

# Influence of Soil Geochemical and Physical Properties on the Sorption and Bioaccessibility of Chromium(III)

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## ABSTRACT

There are numerous Cr(III)-contaminated sites on Department of Defense (DoD) and Department of Energy (DOE) lands that are awaiting possible clean up and closure. Ingestion of contaminated soil by children is the risk driver that generally motivates the likelihood of site remediation. The purpose of this study was to develop a simple statistical model based on common soil properties to estimate the bioaccessibility of Cr(III)-contaminated soil upon ingestion. Thirty-five uncontaminated soils from seven major soil orders, whose properties were similar to numerous U.S. DoD contaminated sites, were treated with Cr(III) and aged. Statistical analysis revealed that Cr(III) sorption (e.g., adsorption and surface precipitation) by the soils was strongly correlated with the clay content, total inorganic C, pH, and the cation exchange capacity of the soils. Soils with higher quantities of clay, inorganic C (i.e., carbonates), higher pH, and higher cation exchange capacity generally sequestered more Cr(III). The amount of Cr(III) bioaccessible from the treated soils was determined with a physiologically based extraction test (PBET) that was designed to simulate the digestive process of the stomach. The bioaccessibility of Cr(III) varied widely as a function of soil type with most soils limiting bioaccessibility to <45 and <30% after 1 and 100 d soil-Cr aging, respectively. Statistical analysis showed the bioaccessibility of Cr(III) on soil was again related to the clay and total inorganic carbon (TIC) content of the soil. Bioaccessibility decreased as the soil TIC content increased and as the clay content decreased. The model yielded an equation based on common soil properties that could be used to predict the Cr(III) bioaccessibility in soils with a reasonable level of confidence.

THE PRESENCE of chromium (Cr) in the environment is widespread due to its usage in many industrial processes. The metallurgic, tanning, and plating industries are just a few examples of very common applications, large and small, which use Cr on a daily basis (Nriagu and Nieboer, 1988). Chromium itself is thermodynamically stable in two oxidative states: cationic Cr with a valence of three, Cr(III), and anionic Cr with a valence of six, Cr(VI). Chromium(VI) is often considered to be mobile in the environment while the more environmentally stable Cr(III) is considered less mobile (Chung et al., 1994; Patterson et al., 1997). There are several factors that contribute to the decreased mobility of Cr(III) in soil: (i) strong adsorption onto the nega-

tively charged soil surfaces, (ii) the ability to form complex molecules with organics found in the soil, and (iii) the formation of oxides and hydroxides and other insoluble minerals in soil (Fendorf and Zasoski, 1992; Losi et al., 1994; Dragun, 1998).

When assessing the risks posed by Cr(VI) and Cr(III), the exposure pathway of most concern is ingestion by children (Paustenbach, 1989; Davis et al., 1990; Sheehan et al., 1991; Skowronski et al., 2001). Chromium(VI) is considered the most harmful of the oxidative states since it is both a mutagen and a carcinogen at low sub-ppm levels (Levis and Bianchi, 1982). Although Cr(III) is generally considered less harmful to human health than its oxidized counterpart, it may be of concern due to its potential to oxidize to Cr(VI) and its ability to accumulate to very high solid phase concentrations in some soils (Fendorf et al., 1992). The bioaccessibility of organic contaminants in soils has been relatively well studied (Linz and Nakles, 1997); however, the bioaccessibility of soil-bound metals such as Cr has received less attention (Ruby et al., 1996; Rodriguez et al., 1999; Skowronski et al., 2001; Stewart et al., 2003), where the bioaccessibility is defined as that amount of contaminant that is soluble due to simulated *in vitro* gastric functions and has the potential to cross the intestinal wall (Hamel et al., 1998). Typically, calculated health risks are inappropriately based on a reference dose derived from studies that use soluble aqueous metal species. The ubiquitous metal-sequestering properties of soil may significantly lower the bioaccessibility of Cr upon digestion, which, in turn may influence the decision for remediation at contaminated sites. Thus, action levels set by state regulators concerning the bioaccessibility of Cr in soil may need to consider specific soil properties instead of using generic guidelines (Proctor et al., 1997).

The intent of this paper is to show that Cr(III) can be strongly sequestered by soil, which in turn influences its bioaccessibility. We developed a simple statistical model based on measured soil properties to estimate the bioaccessibility of Cr(III)-contaminated soils upon ingestion. We show that common soil properties, which are easily obtainable from the National Resource Conservation Service (NRCS) database, can be used to assess Cr(III) bioaccessibility at contaminated sites.

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**Abbreviations:** DoD, Department of Defense; DOE, Department of Energy; PBET, physiologically based extraction test; NRCS, National Resource Conservation Service; CEC, cation exchange capacity; DDI, double deionized; TOC, total organic carbon; TIC, total inorganic carbon; VIF, Variance Inflation Factor; XAS, x-ray adsorption spectroscopy.

## METHODS

### Soil Type and Characterization

A database of metal-contaminated Department of Defense (DoD) sites was obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland. Twenty (20) DoD Army facilities throughout the USA were chosen for consideration based on the high concentration of Cr in their soils and the possible need for remediation (Table 1). Because of the difficulty in obtaining actual contaminated soils from these sites, uncontaminated soils whose properties were similar to the contaminated soils were acquired and treated with Cr(III). The soil series present at the DoD sites of interest were identified using Soil Conservation Survey documents. The USDA-NRCS database was then utilized to locate pedon numbers associated with each soil series. The NRCS was contacted and in most cases 200 g of the A-horizon and the upper B-horizon soil were obtained for each soil series (Table 1). Two additional soils were obtained from the Oak Ridge Reservation in eastern Tennessee, which also had properties similar to DoD sites in the southeast USA. Thirty-five soils were acquired and these encompassed seven major soil orders (Table 1).

