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Factors Controlling the Bioaccessibility of Arsenic(V) and Lead(II) in Soil

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The relative oral bioaccessibility of labile Pb(II) and As(V) added to soils was investigated in a well-characterized soil using a physiologically based extraction test (PBET) to simulate metal solubility in a child's digestive system. The effect of soil and PBET (i.e., simulated stomach and small intestine) pH, soil metal concentration, soil to solution ratio, and soil-metal aging time were investigated. Arsenic bioaccessibility was relatively unaffected by a variation in simulated stomach and small intestine pH over the range 2 to 7 and soil pH over the range 4.5 to 9.4. In contrast, Pb(II) bioaccessibility was strongly dependent on both the simulated stomach, small intestine, and soil pH, showing enhanced sequestration and decreased bioaccessibility at higher pH values in all cases. Although the bioaccessibility of Pb(II) was constant over the concentration range of approximately 10 to 10,000 mg/kg, the As(V) bioaccessibility significantly increased over this concentration range. The bioaccessibility of both arsenic and lead increased as the soil-to-solution ratio decreased from 1:40 to 1:100. Additional lead sequestration was not observed during 6 months of soil aging, but As (V) bioaccessibility decreased significantly during this period.

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***Key Words**: bioaccessibility, bioavailability, extraction, arsenic, lead, soil.*

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INTRODUCTION

Soil ingestion is typically the primary human health exposure pathway at metal-contaminated sites. For residential or recreational land use scenarios, for example, the ingestion of soil by children is almost always the critical exposure pathway. The calculated health risk due to the incidental ingestion of a metal-contaminated soil is a function of several variables: the soil-metal concentration, soil ingestion rate, body weight, exposure frequency and duration, and the oral toxicity (cancer slope factor for carcinogens or the reference dose for non-carcinogens). However, the oral toxicity of metals is often based on toxicological studies where the metal is potentially more bioavailable than metals in soils (e.g., from animal feeding studies with soluble metal salts). Thus, with the exception of Pb, risk assessments implicitly assume a default value of 100% relative bioavailability. In other words, the bioavailability of the metal in the soil is implicitly assumed to be the same as in the dosing medium (e.g., water or food) in the critical toxicity study. The risk assessment methodology for Pb in soils is unique; Pb is the only metal that has an explicit soil bioavailability adjustment.

Metals in soils, however, are often relatively insoluble, requiring aggressive digestion procedures for complete analytical metal recovery. As a result, an oral toxicity value developed from studies using soluble metal species may overstate the risk posed by less-soluble metals in soils. The generally low bioavailability of Pb and As in soils in mining areas has been well documented, and risk assessments based on data from studies using soluble metal salts overestimate the risk posed by these soils (Davis *et al*., 1992). Numerous studies, for example, have shown that Pb in soil (Freeman *et al*., 1994; Casteel *et al*., 1997), mining waste (Dieter *et al*., 1993; Polak *et al*., 1996) and aggregate (Cheng *et al*., 1991; Preslan *et al*., 1996), is much less bioavailable than more soluble Pb species, such as Pb oxide, nitrate, or acetate used in toxicological studies. Relatively low Pb bioavailability is a consequence of Pb speciation and the corresponding solubility constraints (Davis *et al*., 1993) and kinetic limitations to dissolution in the limited residence time of the GI tract (Ruby *et al*., 1992). Similarly, the oral toxicity for As is based on a human epidemiological study of As in drinking water. However, soluble As in drinking water is much more bioavailable than insoluble As in soils, the latter of which is primarily excreted through the feces without being absorbed through the GI tract (Freeman *et al*., 1995). Estimates of risk due to As ingestion in soils in mining areas would overstate the risk unless the lower bioavailability of As in these soils is considered (Davis *et al*., 1996; Davis *et al*., 2001).

In mining-impacted areas, low soil-metal bioavailability might be due to the presence of residual low solubility metal sulfides from the ore body. However, even in non-mining areas, soil metal bioavailability may be lower than for soluble metal species because soils typically bind metals due to sorption to the solid phase and the formation of other secondary solid phases with lower solubility, including authigenic metal sulfides (Barnett *et al*., 1997). For example, the presence of the

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soil matrix significantly reduced the absorption of soluble $CdCl_2$ from the GI tract in rat studies (Schilderman *et al*., 1997). In fact, animals are believed to instinctively consume soils when exposed to contaminants in their diets as a way of decreasing the bioavailability and the effect of these contaminants (Sheppard *et al*., 1995).

The purpose of this article is to describe the results of an investigation into the bioaccessibility of Pb(II) and As(V) added to soils using a physiologically based extraction test (PBET) to simulate soil ingestion. As(V) and Pb(II)-spiked soils were used because (1) the initial metal concentration and speciation could be controlled, (2) changes in bioaccessibility from the initial labile metal could be followed with time, and (3) beginning with labile metals provided insight into the ability of soils themselves to limit metal bioaccessibility, without regard to any unique site-specific speciation. The effects of soil and PBET pH, soil-to-solution ratio, soil-metal concentration, and soil-metal aging time were investigated.

