

Using Nitrogen and Carbon Dioxide Molecules To Probe Arsenic(V) Bioaccessibility in Soils

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Highly specialized personnel and high cost are typically required for in vivo risk assessment of arsenic (As) exposure to humans in As-contaminated soils. Arsenic bioaccessibility in soils, as determined with the aid of in vitro tests, is quite variable, and its magnitude depends upon unidentified soil properties. Use of soil chemical properties is a common practice for construction of As(V) sorption and bioaccessibility models with relative success. We propose a novel As(V) bioaccessibility model, which was tested on 17 soils. The model includes only two parameters characterizing surface properties of soils that are readily determined from N₂- and CO₂-based specific surface areas (SSAs), and total organic carbon (OC) content. We found that N₂ and CO₂ molecules act as As(V) "surrogates", probing easily accessible and relatively difficult to access soil porosity, respectively. Three interrelated linear models were constructed using two terms (CO₂/N₂-based SSAs and OC) that were significant ($p < 0.001$) in explaining 51 and 95% of the variability observed in As(V) sorption and bioaccessibility, respectively. The proposed models successfully predicted bioaccessible As concentrations for 4 out of the 5 soils that were not included in the bioaccessibility models, reaching RMSE values of $\leq 10\%$.

Introduction

The risk of human contact with soil As has greatly increased in the last two decades as residential areas continue to expand into former agricultural land. Geophagia, a Greek term (geo: soil and phagia: eating) may occur from incidental hand-to-mouth activities by children playing in As-contaminated soils. Oral ingestion is the number one exposure route for As in soils, and the adverse effects of As-geophagia on human health, especially to children, are largely dependent upon the relative bioavailability of the As-containing soil particles (1–2). Accurate and relatively simple models are needed for inclusion in risk assessment studies of soil As bioavailability

and bioaccessibility (See Figure S1, Supporting Information). Risk assessment of soil As bioavailability can be performed utilizing data collected from As adsorption and bioaccessibility experiments. Typically, there is a lack of relationship between adsorption and bioaccessibility that has been ascribed to distinct differences between conditions in the soil environment and the human physiology in stomach and intestinal compartments (3).

Arsenic(V) adsorption in soils has been described with several empirical models (Freundlich and Langmuir) (4), as well as models based on the electrical double layer theory (5). The majority of empirical models developed to explain As sorption and bioaccessibility in soils are based on soil chemical properties and tests (pH, oxalate extraction, dithionite–citrate–bicarbonate extraction, etc.) (4–7), and often do not include soil physical properties (3, 8). Soil physical properties, such as specific surface area (SSA), and (micro)porosity are critical in defining chemical reactivity/sorption as expressed by the number of available sorption sites. Nonequilibrium is widely distributed in reactions occurring at the highly heterogeneous soil/liquid interface, suggesting that physicochemical particle heterogeneities are largely associated with their SSA and porosity. As an example, sorption of metalloids, such as As, by different soils may be a nonequilibrium, kinetically (diffusion)-limited process (9). Intraparticle diffusion was the main mechanism explaining the slow As(V) sorption kinetics by granular ferric hydroxide particles that were high in internal SSA (10).

Recent studies showed that SSAs of soils are underestimated by BET-N₂ measurements due to inability of N₂ molecules to diffuse through soil organic matter (SOM) overlayer at low temperatures of the measurements (11–14). Micropore inaccessibility with N₂ gas sorption isotherms at 77.4 K within reasonable equilibration times have necessitated the role of CO₂ molecules in penetrating "buried" and narrow micropores, thus better characterizing microporosity in soils and geosorbent materials (13, 15–16). SSA measurements of soil particles during gas sorption showed that N₂ and CO₂ molecules probe different particle regions and surfaces (13).

N₂-SSA measurements of particles composed of an amorphous mixture of metal hydroxides and organic moieties showed the discrepancy between macroscopic phosphorus (P) sorption data and P parking density (number of PO₄ molecules nm⁻²) (16). In effect, the N₂-based "external" SSA was insufficient to account for sorbed P, whereas CO₂-based SSA measurements more closely matched P sorption data possible due to organic carbon (OC) pore blockage that was only detected with activated sorption of CO₂ at 0 °C (16).