Soils were disaggregated with gentle grinding using a mortar and pestle and sieved to provide a soil fraction <250  $\mu\text{m}$ . It is this smaller size material that is more commonly ingested by children since it adheres more readily to the hand (Sheppard et al., 1995; Rodriguez et al., 1999). Soil properties were obtained from (i) the NRCS database and (ii) repeated or additional measurements in our laboratory. Soil properties included pH, cation exchange capacity (CEC), Fe- and Mn-oxide content, particle size distribution, and total organic and inorganic C (Table 2). Repetitive or additional measurements of soil pH, Fe- and Mn-oxide content, and total organic and inorganic C on all soils were performed to verify the quality of, and provide

**Table 1. U.S. Department of Defense Army bases with their associated soil series designations.**

Army bases by soil order	Facility location by state	Soil series
<b>Ultisol</b>		
Holston AAP	Tennessee	Allen
Fort Gillem	Georgia	Cecil
ORNL†	Tennessee	Minvale
<b>Alfisol</b>		
Seneca AD	New York	Angola
Indiana AAP	Indiana	Crider
Bluegrass Facility	Kentucky	Lawrence
Ft. Knox	Kentucky	Lenberg
Lexington Facility—LBAD	Kentucky	Lenberg
<b>Inceptisol</b>		
Letterkenny AD	Pennsylvania	Berks
ARDEC (Picatinny Arsenal)	New Jersey	Rockaway
Letterkenny	Pennsylvania	Weikert
ORNL†	Tennessee	Montevello
<b>Spodosol</b>		
Stratford Army Engine Plant	Connecticut	Charlton
<b>Mollisol</b>		
Kansas AAP	Kansas	Dennis
Lake City AAP	Missouri	Sibley
<b>Aridisol</b>		
Ft. Wingate	New Mexico	Doakum
Tolle Army Depot	Utah	Kzin
Desert Chem. Depot	Utah	Kzin
Dugway	Utah	Kzin
Hawthorne	Nevada	Oricto
Pueblo Chem. Depot	Colorado	Stoneham
<b>Entisol</b>		
Savanna Depot Activity	Illinois	Wakeland

† Department of Energy sites at the Oak Ridge National Laboratory.

missing information to the NRCS database. In general, data generated in our laboratory was in excellent agreement with the NRCS database. Soil pH was determined using double deionized (DDI) water and 5 mM  $\text{CaCl}_2$  in a 2:1 solution/solid ratio. The pH of the clear supernatant was measured with a microprocessor ionalyzer/901 (Orion Research, Beverly, MA) using a combination glass and Calomel electrode (Beckman, Fullerton, CA). Extractable iron and manganese oxides were determined with dithionite-citrate-bicarbonate (DCB) using the methods of Mehra and Jackson (1960). Total organic carbon (TOC) and total inorganic carbon (TIC) were measured by combustion on a Perkin-Elmer 2400 Series II CHNS/O analyzer. Soil TOC was determined on pretreated samples to remove TIC, which involved a near-boiling, 3 M HCl extraction method on agitated samples. Soil TIC was computed from the difference between total soil C (no pretreatment) and TOC.

### Contaminant Addition to Soil

Ten grams of soil was placed in a 200-mL glass centrifuge vessel along with 100 mL of 500 ppm Cr(III) as  $\text{CrCl}_3$ , pH 4.0. The slurry was agitated on a reciprocal shaker for 2 d, centrifuged, and the supernatant decanted for analysis. This was repeated three more times. After the fourth addition of Cr, the soils were washed three times with DDI water and allowed to air dry. Once the soils were dry, they were gently crushed, homogenized, and then wetted with DDI water to achieve a 30% moisture content. The soils were kept in a container out of direct light and maintained at 30% water content in a moisture saturated environment. Soils were incubated in this manner for the duration of the study (i.e., at least 100 d).

### Determination of Chromium on Soil

Total Cr on the soil was determined using a modification of EPA method 3052. The soil was digested in a CEM microwave, model MDS-81D, with hydrofluoric and nitric acid. Boric acid was added before sample analysis to facilitate the removal of hydrofluoric acid from solution through the formation of fluoroboric acid. Soils from the National Institute of Standards, with known concentrations of solid phase Cr, were also analyzed with each block of analysis. Samples were stored and analyzed for total Cr using inductively coupled plasma.

### In Vitro Bioaccessibility

A physiologically based extraction test (PBET) was adapted from Ruby et al. (1996, 1999; Ruby, personal communication, 2000) to assess the in vitro bioaccessibility of Cr(III) from contaminated soils in humans. The method is designed to simulate the stomach digestive system in humans. The PBET method has been shown to agree with in vivo studies involving Pb-contaminated soils (Ruby et al., 1996) as well as As-contaminated soils (Rodriguez et al., 1999); however, limited data is currently available in the literature that evaluates Cr bioavailability in contaminated soils using in vivo methods (Witmer et al., 1989, 1991; Gargas et al., 1994), and this data does not appear useful for cross-correlating with the results of the current study. Nevertheless, the PBET method can serve as a useful approximation of Cr bioavailability until in vivo studies become available to validate the methods credibility with regard to Cr.