II. Experimental Methods

A. 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). Soil samples were collected from the B- and C-horizon of a weakly developed Inceptisol on the Department of Energy Oak Ridge (Tenn.) Reservation. The soils were air dried and passed through a 250-μm (B-horizon) or 2-mm (C-horizon) sieve. The <250-μm fraction represents the soil fraction most likely ingested as a result of children's hand-to-mouth activities and was adopted after the initial experiments with the C-horizon material were begun. These soils are acidic (pH ~4.2 in a 1:2 g/mL suspension) and heavily coated with Fe-oxides. Some physical and chemical properties of the two soil samples are shown in Table 1.

B. Soil Spiking

Arsenic(V) and Pb(II) were added to the soil from a small volume of concentrated metal stock solution to a 1:10 g/mL suspension in 10^{-3} M $CaCl_2$ solution. In most experiments, the soil slurry was maintained at the natural soil pH (~4.5 in a 1:10 g/mL suspension) by immediately neutralizing the acidity from the metal stock solution with dilute NaOH. The pH of some slurries was changed by adding additional dilute NaOH to study the effect of soil pH on the bioaccessibility of As(V) and Pb(II). After mixing for 48 h, the soil suspension was centrifuged and the supernatant was decanted. The remaining soil was washed twice with distilled

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

Property	B-horizon	C-horizon
Sand (%)	31	31
Silt (%)	50	50
Clay (%)	19	19
pH*	4.2	4.1
Mn (g/kg)**	0.17	0.36
Fe (g/kg)**	22.1	25.8
Organic Matter (%)	0.42	0.55
Inorganic Carbon (%)	0.26	not measured
CEC ($cmol_c/kg$)	14	not measured
Mineralogy (%)***	I(45)IS(20)V(10)K(9) VC(6)M(5)Q(3)F(1)	I(30)IS(25)K(20) S(10) V(10)Q(5)

* The pH of the soil solution was measured in 5 mM $CaCl_2$ in a 1:2 g/mL suspension.
** Dithionite/citrate/bicarbonate extractable.
*** K=kaolinite, V=vermiculite, VC=chloritized vermiculite, I=illite, IS=interstratified 2:1, Q=quartz, G=gibbsite, M=montmorillinite, F=feldspar, S = smectite.

water to remove any traces of the original soluble As(V) or Pb(II) spike. The decanted supernatant and rinse water were filtered through 0.45–μm membrane filter, and the concentration of As(V) and Pb(II) in the filtrate was analyzed using an atomic absorption spectrophotometer equipped with an electrodeless discharge lamp (EDL) for As and a hollow cathode lamp for Pb. The difference between the amount of As(V) or Pb(II) added and that remaining in the supernatant was used to calculate the initial soil concentration. The soil residues from the PBET extraction (below) were also analyzed for Pb and As using EPA Method 3050B to verify a mass balance of ±10%.

The soils were then air-dried and homogenized by mixing. Initial subsamples were taken representing the conditions at 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 bring the soil to field capacity (30% moisture). The open containers 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.

C. Adsorption

The degree of adsorption As(V) and Pb(II) to the soil was measured by adding 5 g/L B-horizon soil and 1 mg/L Pb(II) or As(V) concentrations in 10^{-2} *M* $NaNO_3$

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solution. After adjusting the pH of the initial suspension to between 2 and 12 using dilute HNO_3 or NaOH solutions, the samples were shaken for 48 h at normal room temperature (22 to 25°C). After 48 h, the suspension pH of each sample was measured, and the suspensions were filtered using 0.45-μm filters (Gelman). The concentration of As(V) or Pb(II) in the filtrate was measured using an atomic absorption spectrophotometer as described above.

D. Extractions

The physiologically based extraction test (PBET) used here was adopted from a modification to the original PBET described by Ruby *et al*. (1996). This extraction test has been shown to be predictive of Pb bioavailability in two animal models and is currently being validated for As (Ruby *et al*., 1999). The extraction device 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 variable speed. The sample holder was located in a temperature-controlled water bath. During the 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*) with the pH adjusted to 1.5, 2, 3, or 4 with HCl. These conditions simulated the stomach, because recent research has suggested that Pb and As dissolution in the simulated stomach environment is predictive of Pb and As bioavailability in animals (Ruby *et al*., 1999).

One gram of each air-dried soil was placed in a 125–mL HDPE bottle. Then 40 or 100 mL of 37°C simulated gastric solution was poured in each bottle. After capping, each bottle was placed in the sample holder and rotated end over end at 30 ± 2 rpm for 1 h. After 1 h, the bottles were immediately removed and stood up right for approximately 5 min before taking a portion of the supernatant, which was then filtered with 0.45-μm filter. For all experiments, duplicate or triplicate samples were run and the results were reported as ± one standard deviation unless otherwise noted. The dissolved metal concentration in the filtrate was measured with an atomic absorption spectrophotometer, with the fraction of metal dissolved representing the bioaccessibility (see below). Although the stomach may be important in solubilizing soil-bound metals, systemic absorption occurs in the small intestine, where chemical conditions (especially pH) are significantly different. To examine these effects, the pH of the remaining PBET solution was adjusted to 7 by adding 4 mL of 0.5 *M* $NaHCO_3$, maintaining a constant soil-solution ratio. The bottles were returned to the extractor and rotated end over end at 30 ± 2 rpm for 3 h, when they were sampled and analyzed as described previously. The remaining soil sample was analyzed for As or Pb using acid digestion (see below) to verify mass balance within ±10%.