We hypothesized that N₂ and CO₂ molecules could probe the vast spectrum of internal sorption sites that As(V) molecules occupy in soils with respect to the distance from the particle exterior. N₂ molecules probe surfaces easily accessible by As, such as external surfaces or mineral surfaces devoid of organic moieties. On the other hand, CO₂ molecules probe surfaces that As slowly occupies due to steric/diffusional constraints. At near equilibrium, As(V) sorption and bioaccessibility in soils could be related to SSA measurements with N₂ and CO₂ gases, as well as to the soil OC content. We hypothesized that a combination of physical (SSA) and chemical (TOC) properties might fully explain soil As bioaccessibility. Thus, the objectives of this study were as follows: (i) formulate a comprehensive As(V) sorption and bioaccessibility model that includes both chemical and physical properties of soils comprising a wide range in texture, SSA and OC contents; and (ii) relate the proposed soil

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TABLE 1. Macroscopic Physicochemical Properties and Specific Surface Areas Measured with N₂ and CO₂ Gas Sorption for the 17 Soils Used in This Study^a

soil no.	pH	TOC (g kg ⁻¹)	mg kg ⁻¹				m ² g ⁻¹				textural classification		
			oxalate-As	oxalate-P	oxalate-Fe	oxalate-Al	sand %	silt %	clay %	N ₂ -SSA		CO ₂ -SSA	C-constant
1	6.53	112	0.4	530	8400	3630	70.8	18.1	11.1	4.9	39.8	43	sandy loam
2	6.81	243	0.4	970	4100	1050	73.5	10.6	15.9	3.0	54.3	22	sandy loam
3	6.32	35.8	3.8	200	3000	1450	40.6	33.0	26.4	23.2	31.8	72	loam
4	6.90	91.3	3.1	260	3750	1950	51.8	26.3	21.9	15.4	49.7	51	sandy clay loam
5	6.62	59.5	2.4	350	2000	1800	44.5	19.4	36.1	25.2	38.0	114	sandy clay
6	6.64	22.2	3.6	120	1900	1000	22.7	41.5	35.8	29.5	26.3	79	clay loam
7	6.54	28.9	3.4	170	2700	1200	35.2	23.3	41.5	28.0	28.8	97	clay loam
8	6.41	39.2	3.7	200	3000	1250	35	29.2	35.8	25.1	29.3	81	clay loam
9	6.83	274	13.0	655	7000	1055	42.4	36.2	21.4	16.5	69.1	56	loam
10	6.56	42.2	5.0	250	3400	1255	47.2	23.2	29.6	19.4	30.6	75	sandy clay loam
11	5.9	813	5.0	312	9700	1575	86	9	5	0.5	>50	10	loamy sand/muck
12	4.2	2.45	0.5	9.5	41	65	96	4	0	0.6	2.3	44	sand
13	5.56	23.2	3.8	125	2000	3100	25.4	51.1	27.5	30.3	29.1	95	clay loam/loam
14	6.91	57.8	3.25	220	3100	1800	64	25.3	10.7	24.5	40.3	126	sandy loam
15	7.01	17.3	3.20	215	190	320	43	37	20	18.2	33.7	77	loam/saline
16	6.4	33.2	0.65	180	500	1300	96	2	2	2.1	9.8	33	sand
17	8.6	47.2	0.4	25	120	370	40	36	24	82.9	85.3	396	loam/highly alkaline
mean	6.51	114.3	3.27	281.9	3230	1422	53.8	25.01	21.5	20.55	38.12	86.5	
min	4.20	2.45	0.4	9.5	41	65	22.7	2.0	0	0.5	2.3	10	
max	8.6	813	13	970	9700	3630	96.0	51.1	41.5	82.9	85.3	396	
SD	0.86	195.4	3.0	240	2802	902	23.2	13.6	12.6	19.2	19.9	85.7	

^a The C-constant is the N₂ BET method energetic constant. The first 12 soils were used for model construction and the rest were used for independent validation of the model. The 12 soils varied significantly in physicochemical properties, ranging from sandy to clayey soils, from minimum organic C to mucky soils and variable amorphous Fe and Al content (oxalate extraction). Numbers are the means of two replicates. The CO₂-SSA of soil no. 11 was >50 due to nonequilibrium CO₂ gas sorption that continued beyond typical equilibration times.

properties to soil As bioaccessibility measured by an in vitro stomach phase test.

Materials and Methods

Soils Collection. Surface (0 – 15 cm) soils were collected from several sites around the United States (Illinois, Florida, and Texas). Twelve soils were collected from noncontaminated grassy, forested, and construction sites in the Northwestern Greater Chicago area (13, 17). Five additional soils were also included: a highly organic, mucky soil (Belleglade series) collected from Everglades, FL, a highly saline soil from the arid region of Texas (Orla series), a TX native sand (Euphaua series), the highly alkaline state soil of TX (Houston Black series), and a FL-based acidic fertile soil (Millhopper series) in an attempt to cover a wide span of soil physicochemical properties. According to the USDA textural triangle, these soils encapsulated the majority of textural classes, representing 9 out of the 12 major soil textural classes as defined by USDA (Table 1). The importance of particle size distribution on As bioaccessibility in soils adjacent to CCA-treated utility poles was recently emphasized (18). Soils were air-dried and subsequently passed through a 2-mm sieve.

