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Quantifying the bioaccessibility of chromium contaminated soil

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To the Graduate Council:

I am submitting herewith a thesis written by Melanie A. Stewart entitled "Quantifying the bioaccessibility of chromium contaminated soil." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

Larry D. McKay, Major Professor

We have read this thesis and recommend its acceptance:

Philip Jardine, Kula Misra

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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QUANTIFYING THE BIOACCESSIBILITY OF CHROMIUM CONTAMINATED SOIL

A Thesis
Presented for the
Master of Science Degree
The University of Tennessee, Knoxville

Melanie A. Stewart
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Abstract

There are numerous sites on Department of Defense (DOD) and Department of Energy (DOE) lands along with other industrial facilities that are contaminated with toxic metals such as chromium and are awaiting possible clean up and closure. Ingestion of contaminated soil by children is the usual risk driver that motivates remediation for sites contaminated with toxic metals. The purpose of this study was to investigate the effect of soil properties on the bioaccessibility of Cr(III) and Cr(VI) as a function of contaminant concentration and aging, and to develop a simple statistical model based on common soil properties to estimate the bioaccessibility of Cr(III) contaminated soil upon ingestion.

The A- and upper B- horizons of two well characterized soils were treated with varying concentrations of Cr(III) and Cr(VI) and allowed to age. The bioaccessibility of the contaminated soils was measured using a physiologically based extraction test (PBET) designed to simulate the digestive process of the stomach. Sorption of Cr(III) and Cr(VI) varied significantly as a function of soil type and horizon as well as the oxidation state of the contaminant. Cr(III) showed significantly greater solid phase concentrations than Cr(VI) for any given initial Cr concentration. These results are consistent with one of the expected mechanisms of sequestration of Cr(III) vs. Cr(VI) by the soils: the precipitation of Cr(III) – hydroxides, which can result in the accumulation of large mass fractions of contaminant on mineral surfaces. Overall, bioaccessibility of Cr decreased as the duration of exposure to the soil increased. This occurred for all soils and at all solid phase concentrations, with Cr(III) exhibiting the most pronounced aging effects. The decrease in Cr bioaccessibility was rapid for the first 50 d and then slowed dramatically from 50 to 200 d.

The statistical model for bioaccessibility of Cr(III) was developed using data from thirty-six uncontaminated soils from seven major soil orders which were spiked with Cr(III), aged and then tested using the PBET method. 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 days aging, respectively. Statistical analysis revealed that Cr(III) sequestration by the soils was strongly correlated with the clay, total inorganic carbon (TIC), pH, and Mn-oxide content of the soils. Soils that contained higher quantities of clay, inorganic carbon (i.e. carbonates), higher pH and low Mn-oxide contents generally sequestered more Cr(III). Further statistical analysis showed that the bioaccessibility of Cr(III) on soil was also correlated with the clay content, TIC content, and pH of the soil with bioaccessibility decreasing as the soil TIC content and pH increased and as the clay content decreased. The model was statistically rigorous, passing both a normality test and a constant variance test, with no indication of parameter collinearity. 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. Thus, the model should be useful for assessing Cr(III) bioaccessibility at contaminated site so that the appropriate remediation criteria can be determined.

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Chapter 1

Introduction

Chromium is used in many industrial processes such as electroplating, leather tanning, pulp production and wood preservation, and consequently, can be found throughout the environment (Nriagu and Nieboer, 1988). Human health is the usual risk driver that motivates the likelihood of remediation at Cr contaminated sites. The exposure pathway of concern for chromium contaminated soil is that of ingestion, especially for children who traditionally have greater hand to mouth contact. Chromium is stable in the environment in two main oxidation states: cationic chromium with a valence of three (Cr(III)) and anionic chromium with a valence of six (Cr(VI)). Of the oxidation states Cr(VI) is often expected to have greater mobility in the environment and is considered a carcinogenic and mutagenic agent at low concentrations. The more environmentally stable Cr(III) is expected to be less mobile, but is still considered potentially harmful at high concentrations (Levis and Bianchi, 1982; Chung et al., 1994; Patterson et al., 1997). When regulators establish clean-up criteria for chromium contaminated soils the standards are generally based on the total content of Cr(III) or Cr(VI) and are the same for all soils. The ubiquitous metal sequestering properties of the soils are generally not taken into account (Proctor et al., 1997). A better understanding of the influence of soil sequestration on the bioaccessibility of Cr is needed in order to accurately access the dangers posed by metal contaminated soils.