To measure the pH and the readily soluble and exchangeable concentrations of As and Pb, 1 g of each soil was mixed with 2 mL of 5×10^{-3} *M* $CaCl_2$ solution for

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2 h. After centrifugation (10 min at 2000 rpm), the supernatant was filtered with 0.45-μm filter. Then the pH and metal content of the supernatant were measured. For all soils, blanks (no metal added) were used to correct all data obtained from $CaCl_2$ and PBET extractions.

The absolute oral bioavailability is the fraction of an administered metal dose that reaches systemic circulation from the gastrointestinal tract (Ruby *et al*., 1999). The relative bioavailability is the bioavailability of a metal in one form or media compared with another (e.g., the bioavailability of a metal in soil relative to the bioavailability of the metal in water). In *in vitro* extraction tests, the fraction of metal solubilized and available for absorption is termed the bioaccessibility and is an indicator of the bioavailability of soil-bound metals relative to the soluble metal species on which the oral toxicity is based (Ruby *et al*., 1996). The bioaccessibility of soluble As_2O_5 and $Pb(NO_3)_2 \cdot 6H_2O$ at the same concentration as in the soils was 96.1 ± 0.1% and 99.8 ± 1.1%, respectively. *In vitro* extraction procedures are a more useful tool than expensive and time-consuming animal feeding studies for investigating the effect a number of variables on bioaccessibility/bioavailability.

E. Soil Analysis

In order to verify the mass balance, the residual soil Pb or As was determined using a strong acid extraction method (EPA 3050B; 10 mL of 50% HNO_3, 5 mL of concentrated HNO_3, 2 mL of water + 3 mL of 30% H_2O_2 at 95 ± 5°C) 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 metal amounts remaining on the soil. An analysis of the soil residues from the procedure yielded a mass recovery of 100 ± 10%.

III. Results and Discussion

A. Effect of Aging Time

Figure 1 shows the water-soluble/exchangeable and bioaccessible concentrations of Pb(II) and As(V) in contact with soils from the C-horizon as a function of aging time. The soil rapidly and strongly sequestered both Pb(II) and As(V). The $CaCl_2$–extractable Pb(II) and As(V) was less than 3% of the total soil concentration over all time periods. The bioaccessibility of arsenic was rapidly and dramatically reduced, decreasing from 11.3 ± 0.7% initially to 5.8 ± 0.2% after 6 months, a significant decrease ($p<0.001$). The Pb(II) bioaccessibility was greater than that of arsenic, 62.6 ± 3.2% initially with no further significant sequestration over 6 months. The reductions in bioaccessibility are due to metal-soil interactions rather than preexisting solid phase speciation, as soluble metals were added to the soil

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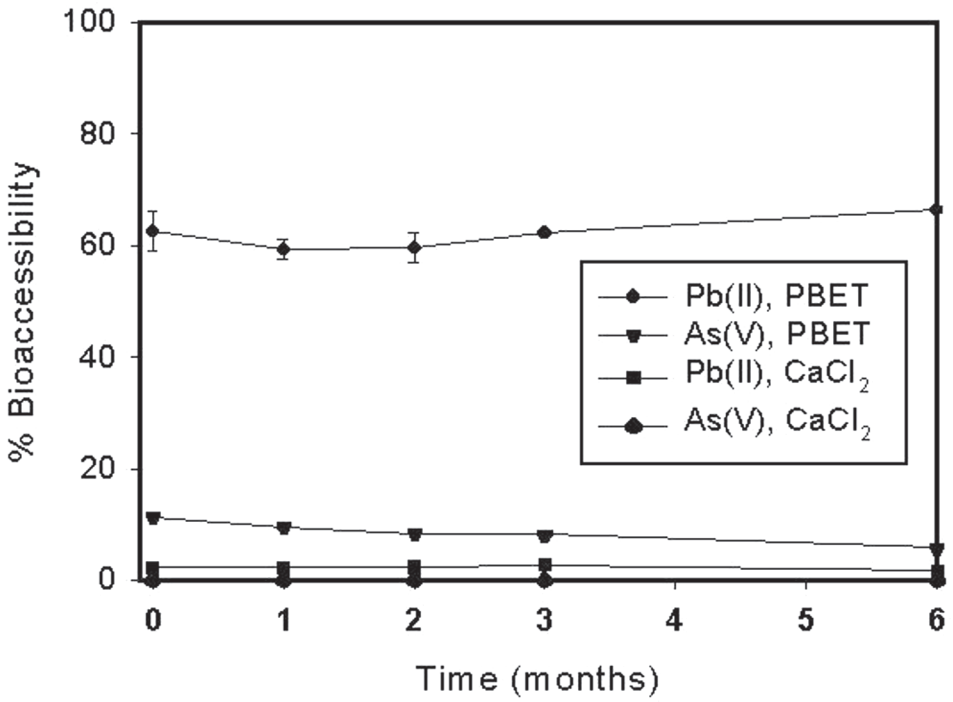

FIGURE 1

Simulated stomach bioaccessibility of As(V) and Pb(II) with aging times (C-horizon soil, pH 2, 1:40 soil/solution ratio). Error bars are ± one standard deviation (n = 2–4).

initially. This is important because it implies a long-term reduction in bioaccessibility as long as the soil properties governing metal sequestration do not change. This is in contrast to long-term changes in metal speciation (e.g., metal sulfide oxidation) that may be a concern in situations where metal speciation, as opposed to soil-metal interactions, is controlling bioaccessibility.