Physicochemical Properties of Soils. Soil pH was measured in 1:1 (w:v) suspensions prepared in a 0.01 M CaCl₂ solution. Total OC of the soils was measured with the loss-on-ignition method after ashing at 440 °C, as per ASTM method D2974-87. Oxalate-extractable As, P, Fe, and Al concentrations were measured by ICP-MS after extraction at a 1:40 solid/solution ratio, following the recommended procedures of Dayton and Basta (19). Oxalate-extractable Fe and Al represents noncrystalline and organically complexed Fe and Al present in the solid (20–21). Soil particle size analysis was performed according to standard protocol procedures (hydrometer method) (22).

Arsenic(V) Spiking to Soils. Na₂HAsO₄·7H₂O (KR Grade, Aldrich, USA) was used to represent As in the form of As(V). The stock As(V) solution was prepared in 0.01 M KCl and the final pH was set to 7 with the aid of 1 N HCl. Representative air-dried (<2 mm) soil samples were reacted with inorganic

As in 1:10 soil/0.01 M KCl solutions at As(V) loads of 50, 100, 250, 500, and 1000 mg As kg⁻¹ for 1 and 10 d to determine As sorption capacities at 23 ± 2 °C. The highest As(V) load (1000 mg kg⁻¹) was used for the soil As bioaccessibility modeling purposes to provide a strong As concentration diffusion gradient. The 1-d reaction time represents typical equilibration time encountered in As sorption experiments in soils (23), although several researchers have shown that As sorption in soils is biphasic in nature and extends beyond 1 d (24–26). The 10-d reaction time was selected in an attempt to represent near-equilibrium As sorption conditions. For all experiments, final pH was not controlled and original soil pH values were maintained with 1 N NaOH/HCl upon soil spiking with the As solution. Suspensions were shaken (120 rpm) during the equilibration period. Following shaking, suspensions were centrifuged (4000g), filtered, and analyzed for total soluble As by ICP-MS. The instrumental detection limit was ~1 ug L⁻¹ with a standard deviation of 0.01 ug L⁻¹.

Sorbed As (mg kg⁻¹ soil) was calculated from the difference between the mass of As initially added to soil solution and the equilibrium mass of As in solution (<0.45 μm filter, and assuming no colloidal As in the filtrate), after 1 or 10 d of reaction with the soil. No mass of As was lost through adsorption to tube walls as it was indicated by soil-free As-containing samples. The amount of As previously sorbed by the soils was determined in soil samples that were reacted with As-free 0.01 M KCl solutions. This amount of As, which was always ≤5 mg kg⁻¹, was subtracted from the residual amount of As after the 1- or 10-d reaction time.

After sorption, the supernatant was carefully removed and soil-containing tubes were filled with d-H₂O to test the ability of d-H₂O on As desorption from the soils (same soil/solution ratio as in adsorption step). Suspensions were shaken at 120 rpm for the same reaction time used earlier during the adsorption step (1 or 10 d). The amount of As desorbed was calculated as the difference between As sorbed and As measured in solution after the desorption step, accounting for entrained soluble As.

Soil Arsenic(V) Bioaccessibility. Samples from the highest initial As load (1000 mg kg⁻¹) used in the sorption experiments were allowed to air-dry before being used in the in vitro test. Arsenic(V) bioaccessibility was measured with the in vitro stomach phase test as described in Sarkar et al. (27). In brief, 1 g of soil was added to 150 mL of gastric solution, and the pH of the suspension was adjusted to 1.8 with 1 N HCl. The gastric phase solution consisted of 0.15 M NaCl and 1% porcine pepsin. The 1:150 (g/mL) solid/solution ratio used here falls within the narrow range of solid/solution ratios (1:100 to 1:500) reported as having no significant effect on soil As bioaccessibility (28). Anaerobic conditions were maintained by passing argon gas through the suspensions. Suspensions were stirred for 1 h at 37 °C to simulate body temperature conditions. After 1 h, 10 mL of supernatant was withdrawn, centrifuged at 4000g for 30 min, and analyzed for bioaccessible As by ICP-MS.