In the current study, triplicate 0.39 g moist samples (0.3 g dry wt) were placed in 50 mL polyethylene tubes to which 30 mL 0.4 M glycine at pH 1.5 and 37°C was added. The slurries were quickly placed in a rotating water bath of 37°C

**Table 2. Select soil chemical and physical properties.†**

	TOC	TIC	Clay	Silt	Fe	Mn	CEC	pH	pH
	%		%		g/kg		cmol/kg	5 mM CaCl <sub>2</sub>	DDI
<b>Ultisol</b>									
Allen A	1.55	0.56	8.7	29.5	6.95	0.31	7.7	4.59	5.05
Allen Ba	0.19	0.09	14.9	28.4	18.96	0.10	1.3	4.30	4.74
Cecil Ap	1.64	0.39	10.2	23.0	6.01	0.06	5.8	4.04	4.47
Cecil Bt1	0.29	0.21	44.8	15.5	32.56	0.11	1.6	4.44	4.48
Minvale Ap	1.89	0.99	6.1	59.0	7.71	1.51	6.0	6.01	6.61
Minvale Bt1	0.10	0.07	23.6	44.2	19.55	0.16	4.0	4.30	5.17
<b>Alfisol</b>									
Lawrence Apl	0.91	0.59	19.5	48.5	11.17	1.35	5.8	4.97	5.27
Lawrence Btl	0.11	0.10	25.8	38.3	17.53	0.29	3.7	4.28	4.91
Angola Ap	3.72	0.96	32.1	56.1	23.28	1.23	6.7	5.29	5.48
Crider Ap	0.55	0.39	22.5	75.8	13.34	0.72	5.6	6.57	6.84
Crider B2lt	0.21	0.13	30.9	67.2	13.38	0.30	5.4	5.27	5.63
Lenberg A	3.41	1.01	49.1	44.5	12.94	1.37	7.9	5.92	6.06
Lenberg Btl	0.36	0.25	64.7	29.5	15.69	0.12	5.5	4.35	4.77
<b>Inceptisol</b>									
Berks A	2.72	1.01	15.7	46.6	13.18	0.15	9.1	3.65	3.91
Rockaway A1	3.54	1.49	12.4	34.8	14.03	0.52	10.6	3.86	3.98
Rockaway B2t	0.21	0.18	12.6	32.1	17.34	0.16	3.7	4.10	4.41
Weikert Ap	3.97	2.37	24.4	56.2	21.41	6.47	13.3	4.44	4.70
Weikert Be	2.01	1.15	23.9	54.3	28.98	5.42	8.0	4.28	4.65
Montevello A	3.55	0.62	6.0	69.0	10.68	1.42	8.0	6.91	7.18
Montevello B	0.42	0.26	19.0	42.2	22.07	0.17	14.0	4.23	4.87
<b>Spodosol</b>									
Charlton A2	2.30	0.40	2.9	28.7	1.33	0.00	11.7	3.15	3.57
<b>Mollisol</b>									
Dennis Ap	1.32	0.89	15.9	66.1	15.11	0.60	8.7	5.82	6.08
Dennis Ba	0.38	0.41	29.7	57.5	24.29	0.59	4.4	4.77	5.28
Sibley A	1.06	0.49	23.5	69.7	8.23	0.67	7.1	6.36	6.66
Sibley B1	0.72	0.52	26.9	68.0	9.11	0.59	6.8	6.36	6.76
<b>Aridisol</b>									
Doakum Ab	0.28	0.08	10.8	24.8	4.74	0.19	6.9	6.94	7.42
Doakum Bt	0.39	0.18	29.3	15.0	6.86	0.16	7.0	6.87	7.39
Kzin A2	3.27	1.35	22.2	44.2	4.07	0.29	13.3	7.74	7.87
Kzin Bk	3.40	1.88	27.0	38.5	3.26	0.18	10.0	7.80	7.88
Oricto A2	0.09	0.94	10.2	34.7	2.92	0.34	13.7	8.72	9.60
Oricto Bt	0.16	1.10	23.2	27.5	3.16	0.29	8.6	9.01	9.60
Stoneham A	1.45	0.71	16.2	41.4	3.40	0.26	10.1	6.43	6.83
Stoneham Bt1	0.66	0.32	21.4	23.2	2.20	0.20	7.8	6.80	7.15
<b>Entisol</b>									
Wakeland Ap	0.92	0.00	23.8	64.7	8.82	0.71	6.1	5.86	6.09
Wakeland Cg1	0.56	0.25	21.1	66.4	9.18	0.80	5.7	5.77	6.07

† TOC, total organic carbon; TIC, total inorganic carbon; CEC, cation exchange capacity; DDI, double deionized.

and agitated at  $30 \pm 2$  rpm for 1 h. Supernatant was separated from the solid via centrifugation. The pH of the supernatant was measured to ensure that the final pH was within  $\pm 0.5$  pH units of the initial pH. This scenario held for all cases. Thus, bioaccessibility was calculated as:

% Bioaccessibility =

$$\left( \frac{\text{Cr in PBET supernatant } (\mu\text{g/mL}) \times 30.0 \text{ mL} \div 0.3 \text{ g dry soil}}{\text{Cr on soil surface (mg/kg)}} \right) \times 100$$

The PBET pH of 1.5 simulates the most aggressive stomach digestive scenario, which is a condition indicative of human fasting. Conditions of higher pH, as a result of food intake, would most likely decrease Cr bioaccessibility even more profoundly than the results presented in the current study, thus offering a potential avenue for future research. Both Ruby et al. (1996) and Yang et al. (2002) found that soil Pb bioaccessibility was strongly pH dependent with soluble Pb decreasing profoundly over a pH range of 1.5 to 4.0.

### Chromium Analysis

The PBET supernatant, soil spiking solution, and equilibrium solution were measured for Cr(VI) and total Cr (Cr<sub>T</sub>).