Positively charged mineral surfaces generally adsorb the Cr anion via electrostatic attraction. Thus, enhanced adsorption of Cr(VI) is favored by conditions of decreasing pH (Zachara et al., 1989). Another important mechanism of Cr(VI) sequestration by soils is the reduction of Cr(VI) to sparingly soluble Cr(III), which is more readily sequestered. Organic matter and surface bound organics are extremely effective at reducing Cr(VI) to Cr(III) under acidic conditions (Bartlett and Kimble, 1976b; Jardine et al., 1999) Sorption of the cationic Cr(III) is favored by conditions of higher pH creating more negative surface sites on soil and organic matter to which Cr(III) can sorb (Sparks, 1995). Further, Cr(III) rapidly precipitates from solution and forms hydroxides on the soil surface at pH conditions above 5.5 (Bartlett and Kimble, 1976a). This paper shows that soils can strongly sequester both anionic and cationic forms of Cr, which, under certain circumstances, dramatically decreases toxic metal bioaccessibility. With all the factors influencing chromium's ability to adsorb to the soil surface, blanket clean-up regulations that ignore the importance of individual soil properties may not be cost-effective or appropriate with regard to human health risk. Thus, action levels need to consider specific soil properties instead of using generic guidelines set by state regulators concerning the bioaccessibility of chromium in soil (Proctor, et al., 1997).

The major chapters of this thesis are briefly outlined below.

Chapter 2 - Effects of Contaminant Concentration, Aging, and Soil Properties on the Bioaccessibility of Cr(III) and Cr(VI) Contaminated Soils: The primary objective of this investigation was to determine the effect of soil properties on the bioaccessibility of

Cr(III) and Cr(VI) as a function of contaminant concentration and aging. The A- and upper B- horizons of two well characterized soils, representative of Cr contaminated soils in the southeastern United States, were treated with varying concentration of Cr(III) and Cr(VI) and allowed to age. A physiologically based extraction test (PBET), that was designed to simulate the digestive process of the stomach, was employed to analyze the bioaccessibility of the contaminated soils and was conducted over a 200 day time period.

Chapter 3 - Influence of Soil Geochemical and Physical Properties on the Sorption and Bioaccessibility of Cr(III): The purpose of this study was to develop a simple statistical model to estimate the bioaccessibility of Cr(III) treated soil based on common soil properties. Thirty-six 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. The bioaccessibility of Cr(III) treated soils was determined with a physiologically based extraction test (PBET).

Chapter 2

Effects of Contaminant Concentration, Aging, and Soil Properties on the Bioaccessibility of Cr(III) and Cr(VI) Contaminated Soils

2.1 Abstract

Contaminated soils at numerous U.S. Department of Defense, Department of Energy, and other industrial facilities often contain huge inventories of toxic metals such as chromium. Ingestion of soil by children is the primary risk that drives the need for remediation. Site assessments are based solely on total soil-metal concentrations and do not consider the potential for decreased bioaccessibility due to metal sequestration by soil. The objectives of this research are to investigate the effect of soil properties on the bioaccessibility of Cr(III) and Cr(VI) as a function of contaminant concentration and aging. The A- and upper B- horizons of two well characterized soils, representative of Cr contaminated soils in the southeastern United States, were treated with varying concentration of Cr(III) and Cr(VI) and allowed to age. The bioaccessibility of the contaminated soils was measured over a 200 day time period using a physiologically based extraction test (PBET) that was designed to simulate the digestive process of the stomach. The sorption of Cr(III) and Cr(VI) varied significantly as a function of soil type and horizon, and the oxidation state of the contaminant. Solid phase concentrations with Cr(III) were significantly greater than Cr(VI) for any given initial Cr concentration. This is consistent with one of the expected mechanisms of Cr(III) sequestration vs. Cr(VI) sequestration by the soils: the formation of Cr(III) – hydroxides, which, can result in the accumulation of large mass fractions of contaminant on mineral surfaces. Overall, Cr bioaccessibility decreased with duration of exposure for all soils and at all solid phase concentrations, with aging effects being more pronounced for Cr(III). The decrease in Cr bioaccessibility was rapid for the first 50 d and then slowed dramatically between 50 and 200 d. In general, the effects of Cr solid phase concentration on bioaccessibility was small, with Cr(III) showing the most pronounced effect; higher solid phase concentrations resulted in a decrease in bioaccessibility. Chemical extraction methods and X-ray Adsorption Spectroscopy analyses suggested that the bioaccessibility of Cr(VI) was significantly influenced by reduction processes catalyzed by soil organic carbon. Soils with sufficient organic carbon had lower Cr bioaccessibility values (~10-20%) due to enhanced reduction of Cr(VI) to Cr(III). In soils where organic carbon was limited and reduction processes were minimal, the bioaccessibility of Cr(VI) dramatically increased (~60-70%).