Specific Surface Area and Surface Properties Measurements. High-resolution (low pressure) SSA measurements were conducted for the untreated (no As added) soils using both N₂ and CO₂ gas sorption isotherm analyses (13, 16). In addition to N₂ and CO₂ SSAs, we have also evaluated BET C-constants that are proportional to the energy of N₂ adsorption, and, thus, indicative of the surface properties of soils. The value of the BET C-constant inversely correlates with the amount of organic carbon per mineral surface area of soils and sediments (13–14, 17). Detailed information for the N₂- and CO₂-based SSA measurements can be found in the Supporting Information.

Multivariable Linear Regression Modeling. Three multivariable linear regression models were used to describe soil As sorption and bioaccessibility, using JMP IN version 5.1 (29). The linear models were constructed on data collected from 12 soils that covered a wide span of physical (SSA) and chemical properties (OC) from different regions of the United States, ranging from sandy to clayey soils, from minimum OC to mucky soils, and variable amorphous Fe and Al content as expressed with oxalate extraction (Table 1). Model 1 included three parameters (TOC, N₂-SSA, and CO₂-SSA) in the following general mathematical formulation: $y = a + b\text{TOC}/\text{N}_2\text{-SSA} + c\text{CO}_2\text{-SSA}$; Model 2 included two parameters (N₂-SSA, and CO₂-SSA) in the following general mathematical formulation: $y = a + b(\text{CO}_2\text{-SSA}/\text{N}_2\text{-SSA}) + c\text{CO}_2\text{-SSA}$; and Model 3 included two parameters (C constant from the BET-N₂ adsorption data, and CO₂-SSA) in the following general mathematical formulation: $y = a + b(\text{BET C-constant}) + c\text{CO}_2\text{-SSA}$. The final values of *a*, *b*, and *c* coefficients in the As bioaccessibility models are shown in Table 3.

In addition, five soils (nos. 13–17, Table 1) randomly selected were not incorporated into the regression models, but they were used to test the validity and predictive power of the models. The predictive power of the proposed models was quantified with the aid of the root-mean-square error (RMSE) function that measured the average error between predicted and observed As sorption and bioaccessibility data (3).

Results and Discussion

General Soil Chemical Properties. Selected physicochemical properties for the 17 soils are shown in Table 1. Soil pH for most of the soils was circumneutral, except for no. 15 which was neutral, and no. 17 which was alkaline. Total organic C content was intentionally highly variable to include both low (2.45 g kg⁻¹) and high (813 g kg⁻¹) extremes, representing sandy to highly organic, mucky soils. Oxalate (200 mM)-extractable As, P, Fe, and Al concentrations are usually associated with the noncrystalline phase of Fe/Al/Mn (hydr)-oxides. Native oxalate-extractable As concentrations of the soils were relatively low (<4 mg kg⁻¹), except soil no. 9 (13

TABLE 2. Arsenic(V) Bioaccessibility and Sorption (1000 mg kg⁻¹ Initial As Load) for the 17 Soils Used in This Study

soil	mg kg ⁻¹			
	sorbed As 1-d	sorbed As 10-d	bioaccessible As, 1-d	bioaccessible As, 10-d
1	627 ± 45	743 ± 66	325 ± 23	413 ± 26
2	326 ± 15	463 ± 26	351 ± 32	495 ± 42
3	373 ± 24	625 ± 61	226 ± 36	355 ± 42
4	338 ± 48	628 ± 26	205 ± 25	405 ± 41
5	411 ± 31	576 ± 19	202 ± 49	386 ± 49
6	434 ± 71	648 ± 42	294 ± 23	331 ± 26
7	326 ± 26	579 ± 48	283 ± 21	330 ± 26
8	320 ± 19	564 ± 41	203 ± 21	355 ± 19
9	368 ± 19	745 ± 42	271 ± 49	523 ± 42
10	369 ± 23	459 ± 24	215 ± 10	354 ± 29
11	526 ± 91	805 ± 41	459 ± 85	640 ± 50
12	152 ± 16	248 ± 23	61 ± 15	263 ± 26
13	405 ± 29	638 ± 45	208 ± 26	332 ± 33
14	418 ± 88	700 ± 49	270 ± 69	432 ± 41
15	147 ± 36	367 ± 29	139 ± 26	295 ± 25
16	308 ± 26	390 ± 36	262 ± 26	266 ± 44
17	421 ± 33	383 ± 37	294 ± 25	383 ± 35

^a As(V) bioaccessibility was measured right after the As(V) sorption experiments that were conducted for 1 or 10 days of reaction. Numbers are the means of two replicates ± one standard deviation. Standard deviation was calculated upon inclusion of both analytical and instrumental (ICP-MS) variability.

mg kg⁻¹) (Table 1). Similarly, oxalate-extractable P concentrations varied among the soils and ranged from 10 – 970 mg kg⁻¹.