Chromium(VI) was measured using a modified *s*-diphenylcarbohydrazide colorimetric method (Bartlett and James, 1979) using a UV-VIS spectrophotometer at wavelength 540  $\mu\text{m}$  (HP model 8453, Palo Alto, CA). Analysis of Cr(VI) was performed immediately on rapidly cooled PBET solutions to avoid possible reduction of Cr(VI) to Cr(III) by glycine (Jardine et al., 1999). Independent studies revealed that Cr(VI) reduction by glycine at 37°C and 1 h was insignificant. Total Cr was measured on a Perkin Elmer AAnalyst 800 atomic absorption spectrophotometer (Wellseley, PA). Standards were made using an atomic absorption Cr standard (EM Industries, Hawthorne, NY). Chromium(III) was calculated as the difference between Cr<sub>T</sub> and Cr(VI).

### Modeling

A multiple regression technique in the statistical software package SigmaStat 2.0 (Jandel Scientific) was used to derive an expression that related Cr(III) sorption and bioaccessibility to common soil properties. The model was run using forward stepwise regression to determine the most salient soil properties for calculating sorption or bioaccessibility. Multiple linear regression was then employed to determine the linear equation to use when computing the Cr(III) sorption or bioaccessibility based on the important soil properties previously ascertained.

## RESULTS AND DISCUSSION

### Influence of Soil Properties on Chromium Sorption

Chromium sorption (i.e., adsorption and surface precipitation) by the 35 soils varied markedly with values ranging from 736 mg/kg to 17 460 mg/kg (Table 3). Sorption of Cr(III) was independent of horizon type where no distinct trend between A- and B-horizons was evident. The majority of the soils adsorbed between approximately 3000 mg/kg to approximately 6000 mg/kg with four soils as high as approximately 18 000 mg/kg. These four soils were all Aridisols and are noted for their high soil pH and for their high TIC content. Observed Cr(III) loading levels on many of these different soil types were similar to those measured on actual contaminated soils from the DoD sites. For example, actual contaminated Kzin soil (Xeric Torriorthents) from the Desert Chemical Depot contained 27 000 mg Cr/kg soil. Artificially contaminated Kzin soils in this study contained approximately 18 000 mg Cr/kg soil.

The large contrast in Cr(III) sorption by the various

soils can be explained by the differences in soil properties. Multiple linear regression showed that four soil properties were important in determining the amount of Cr adsorbed by the soils: pH, total inorganic carbon (TIC) content, clay content, and cation exchange capacity (CEC). The relationship describing Cr adsorption was:

$$\begin{aligned} \text{Cr(III) (mg/kg on soil)} = & -12\,666.3 + \\ & (113.8 \times \% \text{ clay}) + (364.6 \times \text{CEC}) + \\ & (1743.2 \times \% \text{ TIC}) + (1916.7 \times \text{soil pH}) \end{aligned}$$

Chromium(III) sorption by the soils was strongly correlated with these soil properties ( $r^2 = 0.794$ ) suggesting that nearly 80% of the variability in Cr(III) sorption could be described by pH, TIC, clay, and CEC (Table 4). Incorporating the other measured soil properties from Table 2 (e.g., Fe-oxide content, TOC, etc.) did not improve the model fit. In fact, TIC could have been removed from the model if necessary, since the other three independent soil variables could describe approximately 77% of the variability in Cr(III) sorption. The four-parameter model above was statistically rigorous at the 95% confidence level since P values for the independent variables were all  $<0.05$  (Table 4). Thus, it can be concluded that the independent variables, the soil properties, significantly contribute to predicting the dependent variable, Cr sorption. The Variance inflation factor (VIF) also suggested that collinearity between independent variables was not significant (Table 4). Values for VIF that are 1.0 or slightly larger suggest that the variables do not show multicollinearity and that the parameter estimates are reliable. Collinearity becomes an issue when values of VIF exceed 4.0. This model also passed the Normality Test (indicating that the data was normally distributed) and the Constant Variance Test (suggesting that the variance of the dependent variables was constant). One of the most important criteria of a successful model, however, is the true physical significance of the model parameters. Our model suggests that Cr(III) sorption is enhanced by higher soil pH, more TIC (i.e., carbonates), more clay, and higher CEC. For a sparingly soluble cation, such as Cr(III), these soil conditions should enhance sequestration as the model suggests.

The pH of the soil affects the solubility and form of Cr and therefore affects sorption. As the soil pH increases, the amount of Cr on the soil increases. At low pH, Cr(III) is adsorbed or complexed on soil negative charges; at higher soil pH values,  $>5.5$ , Cr precipitates

**Table 3. Chromium(III) solid phase concentrations on the various soils and their corresponding bioaccessibility after 1 and 100 d aging.**

	$C_T$ on soil	1 day % Cr(III) bioaccessible	100 day % Cr(III) bioaccessible
<b>Ultisol</b>	mg/kg		
Allen A	940.32	16.37	8.13
Allen Ba	736.15	31.11	17.98
Cecil Ap	1 342.49	18.84	9.90
Cecil Bt1	2 333.76	41.77	28.34
Minvale Ap	2 261.67	15.88	8.55
Minvale Bt1	1 294.09	54.65	35.52
<b>Alfisol</b>			
Lawrence Ap1	2 586.96	26.03	11.62
Lawrence Bt1	2 359.18	41.48	28.10
Angola Ap	9 408.00	32.40	16.58
Crider Ap	3 719.38	33.90	22.88
Crider B2t	4 247.30	50.30	32.35
Lenberg A	8 169.92	30.27	20.28
Lenberg Bt1	7 254.84	50.89	41.63
<b>Inceptisol</b>			
Berks A	2 275.20	18.77	7.67
Rockaway A1	2 482.08	11.62	6.46
Rockaway B2t	1 525.58	32.96	22.36
Weikert Ap	5 561.77	12.21	5.62
Weikert Be	3 229.97	19.73	10.35
Montevello A	5 925.66	19.03	7.03
Montevello B	2 751.57	47.71	26.23
<b>Spodosol</b>			
Charlton A2	1 721.95	27.65	21.26
<b>Mollisol</b>			
Dennis Ap	3 577.05	19.43	13.67
Dennis Ba	3 521.90	33.61	26.68
Sibley A	4 436.16	29.78	20.50
Sibley B1	4 689.17	36.36	25.37
<b>Aridisol</b>			
Doakum Ab	2 507.82	31.19	16.60
Doakum Bt	5 964.29	39.40	32.77
Kzin A2	16 306.33	17.22	14.00
Kzin Bk	12 452.82	24.03	19.81
Oricto A2	17 460.00	13.66	10.26
Oricto Bt	15 964.28	18.45	16.44
Stoneham A	4 377.44	29.27	18.97
Stoneham Bt1	4 599.44	33.70	24.82
<b>Entisol</b>			
Wakeland Ap	4 262.61	32.33	21.08
Wakeland Cg1	3 802.32	37.68	24.79