2.2 Introduction

Chromium is used in many industrial processes including electroplating, leather tanning, pulp production and wood preservation, and consequently, can be found throughout the environment (Nriagu and Nieboer, 1988). There are two main oxidation states of chromium found in the environment, anionic Cr(VI) and cationic Cr(III). The two forms of chromium have distinct behaviors in subsurface environments. The anionic Cr(VI) is considered to be highly mobile in soils while the Cr(III) cation is believed to be significantly less mobile (Chung et al., 1994; Fendorf et al., 1997). In regards to human health, the two forms of Cr also have major differences, with Cr(VI) considered carcinogenic and mutagenic even at low concentrations while Cr(III) is considered potentially harmful only at high concentrations (Levis and Bianchi, 1982). Human health is the usual risk driver that motivates the likelihood of remediation at Cr contaminated sites. The exposure pathway of concern is usually that of ingestion of contaminated soil, especially for children who traditionally have greater hand to mouth contact. When regulators establish clean-up criteria for chromium contaminated soils, the ubiquitous metal sequestering properties of the soils are not taken into account (Proctor et al., 1997). Instead, the standards are the same for all soils and are usually based on that of a soluble salt of the metal and the assumption that 100% of metal present will be absorbed into the body (Ruby et al., 1999). In order to accurately access the health risk posed by metal contaminated sites, an improved understanding of the influence of soil sequestration on the bioaccessibility of Cr is needed. Hamel et al. (1998) defined bioaccessibility as that amount of contaminant, Cr, which is soluble due to gastric function and has the potential to cross the intestinal wall.

Chromium adsorption in soil occurs under different conditions based on the oxidative state of the Cr ion. The Cr anion, Cr(VI), generally adsorbs to positively charged mineral surfaces via electrostatic attraction. Thus, conditions of decreasing pH result in enhanced adsorption of Cr(VI) (Zachara et al., 1989). Surfaces with proton specific sites, particularly iron oxides, are mostly responsible for Cr(VI) adsorption (Davis and Leckie, 1980; Zachara et al., 1987; 1988). Factors interfering with Cr(VI) adsorption include the presence of SO_4^{2-}, the presence of dissolved inorganic carbon (DIC), and Al substitution for Fe in oxides. With a limited number of positive surface sites in soil there is often competition from SO_4^{2-} and DIC for those sites (Leckie et al., 1980; James and Bartlett, 1983; Zachara et al., 1987; 1988; 1989). Ainsworth et al. (1989) concluded that Al-substitution in oxides reduces the amount of chromate adsorbed due to the difference in the charge characteristics of the surface sites.

Another important mechanism of Cr(VI) sequestration by soils is the reduction of Cr(VI) to sparingly soluble Cr(III). Electron donors such as organic matter and Fe(II) are capable of reducing Cr(VI). Organic matter and surface bound organics are extremely effective at reducing Cr(VI) to Cr(III) under acidic conditions (Bartlett and Kimble, 1976b; Jardine et al., 1999) Likewise, Fe(II) bearing minerals are known to rapidly reduce Cr in soils (Anderson et al., 1994; Peterson et al., 1997). Low soil pH facilitates the reduction reaction through the release of Fe(II) from soils (Eary and Rai, 1991). Iron sulfides also have the ability to rapidly reduce Cr(VI) to Cr(III) suggesting that complete dissolution of Fe(II) does not have to occur before the Cr can be reduced (Patterson et al., 1997). These results imply that the reduction is taking place at the solid-solution interface making FeS an effective reductant of Cr(VI). Fe(II) oxidation is not inhibited by the presence of O_2 at pH values less than 8.0 unless the concentration of Cr(VI) is << 10 μM (Fendorf and Li, 1996). This further reinforces the need for acidic soil conditions in order for Cr(VI) to be reduced to Cr(III).