Arsenic sequestration and availability in soils is largely influenced by the geochemical interactions between As and amorphous metal (oxy)hydroxides, such as Fe/Al phases (23). However, an attempt to correlate oxalate-extractable Fe and Al with the amount of As sorbed by the soils was unsuccessful (*r*² = 0.2) (data not shown). Similar unsuccessful correlation was observed between oxalate-extractable Al concentrations and the amount of As sorbed by 16 soils (8). Particle size analysis showed that soil texture was highly variable among the soils selected for the modeling study, verifying our intent to incorporate most of the soil textural variability observed in U.S. soils.

Specific Surface Areas and Surface Properties. Nitrogen adsorption–desorption isotherms at 77 K and CO₂ sorption–desorption isotherms at 273 K on 12 soils were presented in the previous paper (see Figure S1 and Figure 4, respectively, in ref 13). Sorption data on 5 additional soils were qualitatively and quantitatively quite similar, with only few exceptions. The first one was soil 17 which exhibited microporosity as is evidenced from the high value of 396 for the BET C-constant (Table 1). The second exception was mucky soil 11 with very high TOC content (Table 1). CO₂ sorption–desorption data on soil 11 were widely hysteretic, which is a characteristic of nonequilibrium conditions (30), and prevented reliable estimation of CO₂-based SSA for this soil.

Arsenic(V) Sorption by Soils. Arsenic(V) sorption isotherms illustrated the variable soil As(V) sorption capacities of the soils (see Table S1). Multi-point sorption data for 12 soils were fit to both Freundlich and Langmuir empirical models equally well (data not shown). However, the absence of a plateau during As sorption for most soils and the fact that the use of the Langmuir-based As sorption maxima resulted in no significant improvement of the soil As bioaccessibility model (not shown) urged us to exclude the use of the Langmuir As sorption maxima. Instead, we used the single-point As sorption data collected from the highest initial As load (1000 mg kg⁻¹) (Table 1). Arsenic desorption with d-H₂O from the soils was minimal, since the maximum amount of As desorbed was always <5 mg kg⁻¹ (data not

TABLE 3. Multivariable Linear Regression Models of As(V) Bioaccessibility (in mg kg⁻¹) after 10 Days of Reaction (Soil no. 11, the Mucky Soil, Was Excluded from the Modeling)

	estimate	std error	t ratio	P value	VIF ^a	model R ²
Model no. 1						
intercept (mg kg ⁻¹)	232.8	12.8	18.1	<0.0001		
TOC/N ₂ -SSA (mg m ⁻²)	0.134	0.01	10.75	<0.0001	1.08	
CO ₂ -SSA (m ² g ⁻¹)	4.067	0.32	12.6	<0.0001	1.10	0.95
Model no. 2						
intercept (mg kg ⁻¹)	231.9	11.3	20.6	<0.0001		
CO ₂ -SSA/N ₂ -SSA (mg m ⁻²)	3.46	1.06	3.28	0.004	1.07	
CO ₂ -SSA (m ² g ⁻¹)	3.75	0.30	12.2	<0.0001	1.07	0.93
Model no. 3						
intercept (mg kg ⁻¹)	268.3	21.3	12.6	<0.0001		
BET C-constant	-0.46	0.21	-2.17	0.04	1.16	
CO ₂ -SSA (m ² g ⁻¹)	4.0	0.32	12.25	<0.0001	1.17	0.90

^a The variance inflation factor (VIF) is a measure of how the individual independent variables correlate with each other and show the redundancy of the model. A value close to 1 indicates the absence of redundancy.

shown). Apparently, sorbed As was chemisorbed on soil particle surfaces, since d-H₂O was incapable of breaking apart inner-sphere complexes.

Single-point As sorption data for the highest initial As load (1000 mg kg⁻¹) suggested that As sorption by soils was kinetically limited (Table 2). With the exception of soil no. 17 (highly alkaline soil; pH = 8.6), As(V) sorption significantly (paired *t*-test at 95% confidence level) increased from 1- to 10-d of reaction for all soils (Table 2). Using the same maximum initial As load (1000 mg kg⁻¹), As sorption by soils was characterized by an initial fast (up to 1-d), followed by a slower, sorption stage that continued up to 21-d (24). Hysteretic As sorption by soils is common, following a pattern similar to that of its chemical analog, i.e., P (31). One- to two-day reaction times are typically used in batch As sorption isotherm studies, often underestimating the true soil As sorption capacity. Arsenate sorption kinetics by a granular ferric hydroxide showed that from 3 to > 15 d were required to reach pseudo-equilibrium (10). Assuming a continuous diffusion gradient that slowly migrates through mineral/organic C coated pore surfaces, As sorption maxima and bioaccessibility are severely affected.