**Table 4. Parameter estimates, standard errors, and statistics obtained from a multiple linear regression analysis that related soil properties to Cr(III) sorption.†**

Parameter	Value	SE	P	VIF
Intercept	-12 666.3	1 794.5	<0.001	-
% Clay	113.8	30.4	<0.001	1.119
pH in DDI	1 916.7	250.7	<0.001	1.079
CEC, cmol/kg	364.6	155.7	0.026	1.902
% TIC	1 743.2	850.1	0.049	1.670
$r^2$	0.794		<0.001	

† DDI, double deionized; CEC, cation exchange capacity; TIC, total inorganic carbon; VIF, Variance Inflation Factor.

as hydroxides covering the surface of the soil (Bartlett and Kimble, 1976). It was presumed by Bartlett and Kimble (1976) and James and Bartlett (1983) that the Cr(III) precipitate consisted of macromolecules with Cr ions in six coordination with water and hydroxy groups. Studies by Fendorf et al. (1994) and Fendorf and Sparks (1994), using x-ray adsorption spectroscopy (XAS), showed that with a low Cr(III) surface coverage the principle mechanism was adsorption with an inner-sphere monodentate complex on the silica. With increased surface coverage (>20%), precipitation likely occurred and became the dominant sorption mechanism.

As with pH, TIC or carbonate content in soils enhanced Cr(III) sorption. The mechanism of increased sequestration is most likely a localized pH effect at the carbonate surface, which promotes the formation of Cr(OH)<sub>3</sub> species. The localized pH effect is the most plausible scenario since there was no correlation between soil pH and soil TIC, thus explaining why collinearity was not a problem for these parameters when the model was fit to the Cr(III) sorption data. Several acidic Inceptisols derived from interbedded limey shales and limestone have relatively large residual carbonate contents (Table 2), due to the slow dissolution of local scale dolomite, and this may serve to enhance Cr(III) sequestration in these systems, even though the overall bulk soil pH is acidic.

The model also shows a positive correlation between the amount of Cr adsorbed and the soil clay content and CEC. This was expected since clay minerals tend to be dominated by negatively charged sites on the surface due to isomorphous substitution (Klein and Hurlbut, 1993). These negatively charged sites attract the cation Cr<sup>3+</sup> and a weak, electrostatic bond is formed. The more negatively charged sites that are available (i.e., larger CEC), the greater propensity for Cr(III) sorption. Further, clay minerals typically have a large surface area that is capable of accommodating large quantities of Cr<sup>3+</sup> and Cr(OH)<sub>3</sub> precipitated phases. The more surface area a soil has, the more reactive sites the soil has, and consequently the more Cr that will adsorb to the soil.

### Influences of Soil Properties on Chromium Bioaccessibility

The bioaccessibility of Cr(III), as measured by the PBET method, varied widely as a function of soil type with most soils limiting bioaccessibility to <45% and <30% after 1 and 100 d soil-Cr aging, respectively (Table 3, Fig. 1a–e). Bioaccessibility values were consistently higher for 1 d aging vs. 100 d aging. For all soils the percent bioaccessibility ranged from 3.0 to 54.7% at Day 1 and 1.5 to 35.5% at 100 d (Table 3, Fig. 1a–e). The aging effect is related to the enhanced stability of Cr on the soil surface with time. Structural reorientation of Cr surface bonds or slow precipitation reactions can account for the stronger sorption of Cr at longer times (Karthein et al., 1991). Previous studies by Stewart et al. (2003) have shown that aging effects are insignificant after 100 d and that the 100 d data are most relevant

to actual DoD-contaminated soils. In general, the A-horizon soils had the lowest percent bioaccessible values, even when they adsorb more Cr(III) on the soil vs. the B horizons (Table 3). Bioaccessibility did not appear to be a function of soil order, suggesting that detailed soil series data, as is used in the current study, was necessary for predictive purposes (Table 3, Fig. 1a–e). Chromium(VI) was also measured in the PBET extractant to monitor for oxidation of Cr(III) to Cr(VI). The proportion of bioaccessible Cr that was Cr(VI) was always <1%, suggesting that oxidation reactions were minimal or that any oxidation products of Cr(VI) were tightly held by the soil. These results are consistent with the data presented by Stewart et al. (2003), which showed limited bioaccessibility of Cr(VI) in several soils.