Cationic Cr(III) also adsorbs to soil through a variety of mechanisms. The pH of the soil has a strong influence on Cr(III) adsorption since changes in pH affect the variable charge on minerals and organic matter. Conditions of higher pH creates more negative surface sites on soil mineral surface and organic matter to which Cr(III) can sorb (Sparks, 1995). Further, at pH conditions above 5.5, Cr(III) rapidly precipitates from solution and forms hydroxides on the soil surface (Bartlett and Kimble, 1976a). These hydroxides have low solubility and therefore are not likely to dissolve and re-enter the soil solution (Losi, et al., 1994).

With all the highly variable factors influencing chromium's ability to adsorb to the soil surface, blanket clean-up regulations that ignore the importance of individual soil properties may not be accurate with regard to human health risk. The objective of this research was to investigate the effect of soil properties on the bioaccessibility of Cr(III) and Cr(VI) as a function of contaminant concentration and aging. We show that soils can strongly sequester both anionic and cationic forms of Cr, which, under certain circumstances, dramatically decreases toxic metal bioaccessibility.

2.3 Methods

2.3.1 Soil Type and Characterization

The A and upper B horizons of two soils were obtained from the Melton Valley and Walker Branch watersheds on the Oak Ridge Reservation (ORR) in eastern Tennessee. The soils are representative of Cr contaminated sites common to the southeastern U.S. Selected physical and geochemical properties of these soils are listed in Table 2.1. The Melton Valley soil is an acidic Inceptisol derived from interbedded shales and limestone (Driese et al., in press; Jardine et al.; 1999; Kooner et al., 1995). The soils are extensively weathered and devoid of carbonates. Illites dominate the < 2μm clay fraction

Table 2.1 Select soil physical and geochemical properties

	Sampling depth (cm)	Particle size analysis			Organic matter content (%)	pH (5mM $CaCl_2$)	pH (DDI)	Fe (g/kg)	Mineralogy of <2 μm clay fraction *
		Sand (%)	Silt (%)	Clay (%)					
Melton A	0 - 4	56.2	30.0	13.8	3.97	6.91	7.18	10.68	
Melton B	4 - 10	30.8	50.4	18.8	0.73	4.23	4.87	22.07	$I_{45}IS_{20}V_{10}K_9VC_6M_5Q_3F_1$
Walker A	0 - 3	34.9	58.9	6.2	1.89	6.01	6.61	7.71	
Walker B	10 - 20	32.2	44.2	23.6	0.10	4.30	5.17	19.55	$K_{27}V_{27}VC_{14}Q_{13}I_{10}IS_5G_3F_1$

* K = kaolinite; V = vermiculite; VC = chloritized vermiculite; I = illite (soil mica); IS = interstratified 2:1; Q = quartz; G = gibbsite; M = montmorillite; F = feldspar. Sunscripts refer to the percent by weight of each mineral

and the clays are heavily coated with amorphous Fe – oxides and goethite. The pH and cation exchange capacity (CEC) values of these soils range from 4 to 7 and 10 to 20 cmol$_c$ kg^{-1}, respectively (Jardine et al., 1989). Walker Branch soils are an acidic Ultisol that has been weathered from the Knox Group (Arnseth and Turner, 1988), a dolostone sequence with occasional interbeds of limestone and shale. The soils are also extensively weathered and devoid of carbonates. Kaolinite dominates the < 2μm clay fraction and the clays are heavily coated with hematite and maghemite. The pH and cation exchange capacity (CEC) of these soils range from 4 to 6 and 4 to 6 cmol$_c$ kg^{-1}, respectively (Jardine et al., 1989). All soils were dried in an oven at 40°C and crushed with a mortar and pestle to pass a 250 μm sieve.

2.3.2 Contaminant Addition to Soil

Ten grams of the soil and 100 ml of chromium solution were placed in a 200 ml glass centrifuge vessel, shaken, and allowed to equilibrate for 2 days. The spiking concentrations for Cr(VI), as K_2CrO_4, were 1000, 250, and 50 ppm at a pH of 6.0 and for Cr(III), as $CrCl_3$, were 500, 200, and 50 ppm at a pH of 4.0. After a 2 day equilibration period the slurries were centrifuged and the supernatant was discarded (Appendix 1). The soils were then rinsed with double dionized (DDI) water 3 times to remove chromium in the pore water and allowed to air dry. Once the soils were dry, they were gently crushed, homogenized, and then rewetted with DDI water to 30% moisture. The soils were kept in a container out of direct light and maintained at 30% water content in a moisture saturated environment.