Arsenic(V) bioaccessibility as measured by the *in vitro* gastric phase test was quite variable, ranging from 40 to ~100% of the total amount of As sorbed by the soils (Table 2). The reduced (<100%) soil As bioaccessibility values for the majority of soils suggest near-equilibrium conditions with respect to As sorption. Although equilibrated in the lab for 10-d, this soil dataset does not hold the characteristics of a freshly As-amended soil where bioaccessibility is typically equal to the amount of As added (100%) (4). Historic As-contaminated soils exhibit reduced soil As bioaccessibility values (1.2 – 19%) (4, 32).

Similarly to sorption, As(V) bioaccessibility was kinetically affected, as well, showing an overall increase (Table 2). This increase in As(V) bioaccessibility with time was explained simply on the basis of the amount of As sorbed within a specific reaction time interval. Despite the observed kinetic effect on both As sorption and bioaccessibility values for the soils, there was no significant (*p* > 0.05) correlation between As sorption and bioaccessibility either after 1- or 10-d of sorption reaction time (*r*² = 0.35 and 0.41, respectively) (data not shown). The absence of a relationship between As(V)

sorption and bioaccessibility measurements was also observed for a larger set of soils (3).

Arsenic Sorption/Bioaccessibility Model. The absence of a relationship between adsorption and bioaccessibility data led us to construct a model that was based on representative soil chemical (TOC) and physical properties (SSA). The model is based on the concept of As intraparticle diffusion (10, 33) and the effect of organic C moieties (18) on retarding As sorption and bioaccessibility. We used a potential surrogate for As(V), that is a gas molecule (either N₂ or CO₂) that can probe both easily accessible and difficult-to-access sorption sites within soil aggregates or single soil particles.

SSA values of the soils using the N₂ and CO₂ sorption data are listed in Table 1. For the majority of the soils, CO₂ SSAs > N₂ SSAs (Table 1). Soils (no. 6, 7, 8, 12, and 17) exhibited practically no difference between SSAs calculated with either N₂ or CO₂, being consistent with their physicochemical properties: high mineral clay content and/or relatively low TOC content (Table 1). Based on these properties, we have constructed 3 interrelated models (Table 3 and Table S2) consisting of the following parameters: TOC, N₂- and CO₂-based SSA, and the BET C-constant. Ravikovitch et al. (13) demonstrated that CO₂ adsorption per unit of BET-N₂ surface area (CO₂-SSA/N₂-SSA) correlates well with TOC/N₂-SSA. Also, it has been shown that BET C-constant correlates with the TOC/N₂-SSA (13–14). Autocorrelation between the independent variables of the three proposed models was negligible because calculated variance inflation factor (VIF) values were very close to 1 (Table 3). The multivariable regression analysis for the As(V) sorption data collected after 1-d of reaction, utilizing 2 factors (TOC/N₂-SSA and CO₂-SSA) showed that the model was unsuccessful in explaining the variability in As(V) sorption (*R*² = 0.25) (see Supporting Information Table S2). However, the use of the 10-d As(V) sorption data improved the performance of the proposed model (*R*² = 0.51) (Table S2). No further improvement in the model prediction was achieved using Models 2 and 3 (data not shown). Yang et al. showed that the log Fe oxide content (*p* < 0.001) increased As(V) adsorption by 36 soils over a 48-h reaction period (3). All of the soil properties included in Yang et al. (3) model explained only 66% (*r*² = 0.66) of the variability in the amount of As(V) adsorbed by the soils.