As demonstrated by Stewart et al. (2003), bioaccessibility values leveled off and reached near equilibrium after the first 50 to 100 d. Thus, the 100 d bioaccessibility data is most appropriate for use in the modeling endeavor. Stepwise multiple regression indicated two combinations of variables considered instrumental in predicting the bioaccessibility of Cr(III) in soils: (i) % clay and % TIC and (ii) % clay and % TOC. Using the independent variables from Table 2, the most significant model revealed that the bioaccessibility of Cr(III) on the soils was correlated with clay and TIC of the soil (Table 5). The relationship describing Cr(III) bioaccessibility was:

$$\% \text{ Cr(III) bioaccessible} = 16.02 + (0.426 \times \% \text{ clay}) - (9.56 \times \% \text{ TIC})$$

with an  $r^2$  value of 0.722, which indicated that as much as 72% of the variability in Cr bioaccessibility was explained by the model (Fig. 2). The model was statistically rigorous at the 99% confidence level since P values for the independent variables were well below 0.01, indicating that they all contributed to predicting the % bioaccessible Cr(III) (Table 5). Values for VIF were all nearly 1.000, indicating that there was no redundant information in the other independent variables, i.e., soil properties, and that collinearity between independent variables was not of concern. This indicated that parameter estimates in the model were reliable, which is in agreement with the low standard errors on the estimated values (Table 5). The model also passed the Normality Test and the Constant Variance Test, suggesting that the data was normally distributed around the regression line and that the variance present in the dependent variable is constant. Most important, however, is the true physical significance of the model parameters. The model suggests that Cr(III) bioaccessibility decreases as the TIC content increases and as the clay content decreases. As shown with the Cr sorption data, Cr(III) sequestration is enhanced by soils with high levels of TIC. The presence of TIC promotes the formation of solid phase Cr(III)-hydroxides that are sparingly soluble, even under acidic conditions. These hydroxides [i.e., Cr(OH)<sub>3</sub>] precipitate and cover the surface of the soil and are not easily bioaccessible even in the presence of the low pH in the simulated stomach fluid of the PBET. Conse-

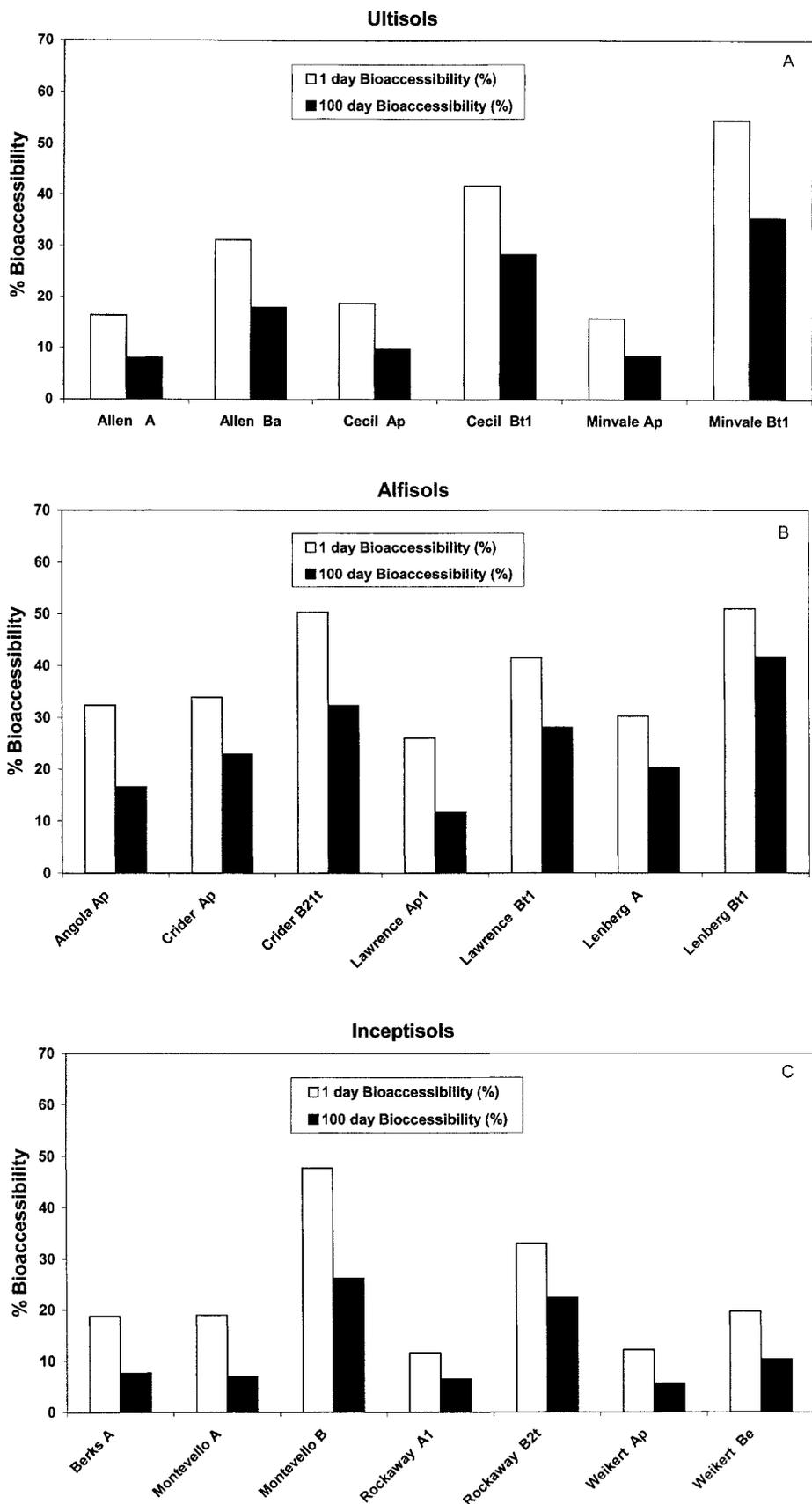


Fig. 1. Percentage Cr(III) bioaccessibility after 1 and 100 d Cr-soil aging for (a) Ultisols; (b) Alfisols; (c) Inceptisols; (d) Spodosols, Mollisols, Entisols; and (e) Aridisols.