2.3.3 *In Vitro Bioaccessibility*

A physiologically based extraction test (PBET) was adapted from Ruby et al. (1996; 1999; Ruby, 2000, personal communication) to assess the in vitro bioaccessibility of Cr(III) from contaminated soils in humans. Sampling was conducted on the treated soils that had been allowed to age in the storage container to 1, 21, 50, 100, and 200 day after initial treatment and subsequent wetting of the treated soils. Triplicate 0.39 g moist samples (0.3 g dry weight) were placed in 50 ml polyethylene tubes to which 30 ml of 0.4 M glycine at pH 1.5 and 37°C was added. The slurries were quickly placed in a rotating water bath at 37°C and agitated at 30±2 rpm for 1 hour. The method was designed to simulate the stomach digestive system in humans. Supernatant was separated from the solid via centrifugation (Appendix 1). The pH of the supernatant was measured to ensure that the final pH was within ± 0.5 pH units of the initial pH. This scenario held for all cases. Bioaccessibility was calculated as:

$$\%\,\text{Bioaccessibility} = \left(\frac{\text{Cr in PBET supernatant (mg/L)} \times 0.03\text{L} \div 0.3\text{g dry soil}}{\text{Cr on soil surface (mg/kg)}} \right) \times 100$$

2.3.4 *Chromium Analysis*

The PBET supernatant was measured for Cr(VI) and Cr total (Cr_T). Cr(VI) was measured using a modified *s*-diphenylcarbohydrazide colormetric method (Bartlett and James, 1979) with a UV-VIS spectrophotometer at a wavelength of 540 μm (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 hr was insignificant. Total chromium was measured on a Perkin Elmer AAnalysist 800 atomic absorption spectrophotometer (Wellseley, PA). All standards used were made from an atomic absorption chromium standard (EM Industries, Hawthorne, NY). Cr(III) was calculated as the difference between Cr_T and Cr(VI).

2.3.5 Determination of Chromium on Soil

Total chromium 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 in order to facilitate the removal of hydrofluoric acid from solution. 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 chromium using Inductively Coupled Plasma.

2.3.6 Chromium Solid Phase Speciation

2.3.6.1 X-ray Adsorption Spectroscopy (XAS)

Solid phase Cr was speciated using X-ray adsorption near-edge structure (XANES) spectroscopy, which was conducted at the Stanford Synchrotron Radiation Laboratory (SSRL) under dedicated running conditions. Scans were recorded from –200 to 300 eV around the K-edge of chromium (5989 eV), with 0.2-eV steps across the white-line and main-edge region. Energy selection was accomplished with a Si(*220*) double-crystal monochromator, with a 1-mm (h) x 20-mm (w) beam. Adsorption was measured by a proportional fluorescent X-ray production using a 13-element Ge detector (Cramer et al. (1988). Mass fractions of Cr(III) and Cr(VI) were determined for each soil using

XANES spectroscopy by placing the soil in a 4- x 4- x 40-mm slot cut in an acrylic plate that was sealed with Kapton. The proportion of Cr(VI) relative to total chromium was then determined by the ratio of the white-line amplitude to the total atomic cross section and comparison to standard curves as described by Patterson et al. (1997).

2.3.6.2 Chemical Extraction

In an effort to indirectly quantify Cr(VI) reduction processes on the soils, sorption isotherms were constructed and the solid phase extracted with SO_4^{2-}. Since SO_4^{2-} competes well for Cr(VI) sorption sites, but does not compete well for Cr(III) sorption sites, an indirect measure of the reduction of Cr(VI) to Cr(III) should be possible. Approximately 1 g soil was placed in preweighed centrifuge tubes and the soils treated with 15 ml of varying concentrations of Cr(VI) in 5 mM $CaCl_2$ that were adjusted to the pH of the soil. Samples were allowed to equilibrate on the shaker for 48 hours. Soils were centrifuged and supernatant was saved for analysis. The Cr(VI) was extracted from soils with 3 sequential washings of 0.05 M Na_2SO_4. The equilibrium solutions and extraction solutions were analyzed for both Cr(VI) and Cr(III). The chromium extract was corrected for pore water Cr of the equilibration step.