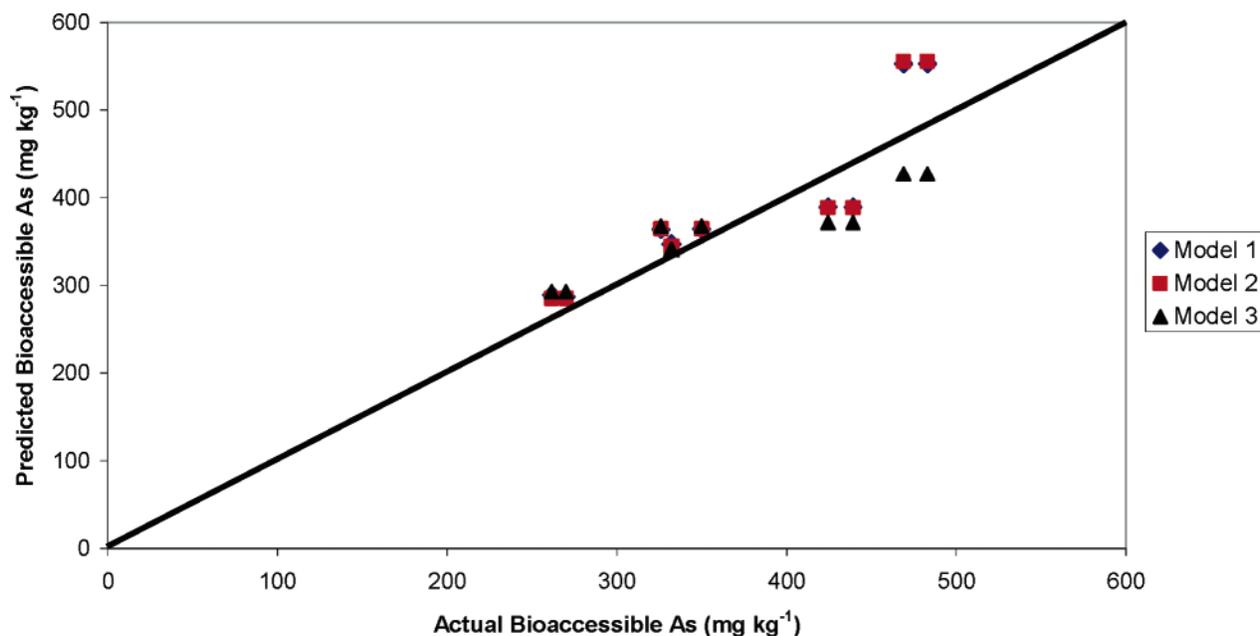


FIGURE 1. Multivariate regression model performance test using five (two replicates each) independent soils that were not used in model construction. The three proposed models accurately predicted As(V) bioaccessibility (RMSE $\leq 10\%$) for four out of the five soils randomly selected for model verification. The ability of the models in predicting As bioaccessibility for the fifth soil (no. 17) was relatively reduced (RMSE = 16%). This soil was a highly alkaline soil (pH 8.6), whereas the rest of the soils were acidic/circumneutral.

Similar multivariable analysis was also conducted for soil As(V) bioaccessibility from data obtained either after 1- or 10-d of equilibration (Table 3). Using the 1-d data, all three models were deemed unsuccessful in predicting soil As bioaccessibility (all $R^2 \leq 0.55$; Table S3). However, use of the 10-d equilibration bioaccessibility data resulted in a highly significant ($p < 0.001$) ability of all three models to explain 95, 93, and 90% of the variability in As bioaccessibility, respectively (Table 3) (Figure S2). The Model 2 gave equally good prediction as Model 1, having the advantage that it does not require TOC data. It is able to predict As(V) bioaccessibility based on N_2 and CO_2 sorption data alone.

The fact that the proposed models performed better upon use of the 10-d instead of the 1-d As(V) bioaccessibility data suggests that As bioaccessibility is kinetically limited, likely due to steric and diffusional limitations. Steric/diffusional constraints in soil particles may be imposed by organic moieties (fulvic and humic acids) residing in the internal pore network. Recently, soil OC was positively correlated to As bioaccessibility in soils adjacent to CCA-treated utility poles ($R^2 = 0.36$; 18). Since N_2 and CO_2 gas sorption isotherms were conducted at near-equilibrium conditions (with the exception of CO_2 sorption on the mucky soil no. 11 with high TOC), it is reasonable to expect a better correlation between As bioaccessibility measured at near equilibrium conditions (10-d data, instead of 1-d) with the N_2 - and CO_2 -based SSAs; for this reason, soil no. 11 was excluded from further mathematical formulation of the models.

Five soils randomly selected (no. 13–17) were included in the predictive power test of the proposed models. Arsenic(V) bioaccessibility was then predicted for these soils, using the model formula that was based on bioaccessible As data collected after 10 d (Table 3). The proposed models successfully predicted bioaccessible As concentrations for four out of the five soils, reaching RMSE values of $\leq 10\%$ (Figure 1). Relative to the other soils, the predictive power of As bioaccessibility for soil no. 17 was slightly reduced (RMSE = 16%). This soil was the only highly alkaline soil (pH = 8.6), since the rest of the soils were acidic/circumneutral. The performance of the proposed models was not significantly ($p > 0.05$) improved upon inclusion of soil pH values,

being consistent with the absence of relationship between As bioaccessibility and soil pH (34). It should be also noted that soil no.17 exhibits the lowest TOC/ N_2 -SSA of all the soils studied in this work (TOC/ N_2 -SSA = 0.57 mg m^{-2}). In addition, it is microporous as it follows from high BET C constant, $C = 396$ (Table 1).