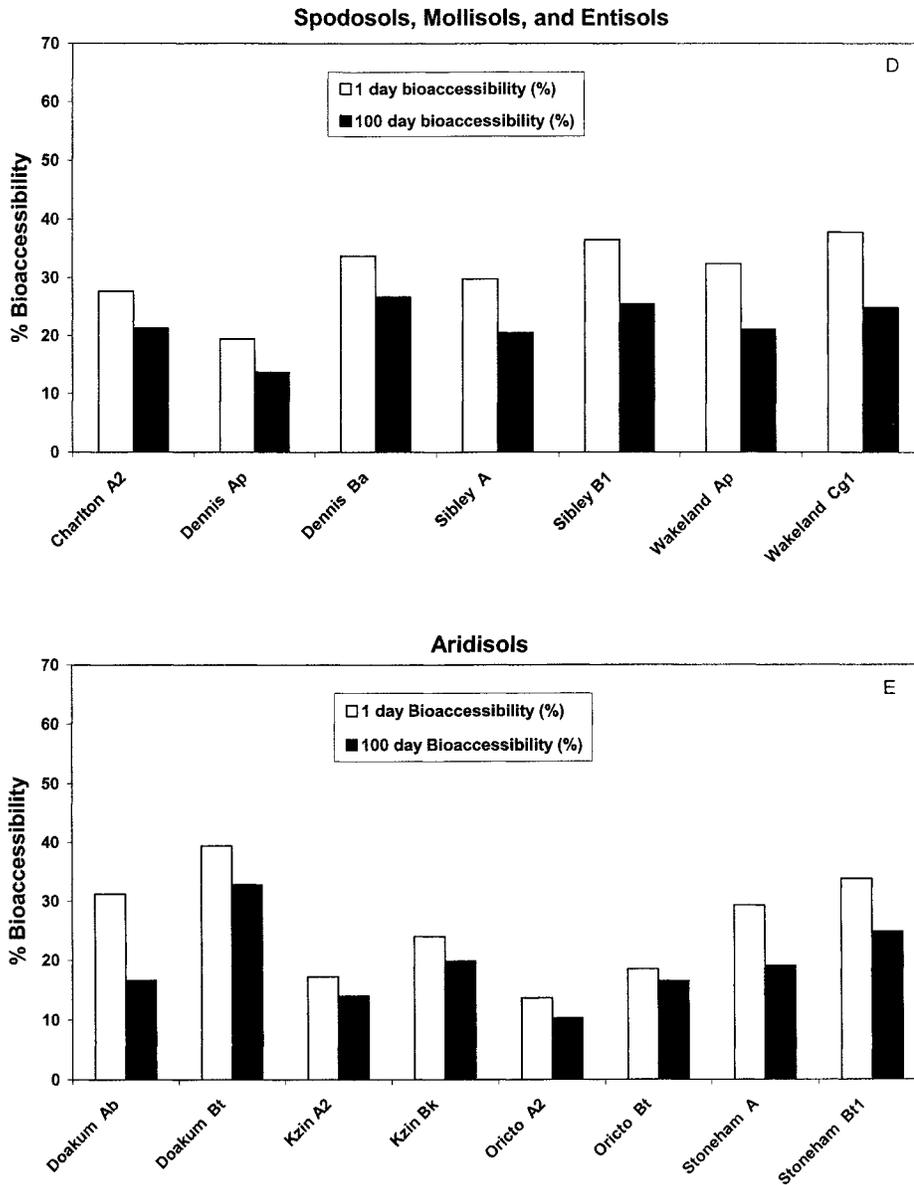


Fig. 1. Continued.

quently as the TIC content increases the bioaccessibility of Cr(III) in soil decreases. As shown with the Cr sorption data the clay content on the soil was also correlated with the amount of Cr sequestration and thus should be important in determining bioaccessibility. The bioaccessibility model suggested that, as the clay content of the soils increased, the percent of Cr on the soil that is bioaccessible also increased. Since the mechanism of Cr retardation on clay minerals is primarily weak electrostatic bonds, these bonds are easily broken under the conditions of the PBET, allowing Cr to desorb from the soil and be released into solution during the simulated digestion.

Stepwise multiple regression analysis also indicated that Cr(III) bioaccessibility was significantly correlated with clay and TOC content of the soil (Table 6). The relationship describing Cr(III) bioaccessibility was:

$$\% \text{ Cr(III) bioaccessible} = 15.54 + (0.408 \times \% \text{ clay}) - (3.78 \times \% \text{ TOC})$$

with an  $r^2$  value of 0.674. This relationship was similar to the clay/TIC model where higher quantities of TIC and TOC resulted in decreased Cr(III) bioaccessibility. When clay, TIC, and TOC were used in the same model, the contribution of TOC was not significant at the 90%

**Table 5. Parameter estimates, standard errors, and statistics obtained from a multiple linear regression analysis that related soil properties (clay and TIC) to percent Cr(III) bioaccessibility.†**

Parameter	Value	SE	P	VIF
Intercept	16.02	1.99	<0.001	-
% Clay	0.426	0.0671	<0.001	1.002
% TIC	-9.56	1.54	<0.001	1.002
$r^2$	0.722		<0.001	

† TIC, total inorganic carbon; VIF, Variance Inflation Factor.