2.4 Results and Discussion

2.4.1 Influence of soil properties on Cr sorption

As expected, soils treated with solution containing Cr(III) adsorbed 2 to 10 times more Cr than those treated with Cr(VI) (Table 2.2). This results from a larger cation exchange

Table 2.2 Solid phase concentration of Cr on soil (mg/kg) after treatment with solutions containing various concentrations (ppm) of Cr(III) or Cr(VI)

Cr(III)	500 ppm	200 ppm	50 ppm
Melton A	4479.42	1823.26	426.42
Melton B	2002.91	1430.68	452.02
Walker A	2421.67	1779.01	451.00
Walker B	1276.05	1070.32	445.20

Cr(VI)	1000ppm	250ppm	50ppm
Melton A	386.47	199.21	91.28
Melton B	269.14	219.86	150.00
Walker A	391.83	244.24	100.22
Walker B	423.48	330.53	218.25

capacity versus anion exchange capacity and the propensity for Cr(III) to precipitate on mineral surfaces at pH values above 5.5. The adsorption of both Cr species became more similar on the WB B-horizon soil since acidic conditions and abundant Fe-oxides provided positive surface charges, thereby enhancing Cr(VI) sorption (Appendix 2). Thus, mineral phases, particularly iron oxides, with proton-specific surface sites may effectively adsorb Cr(VI) at low to medium soil pHs (Zachara et al., 1987;1988;1989; Leckie et al., 1980; Davis and Leckie, 1980; Mayer and Schick, 1981). The A-horizon soils had a higher pH and organic matter content creating an environment that was not conducive to Cr(VI) adsorption.

In the case of Cr(III) the patterns of adsorption were reversed, where the A-horizon soils typically adsorbed more Cr than the B-horizon soils (Appendix 2). The A-horizon soils characteristically had higher pH creating an environment that favored Cr(III) adsorption. Deprotonation of oxides and organic matter occurs in soils with higher soil pH values, which results in more negatively charged sites that attract cations such as Cr(III). Also, when the soil pH is above 5.5, as with the two A-horizon soils used here, the Cr(III) most likely precipitates from solution as hydroxides creating a surface coating on a variety of soil mineral surfaces (Bartlett and Kimball, 1976a). This suggests that larger solid phase concentrations of Cr(III) can often be expected in soils with higher pH and abundant inorganic and organic carbon as shown in Chapter 3.

2.4.2 Influence of aging

PBET results show chromium bioaccessibility decreased with time for all soils tested and at all solid phase concentrations, with aging effects being most pronounced for Cr(III) (Figures 2.1 and 2.2). The decrease in bioaccessibility was rapid for the first 50 d and slowed dramatically as the aging period approached 200 d. As the soils age they are most likely approaching a state of equilibrium between the solution phase Cr and the surface of the soil. The aging effect is related to the enhanced stability of Cr on the soil surface with time. Structural reorientation of Cr surface bonds or, in the case of Cr(III), slow precipitation reactions can account for the stronger sorption of Cr at longer times. The greater aging effect observed for Cr(III) vs. Cr(VI) is most likely related to the nature of the Cr(III) surface bond which tend to form an inner-sphere monodentate complex. This is a strong bond that can be maintained even in the low pH conditions of the PBET (Fendorf et al., 1994; Fendorf and Sparks, 1994). The chromium hydroxides ($Cr(OH)_3$) that are commonly thought to be precipitated on the soil surface have low solubility and are not easily redissolved into solution even under the conditions of the PBET.

2.4.3 Influence of solid phase concentration on Cr bioaccessibility

In general, the effect of Cr solid phase concentration on bioaccessibility was small, with Cr(III) showing the most pronounced effect. No obvious trends were noted for Cr(VI), whose bioaccessibility remained relatively constant at different solid phase concentrations on any given soil (Figure 2.2). For Cr(III), in the A-horizon soils (Figure 2.1), higher bioaccessibility was noted for soils that were treated with 50 ppm Cr(III) relative to the higher concentration treatments. This is most likely related to the fact that

Figure 2.1 Bioaccessibility of Cr(III) treated soils. Aging and solid phase concentration effects for 4 soils treated with varying concentrations of Cr(III) (500, 200, and 50 ppm). (a.) Melton Valley A-horizon soil, (b.) Melton Valley B-horizon soil, (c.) Walker Branch A-horizon soil, and (d.) Walker Branch B-horizon soil.