B. Effect of Simulated Gastrointestinal pH

The pH of the stomach is variable, ranging from approximately 2 (fasting) to 4 to 5 after eating (Ruby *et al*. 1996). To examine the potential effects of different pH conditions in a simulated stomach, the bioaccessibility of As(V) and Pb(II) were measured at four different pH values. Figure 2a shows a comparison of the bioaccessibility of As(V) and Pb(II) in freshly spiked B-horizon soil at four different simulated stomach pH values. The bioaccessibility of arsenic was constant at 25.9 ± 6.8% with pH over the range 1.5 to 4. The differences between the bioaccessibility in the B-horizon (Figure 2a) and C-horizon (Figure 1) may be due

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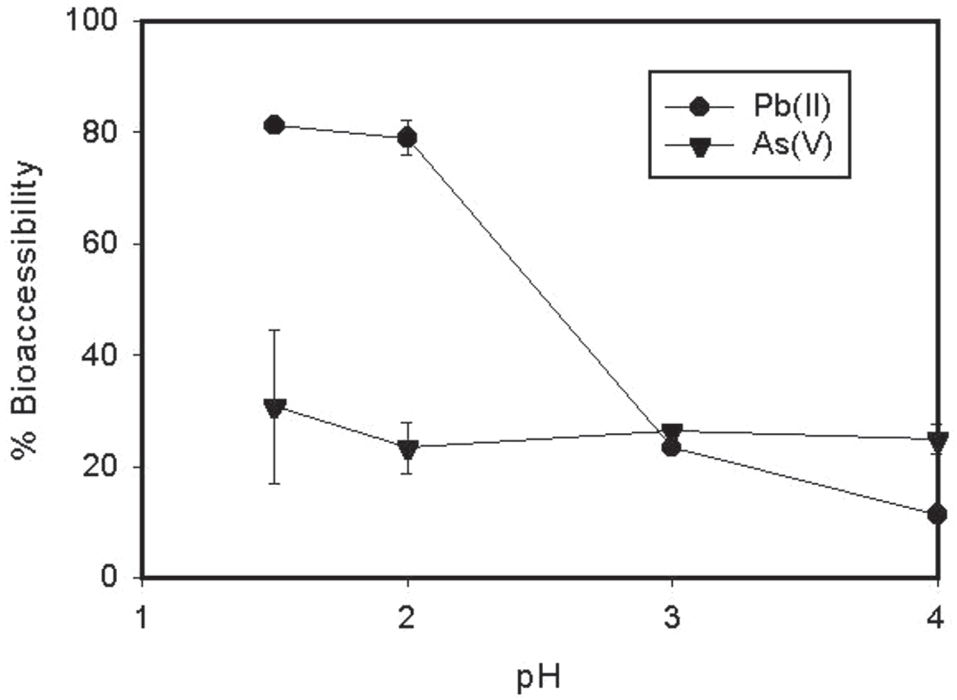

FIGURE 2A

Simulated stomach bioaccessibility of As(V) and Pb(II) from fresh soil with variation of pH of PBET solution (B-horizon soil, 1:40 soil/solution ratio). Error bars are ± one standard deviation (n = 2–3).

to differences in particle size used (<250 μm vs. <2000 μm) or small changes in the amount and reactivity of Fe or other metal-sequestering solid phases. The Pb(II) bioaccessibility, in contrast to As(V), exhibited a greater pH dependence. At pH 1.5, 81.1 ± 1.3% of lead was bioaccessible, while only 11.1 ± 0.7% was bioaccessible at pH 4. This result suggests that the bioaccessibility of lead is strongly affected by the stomach pH. Thus, an eightfold variation in bioaccessibility is possible due to a daily variation in stomach pH. This phenomenon illustrates another source of uncertainty that must be considered in conducting a risk assessment. From studies of the bioavailability of soil-borne lead in adults, Maddaloni *et al*. (1998) reported a great difference in lead absorption between fasting (26.1%) and after eating (2.5%).

After approximately 2 h of residence time in the stomach, food enters the small intestine where the pH increases to approximately 7 (Ruby *et al*., 1996). Although the overall dissolution of Pb(II) and As(V) may be controlled by the stomach, it is not clear that all the metals dissolved in the stomach may be absorbed, because the proximal area of the small intestine is known as the primary region of heavy metal

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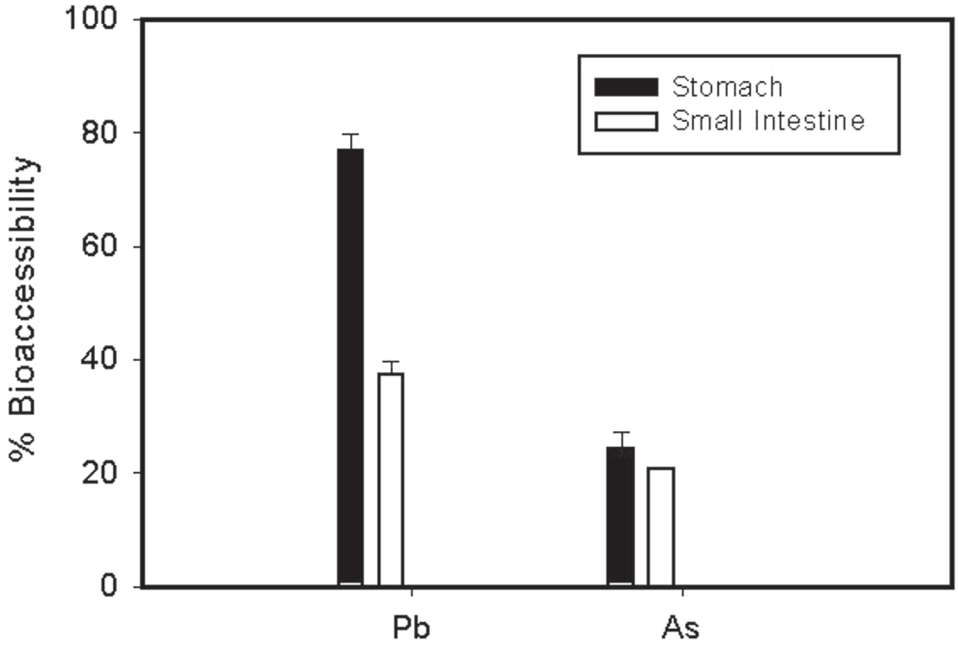

