaccessibility by promoting greater sequestration, that is, stronger bonding with the soil over time. There was no evidence that this aging effect at pH < 6 was related to bonding on Fe oxides. The carbonate content of the soil (TIC) also influenced the bioaccessibility of As(V), for which soils with higher TIC exhibited more bioaccessibility. This relationship is most likely the result of a localized pH effect near the carbonate surface, where higher pH discourages sequestration, resulting in greater bioaccessibility. The variance inflation factor (VIF) indicated all three variables were important in their own right, with no indication of collinearity (Table 3). However, removing the TIC as an independent variable from the model only slightly decreases the variance in bioaccessibility explained by the model ($r^2 = 0.743$, model 2). Thus, the pH and Fe oxide content can explain nearly 75% of the variability in As(V) bioaccessibility (Figure 5a). The molecular nature of the As(V) interactions in these soils is currently being investigated by synchrotron-generated X-ray absorption spectroscopy (XAS) to correlate these macroscopic observations with molecular-scale speciation.

One of the primary objectives of this study was to develop a simple statistical model to predict the steady-state bioaccessibility of soluble As(V) added to soil. To quantify the ability of the developed model(s) to independently estimate bioaccessibility, 5 (nos. 3, 9, 23, 25, 34) of the 36 soils (one each from the five different soil types with more than two samples) were selected at random and excluded from the multivariable regression analysis. The resulting multivariable regression models were then used to independently predict the steady-state bioaccessibility of As(V) in these five soils. Model 1 was able to predict the steady-state bioaccessibility of these five soils within a RMSE of 8.2% (Figure 5b). Removing the independent variable TIC from the model (model 2)

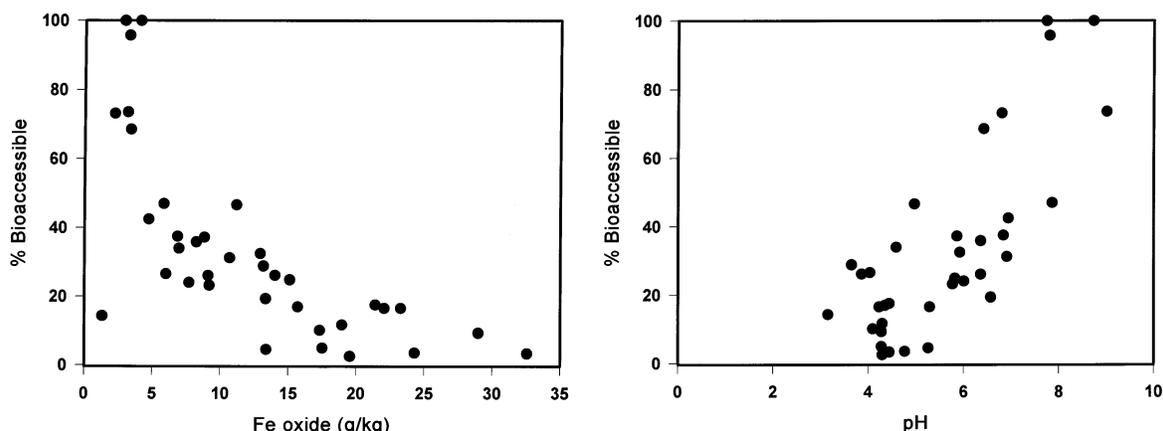


FIGURE 4. (A) Percentage of bioaccessible As(V) versus the Fe oxide content. (B) Percentage of bioaccessible As(V) versus pH.