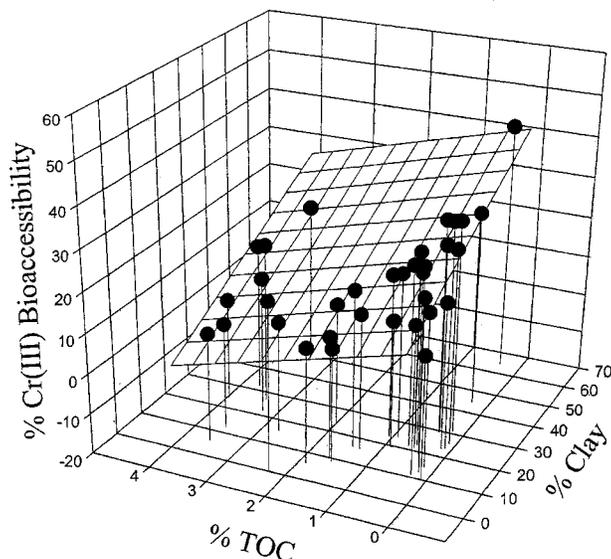


Fig. 2. The observed (data points) and model fitted (grid surface) relationship between the two most significant independent variables (% clay and TIC) and % Cr(III) bioaccessibility using the model: % Cr(III) bioaccessible = 16.02 + (0.426 × % clay) – (9.56 × % TIC) an  $r^2$  value of 0.722.

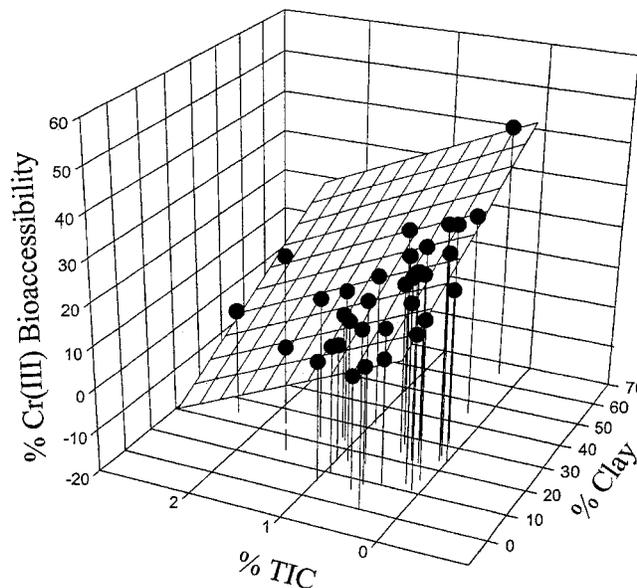


Fig. 3. The observed (data points) and model fitted (grid surface) relationship between the two independent variables (% clay and TOC) and % Cr(III) bioaccessibility using the model: % Cr(III) bioaccessible = 15.54 + (0.408 × % clay) – (3.78 × % TOC) with an  $r^2$  value of 0.674.

confidence level ( $P = 0.115$ ). This scenario may be an artifact of our limited data set, where the most appropriate model, in fact, includes both TIC and TOC along with clay content. A more extensive data set will be necessary to test this hypothesis. Nevertheless, the model using clay and TOC was statistically rigorous at the 99% confidence level since  $P$  values for the estimated parameters were  $<0.01$  and the VIF values are approximately 1.000, indicating that the variables all contribute significantly to the equation and that no multicollinearity was present among the independent variables. This model passed the Normality Test and the Constant Variance Test. The model suggested that as the clay content decreased and the TOC content increased, the % Cr(III) bioaccessible decreased (Fig. 3). The trend regarding clay content is consistent with the previous model and the limited bioaccessibility of Cr in the presence of higher system organic C is conceptually correct. Organic matter found in soil is a major contributor to the overall negative charge in soils and thus is an important sorbent for heavy metal cations (Sparks, 1995). Organic matter has the ability to form strong bonds with the Cr(III) with the metal not readily released during the PBET process. As Cr(III) is considered a Lewis hard acid, it forms stable complexes with the carboxyl group of the organic matter (Sparks, 1995). These bonds are stable

and not easily broken. The current model again explains more than 67% of the variability in Cr(III) bioaccessibility and should be useful for soils low in carbonate (TIC).

### ENVIRONMENTAL SIGNIFICANCE

This study has shown that site assessments of soil metal bioaccessibility based solely on total soil metal concentrations may not accurately reflect the risk posed by the soils. The sequestering properties of soil significantly lower the percent of Cr bioaccessible upon ingestion of the otherwise labile Cr. Chromium(III) can be immobilized as strongly bound species on clay and organic matter, and Cr-hydroxide precipitates on soil mineral surfaces. It has been shown that common soil properties are strongly correlated with Cr(III) bioaccessibility. The availability of these soil properties is commonplace (e.g., NRCS database), which allows the percent bioaccessibility of Cr(III) to be estimated for a variety of contaminated sites whose remediation is pending. The ability to rapidly assess metal bioaccessibility in soils will facilitate decision making strategies regarding the need for more detailed and expensive site-specific bioavailability (e.g., animal feeding) studies, which are designed to assess actual clean-up needs at contaminated DoD sites and other sites to a level safe for human use. Such in vivo studies are lacking with regard to Cr, but research in this area is currently underway (M.V. Ruby, personal communication, 2002).

Table 6. Parameter estimates, standard errors, and statistics obtained from a multiple linear regression analysis that related soil properties (clay and TOC) to percent Cr(III) bioaccessibility.†

Parameter	Value	SE	P	VIF
Intercept	15.54	2.16	<0.001	–
% Clay	0.408	0.073	<0.001	1.010
% TOC	–3.78	0.711	<0.001	1.010
$r^2$	0.674		<0.001	

† TOC, total organic carbon; VIF, Variance Inflation Factor.

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