FIGURE 2B

Simulated stomach (pH 2) and small intestine (pH 7) bioaccessibility of As(V) and Pb(II) from fresh B-horizon soil (1:40 soil/solution ratio). Error bars are ± one standard deviation (n = 2–3).

absorption (Ashmead *et al*., 1985). To simulate the small intestine, the pH of the extraction solution was increased to 7 by the addition of $NaHCO_3$. Metal bioaccessibility in the simulated small intestine following digestion is shown in Figure 2b. The bioaccessible As was not significantly affected as the pH of the extraction solution was changed from 2 to 7, suggesting that the pH is not a major controlling parameter for the dissolution of As(V) from this soil at this pH range. However, lead bioaccessibility decreased significantly ($p<0.01$) from $76.7 \pm 3.1\%$ to $37.4 \pm 2.3\%$. As the small intestine is the major region of heavy metal absorption, the bioaccessibility of Pb in the stomach may be greater than the actual bioavailability.

The pH-dependent bioaccessibility of As(V) and Pb(II) can be understood in terms of standard geochemical phenomena. For example, cationic metals (e.g., Pb(II)) typically partition to solids to a greater degree at higher pH, while anionic metals (e.g., As(V)) exhibit the opposite behavior, as shown in Figure 2c. Therefore, the lower bioaccessibility of Pb(II) at higher pH may be due to the same factors (e.g., pH-dependent sorption) that favor Pb(II) adsorption at higher pH. In contrast, As(V) bioaccessibility was relatively independent of simulated stomach

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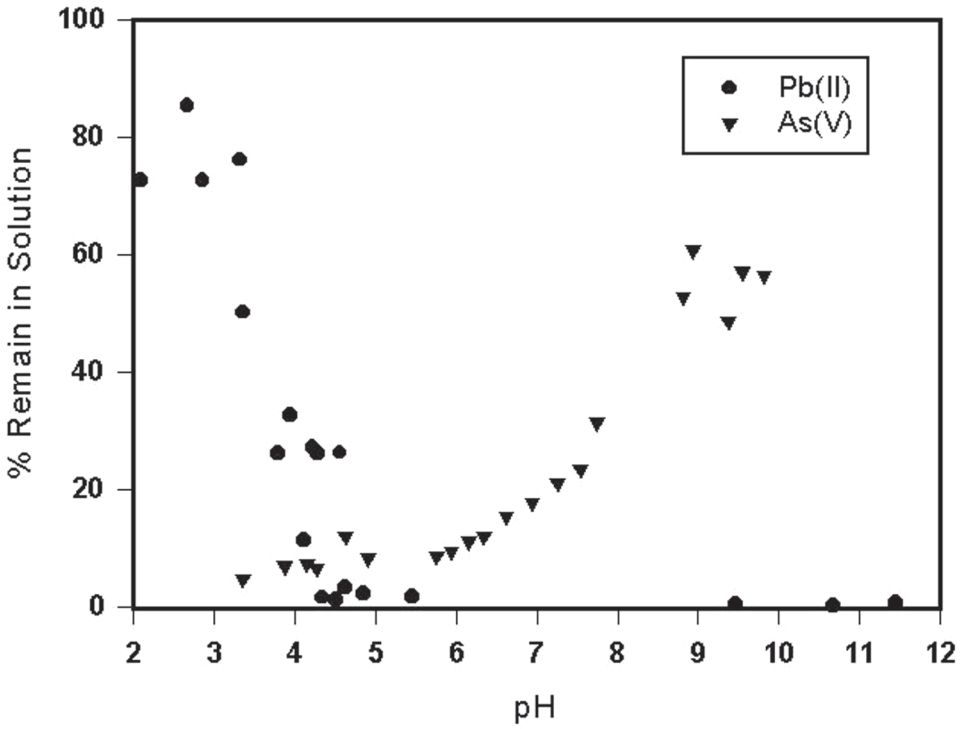

FIGURE 2C

Pb(II) and As(V) adsorption onto B-horizon soil as a function of pH (5 g/L soil; 1 mg/L Pb(II) and As(V); I = 0.01 M $NaNO_3$).

and small intestine pH, which is consistent with a relatively little variation in adsorption from pH 2 to 7 (Figure 2c).