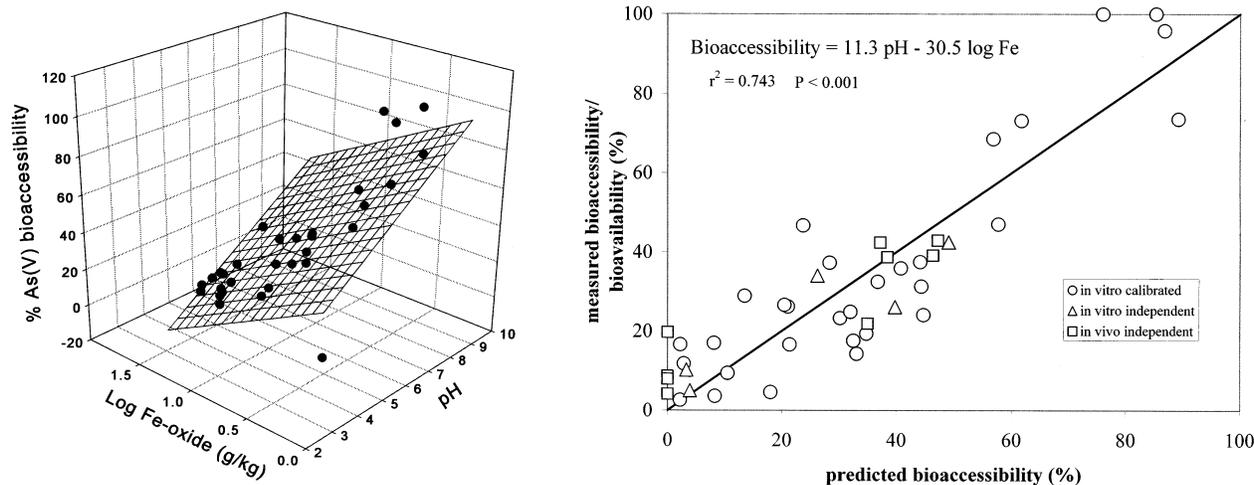


FIGURE 5. (A) Observed (data points) and model-fitted (grid surface) relationship between bioaccessibility, pH, and log Fe oxide content (model 2). (B) Measured bioaccessibility or bioavailability versus predicted bioaccessibility.

increased the RMSE of the predictions only to 10.9%. Previously, Rodriguez et al. (15, 28) reported *in vivo* bioavailability measurements (determined from swine dosing trials) from 15 As-contaminated soils. Subsamples of 9 of these soils (soils 1–4 and 6–10 from ref 15) were obtained from the authors, and the DCB-extractable Fe oxides were measured as described above. Using the pH values reported by Rodriguez et al. (15) and the DCB-extractable Fe oxides measured on the subsamples, the As bioavailability was predicted using model 2 and compared to the values reported by Rodriguez et al. (15, 28). Model 2 was able to predict the *in vivo* bioavailability of these nine soils within an RMSE of 9.5% (Figure 5b). In using model 2, predicted values of bioavailability < 0 (a physical impossibility) were assigned a value of zero.

The results of this investigation have revealed several important factors governing As(V)–soil interactions relevant to contaminated sites. First, there was a wide range in measured As(V) adsorption, sequestration, and bioaccessibility. The Fe oxide content was the most important (and only statistically significant) soil property governing As(V) adsorption over the initial 48 h. Approximately one-half of the soils exhibited a significant reduction in bioaccessibility while being aged for 6 months at 30% moisture content. Further reductions in bioaccessibility had generally been completed by 6 months. The pH was the most important (and only statistically significant) soil property influencing the reduction in bioaccessibility over 6 months, with soils with pH values < 6 generally exhibiting significant reductions over time. In contrast, soils with pH > 6 generally did not sequester As(V) significantly over time. Both Fe oxide content and pH and, to a lesser extent, TIC significantly influenced the steady-state bioaccessibility measured after 6 months.

These results indicate many soils, particularly those with high Fe oxide content and low pH, may reduce As(V) bioaccessibility relative to soluble As(V). Because the allowable inorganic intake of As(V) is based on soluble As in drinking water, the calculated risk to children consuming As-contaminated soils may be overestimated unless site-specific bioavailability is considered. The quantitative models presented here can be used to predict otherwise soluble As(V) bioaccessibility in soil within an RMSE of 6.3–10.9%. In addition, the model was able to predict the *in vivo* bioavailability of As from nine contaminated soils to within a RMSE of 9.5%. Estimates of As(V) bioaccessibility can be used to prioritize sites and justify more-detailed site-specific bioavailability (e.g., animal dosing) studies. Finally, these results demonstrate that fundamental As(V)–soil interactions

may limit otherwise soluble As(V) bioaccessibility without relying on any particular As speciation (e.g., in sulfides) that is difficult to measure and may be subject to change over time. Estimates of bioaccessibility based on soil properties are, by definition, valid unless the major soil properties change. Because most soils have evolved a particular set of physicochemical properties as a result of interactions over a relatively long period of time (e.g., thousands to hundreds of thousands of years), major soil properties are unlikely to change over relatively short time spans (e.g., human lifetimes) unless conditions change dramatically (29). Thus, major soil properties are arguably the most stable aspect of soils, and reductions in metal bioavailability as a result of these soil properties would be correspondingly stable.

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