Our results show that the CO_2 -based SSA is one of the most important parameters for predicting As(V) bioaccessibility in soils. It appears in all three empirical models that we have formulated. While CO_2 -SSA alone is not sufficient to predict As bioaccessibility in a suite of different soils, it is useful to elucidate its role. Using the whole set of soils (except soil no. 11), the correlation between As(V) bioaccessibility and CO_2 -SSA parameter alone is quite poor ($R^2 = 0.56$). However, the correlation improves significantly ($R^2 = 0.86$) after excluding microporous soil no. 17. Since CO_2 has high affinity to OC domains (13), CO_2 -SSA is positively correlated with TOC, and As(V) bioaccessibility is also positively correlated with OC content ($R^2 = 0.78$). One of the possible explanations is that the fraction of As(V) bound to SOM is more readily extractable in *in vitro* bioaccessibility tests as opposed to the mineral (alumina and iron) bound fraction.

Implications. The proposed work goes beyond the so-far developed empirical modeling to predict As bioaccessibility in soils by combining chemical properties, such as TOC, with physical parameters (SSA) already recognized for their importance in sorption processes, but never included in modeling schemes. Chemical-properties-based As bioaccessibility models rely mostly upon the Fe soil content and pH (3). An attempt to correlate oxalate-extractable Fe and Al concentrations (a measure of the amorphous Fe/Al hydroxide content) with the N_2 and CO_2 SSA values of the soils was deemed unsuccessful ($R^2 = 0.1$), suggesting that SSA measurements probe distinctly different sorption sites and regions within soil particles. Despite the similar empirical nature with the chemical-properties-based As bioaccessibility models, our approach provides a semi-mechanistic insight on As bioaccessibility in soils by probing the internal morphology and pore network of complex and highly heterogeneous soil particles.

The multi-elemental composition of soil particles in combination with particle coatings in the form of inorganic oxides and/or organic moieties severely perplexes the SSA and porosity of these particles (35). Spatially variable SSA and porosity may result in nonuniform distribution of the As concentration gradient that promotes unbalanced mass transfer with subsequent As diffusion limitations. The experimental section of the proposed model was carefully designed to capture the potential kinetically (diffusion)-limited As sorption processes. Adequate reaction time, As concentration gradient, and water availability are necessary prerequisites for maximizing As diffusion coefficients and overcoming potential diffusion constraints. We used 1- and 10-d reaction intervals to better demonstrate the role of kinetics on the magnitude of sorbed and bioaccessible As by soils via advection and diffusion mechanisms. During this equilibration time, 100% water availability ensured facilitation of As transport to all available pore spaces within the soil particles, while the sufficiently high initial As load (1000 mg kg⁻¹) created a strong As concentration diffusive gradient. Our approach may have created soil conditions that represent near-equilibrated or pseudo-equilibrated As-contaminated soil conditions where soil-As occupies not only external, but also internal, sorption sites that are characterized by distinctly different degrees of As bioaccessibility.

In field As-contaminated soils, where added As may not exceed a total of 0.1% by weight (this study), measured N₂ and CO₂ SSAs will likely not be influenced by the presence of As. Earlier studies on the effect of sorbed P by drinking-water treatment residuals (WTRs) on the measured N₂ and CO₂ SSAs, showed that in some cases, P addition (1% by wt.) had no effect on the measured SSAs, whereas in others, there was a negative effect of added P (16). There was no significant correlation between the amount of sorbed P with the N₂ or CO₂-based SSA (16). However, the total P load (1% by wt.) used by Makris et al. (16) seems highly unlikely to be encountered in field As-contaminated soils.

One of our current priorities is to further validate the proposed model in actual As-contaminated sites varying in soil physicochemical properties. Results from this set of soils are encouraging but in need of verification with ongoing in vivo data. Our intention is to provide stakeholders, consultants, and regulators with a simple, yet accurate, tool to conduct risk assessment studies that will potentially complement in vivo data and reduce cleanup cost associated with As-contaminated sites.

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Supporting Information Available

One table showing multi-point As(V) sorption isotherms for the soils and two tables showing multivariable regressions modeling for As(V) sorption and bioaccessibility utilizing 1-d data. One flow chart identifying the major components of a standard risk assessment protocol of soil As bioavailability. One figure on the performance of the proposed model predicting soil As bioaccessibility. Text describing the details on the SSA measurements of the soils. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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