C. Effect of Soil pH

B-horizon soil was used to study initial soil pH effects on metal bioaccessibility. As shown in Figure 3, the effect of soil pH on As(V) and **Pb(II) bioaccessibility was different.** Although As(V) sorption increased sharply from pH 7 to 9 (Figure 2c), the variation of As(V) bioaccessibility was relatively small over the pH range 4.5 to 9. These results indicate that the As(V) bioaccessibility in this soil is controlled by the simulated stomach and small intestine pH rather than the initial soil pH, possibly reflecting relatively rapid pH-dependent partitioning in the solution phase (i.e., As(V) partitioning responds relatively rapidly to solution pH independent of initial soil pH). In contrast, Pb(II) bioaccessibility significantly ($p<0.02$) decreased from $76.7 \pm 3.1\%$ to $47.2 \pm 3.2\%$ at higher soil pH, reflecting

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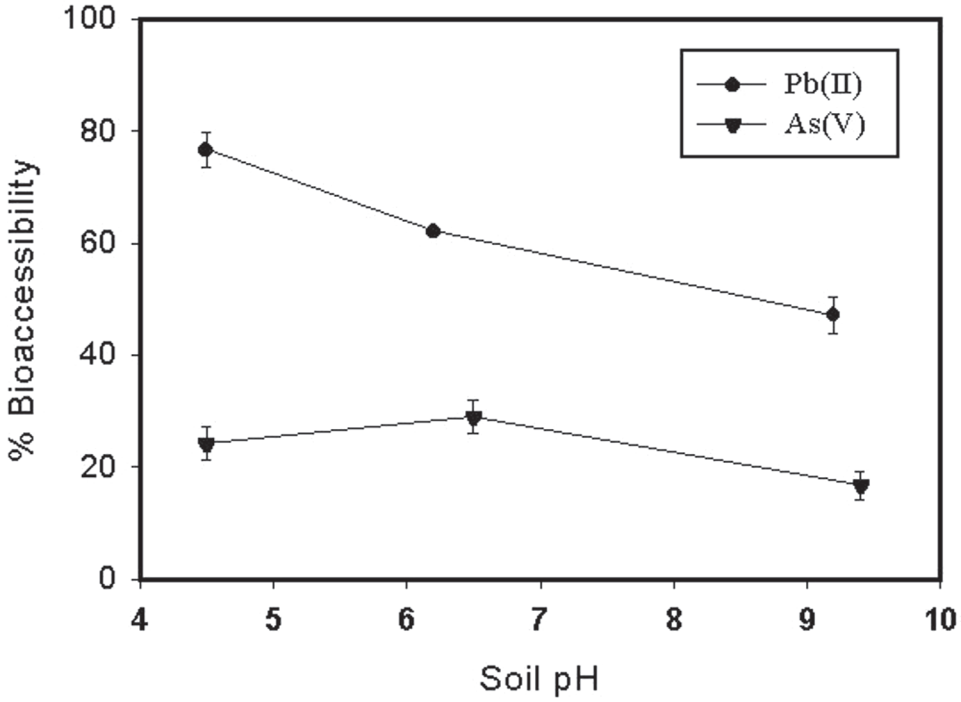

FIGURE 3

Simulated stomach bioaccessibility of As(V) and Pb(II) with variation of soil pH (fresh B-horizon soil, pH 2, 1:40 soil/solution ratio). Error bars are ± one standard deviation (n = 2–3).

the same pattern as typical cationic-type adsorption (Figure 2c). These results indicate that the binding of Pb(II) in the soil is influenced by the initial soil pH, and that the Pb(II) bioaccessibility depended on both the simulated stomach (Figure 2a) and soil (Figure 3) pH. In contrast, the As(V) bioaccessibility was relatively independent of both the simulated stomach (Figure 2a) and soil (Figure 3) pH.

D. Effect of Concentration

Figure 4 shows the bioaccessibility of Pb(II) and As(V) as a function of soil metal concentration. The current risk assessment methodology implicitly assumes that the bioavailability is independent of the concentration by using a constant relative bioavailability adjustment factor. However, metals often partition to the solid phase in a nonlinear manner (i.e., the fraction of metal sorbed decreases with increasing concentration). In order to investigate the accuracy of using a constant bioaccessibility, Pb(II) and As(V) bioaccessibility were measured over almost three orders of magnitude of concentration (10 to 10,000 mg/kg). Pb(II)

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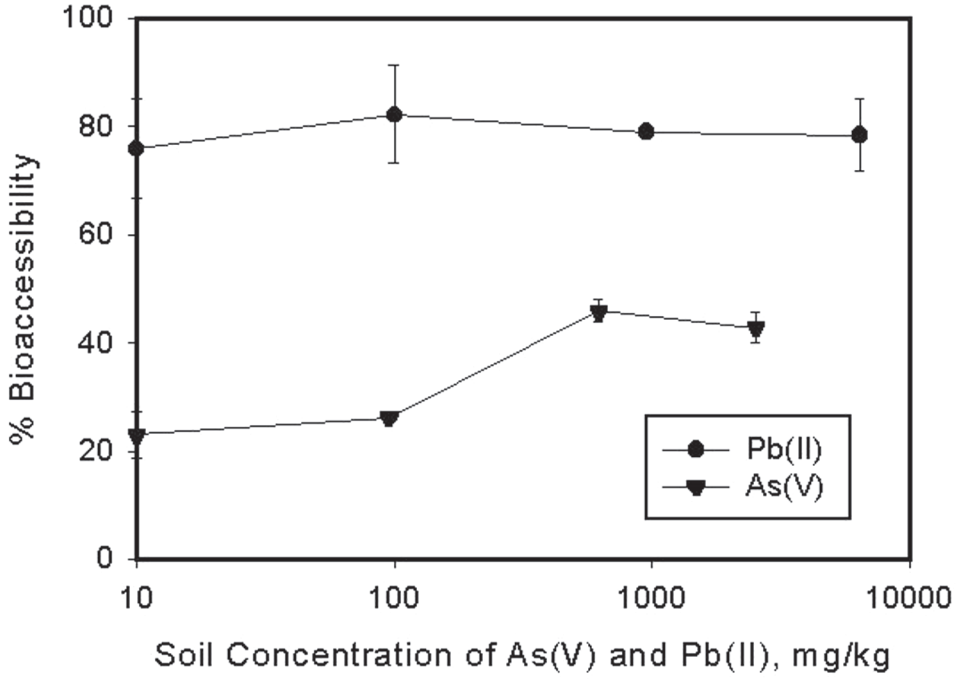

FIGURE 4

Simulated stomach bioaccessibility of As(V) and Pb(II) with variation of initial concentration (fresh B-horizon soil, pH 2, 1:40 soil/solution ratio). Error bars are ± one standard deviation (n = 2–3).

bioaccessibility was relatively insensitive to the concentration of lead, yielding 78.7 ± 6.8% bioaccessibility over all concentration ranges. However, As(V) bioaccessibility significantly ($p<0.05$) increased from 23.0 ± 4.2% to approximately 42.8 ± 2.7% as the concentration of As(V) increased from approximately 10 to 1000 mg/kg, illustrating another potential source of uncertainty introduced in risk assessments by using a constant bioavailability adjustment.

E. Effect of Soil to Solution Ratio

The soil to solution ratio in the stomach will not be constant over time due to the ingestion of different amounts of soil on varying occasions and because the volume of fluid in the stomach depends on the fasting condition of the child. As a result, the bioaccessibility of As(V) and Pb(II) was investigated as a function of soil to solution ratio (Figure 5). The bioaccessibility increased from 30.8 ± 13.8 to 53.2 ± 0.9 for As(V) and from 81.8 ± 1.8 to 91.0 ± 2.1 for Pb(II) with decreasing soil

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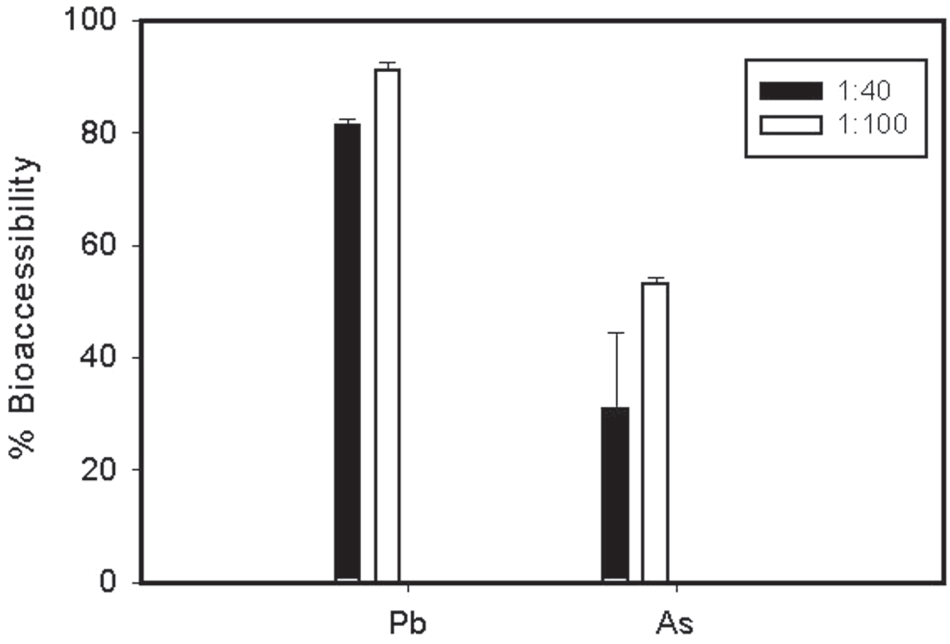

FIGURE 5

Simulated stomach bioaccessibility of As(V) and Pb(II) from fresh B-horizon soil (pH 1.5, 1:40 and 1:100 soil/solution ratio). Error bars are ± one standard deviation (n = 2).

to solution ratio. The same trend was observed in soluble and exchangeable Pb(II) in the $CaCl_2$ solution, especially for aged soil samples. Hamel *et al*. (1998) reported that the effect of the soil to solution ratio on lead and arsenic bioaccessibility depended on the soil sample. Although a higher bioaccessibility of Pb and As from Jersey City soil was observed as the soil to solution ratio decreased from 1:100 to 1:5000, a relatively constant bioaccessibility of Pb(II) and As(V) was observed with Montana soils over all soil to solution ratios tested.

IV. Summary and Conclusions

These results have illustrated several salient aspects of Pb(II) and As(V) bioaccessibility. First, the soils decreased both Pb(II) and especially As(V) bioaccessibility solely as a result of soil-metal interactions and not as a result of any specific preexisting metal speciation. Reduced Pb(II) and As(V) bioaccessibility then can be a result of the fundamental nature of soil-metal interactions rather than site-specific speciation (e.g., metal sulfides from ore bodies). These results also promote greater confidence in the long-term ability of soil to lower Pb(II) and

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As(V) bioaccessibility as long as the soil properties governing metal sequestration remain constant. This might not be the case if the reduced Pb(II) or As(V) bioaccessibility was due to unique metal speciation that was subject to change over time (e.g., oxidation of metal sulfides in surface soils). In fact, the As(V) bioaccessibility significantly decreased over a 6-month aging period. Second, Pb(II) bioaccessibility significantly depended on the pH of both the simulated GI fluid and the soil, showing enhanced sequestration and reduced bioaccessibility at higher pH values. In contrast, neither soil nor GI pH significantly affected As(V) bioaccessibility over the range of GI pH from 2 to 7 and soil pH from 4.5 to 9.4. Third, although Pb(II) bioaccessibility was not significantly influenced by soil-metal concentration over the range 10 to 10,000 mg/kg, the As(V) bioaccessibility significantly increased over this same concentration range. Thus, the use of a concentration-independent bioaccessibility/bioavailability factor in a risk assessment for As(V) may not be warranted. Finally, both Pb(II) and As(V) bioaccessibility increased with decreasing soil to solution ratio, illustrating another degree of uncertainty in estimating the risk of soil ingestion at metal-contaminated sites.

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REFERENCES

Ashmead, H. D., Graff, D. J., and Ashmead, H. H. 1985. *Intestinal Absorption of Metal Ions and Chelates*, pp. 76–77. (Ed.) Charles C Thomas, Springfield, IL.

Barnett, M. O., Harris, L. A., Turner, R. R., Stevenson R. J., Henson, T. J., Melton, R. C., and Hoffman, D. P. 1997. Formation of mercuric sulfide in soil. *Environ. Sci. Technol.* **31**, 3037–3043.

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., and Turk, J. R. 1997. Bioavailability of lead to juvenile swine dosed with soil from the smuggler mountain NPL site of Aspen, Colorado. *Fundam. Appl. Toxicol.* **36**, 177–187.

Cheng, Y. L., Preslan, J. E., Anderson, M. B., and George, W. J. 1991. Solubility and bioavailability of lead following oral ingestion of vitrified slagged aggregate. *J. Hazard. Mater.* **27**, 137–147.

Davis, A., Drexler, J. W., Ruby, M. V., and Nicholson, A. 1993. Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. *Environ. Sci. Technol.* **27**, 1415–1425.

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

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Davis, A., Ruby, M. V., Bloom, M., Schoof, R., Freeman, G., and Bergstrom, P. D. 1996. Mineralogic constraints on the bioavailability of arsenic in smelter-impacted soils. *Environ. Sci. Technol.* **30**, 392–399.

Davis, A., Sherwin, D., Ditmars, R., and Hoenke, K. A. 2001. An analysis of soil arsenic records of decision. *Environ. Sci. Technol.* **35**, 2401–2406.

Dieter, M. P., Matthews, H. B., Jeffcont, R. A., and Mosemers, R. F. J. 1993. Comparison of lead bioavailability in F344 rats fed lead acetate, lead-oxide, lead sulfide, or lead ore concentrate from Skagway, Alaska. *J. Toxicol. Environ. Health* **39**, 79–93.

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

Freeman, G. B., Schoof, R. A., Ruby, M. V., Davis, A. O., Dill, J. A., Liao, S. C., Lapin, C. A., and Bergstrom, P. D. 1995. Bioavailability of arsenic in soil and house dust impacted by smelter activities following oral administration in cynomolgus monkeys. *Fundam. Appl. Toxicol.* **28**, 215–222.

Hamel, S. C., Buckley, B., and Lioy, P. J. 1998. Bioaccessibility of metals in soils for different liquid to soild ratios in synthetic gastric fluid. *Environ. Sci. Technol.* **32**, 358–362.

Maddaloni, M., Lolacono, N., Manton, W., Blum, C., Drexler, J., and Graziano, J. 1998. Bioavailability of soilborne lead in adults, by stable isotope dilution. *Environ. Health Perspect.* **106**, 1589–1594.

Polak, J. E., Oflaherty, E. J., Freeman, G. B., Johnson, J. D., Liao, S. C., and Bergstrom,
P. D. 1996. Evaluating lead bioavailability data by means of a physiologically based lead kinetic model. *Fundam. Appl. Toxicol.* **29**, 63–70.

Preslan, J. E., Chang, C. Y., Schiller, N. K., and George, W. J. 1996. Bioavailability of lead from vitrified slagged aggregate. *J. Hazard. Mater.* **48**, 207–218.

Ruby, M. V., Davis, A., Kempton, J. H., Drexler, J. W., and Bergstrom, P. D. 1992. Lead bioavailability-dissolution kinetics under simulated gastric conditions. *Environ. Sci. Technol***. 26**, 1242–1248.

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

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., and Chappell, W. 1999. Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environ. Sci. Technol.* **33**, 3697–3705.

Schilderman, P. E., Moonen, J. C., Kempkers, P., and Kleinjans, J. C. S. 1997. Bioavailability of soil-adsorbed cadmium in orally exposed male rats. *Environ. Health Perspect.* **105**, 234–238.

Sheppard, S. C., Evenden, W. G., and Schwatz, W. J. 1995. Ingested soil bioavailability of sorbed lead, cadmium, cesium, iodine, and mercury. *J. Environ. Qual.* **24**, 498–505.

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