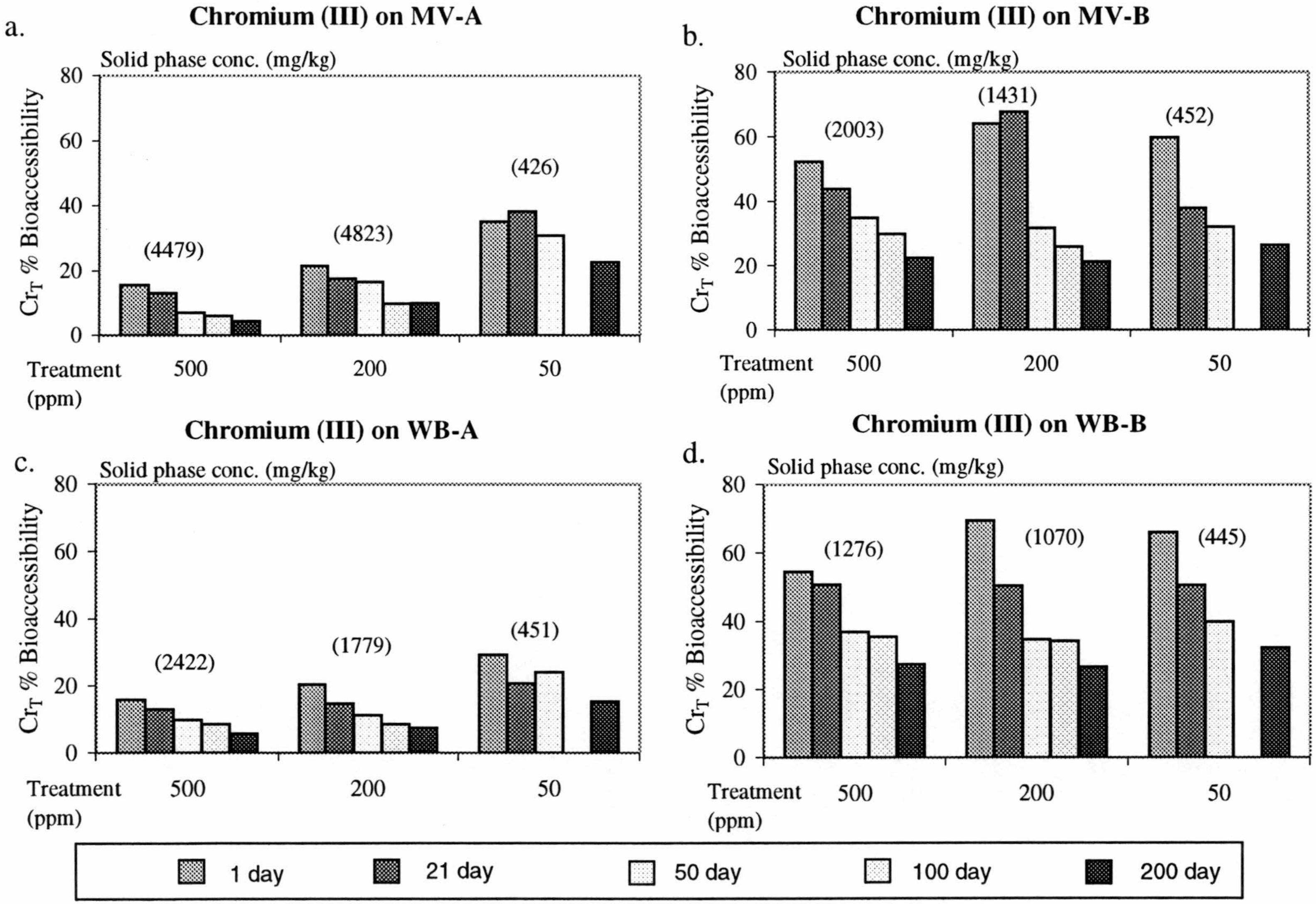
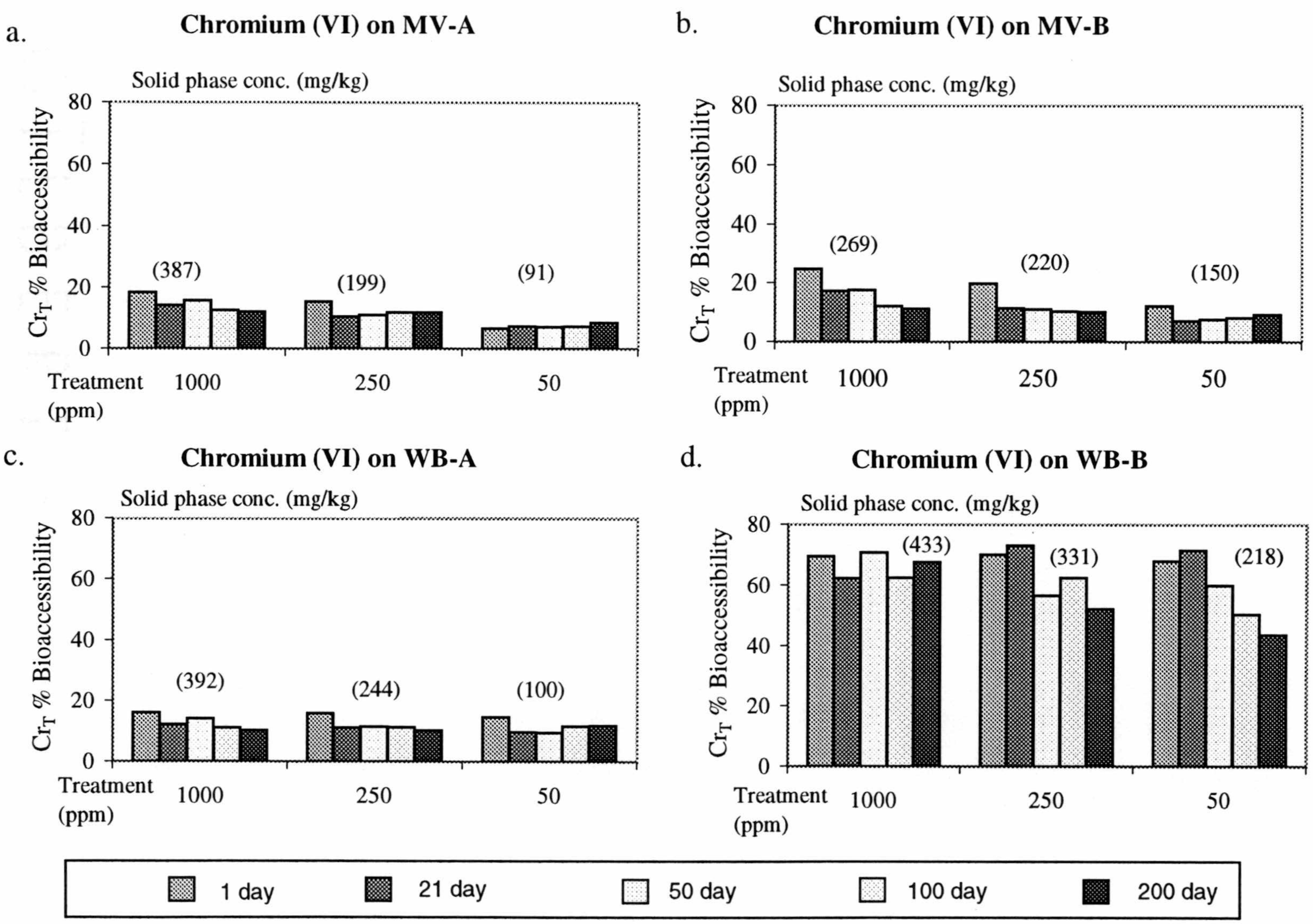

a.
Chromium (III) on MV-A
Solid phase conc. (mg/kg)
Cr_T % Bioaccessibility
80
60
40
20
0
(4479)
(4823)
(426)
Treatment (ppm)
500
200
50
b.
Chromium (III) on MV-B
Solid phase conc. (mg/kg)
Cr_T % Bioaccessibility
80
60
40
20
0
(2003)
(1431)
(452)
Treatment (ppm)
500
200
50
c.
Chromium (III) on WB-A
Solid phase conc. (mg/kg)
Cr_T % Bioaccessibility
80
60
40
20
0
(2422)
(1779)
(451)
Treatment (ppm)
500
200
50
d.
Chromium (III) on WB-B
Solid phase conc. (mg/kg)
Cr_T % Bioaccessibility
80
60
40
20
0
(1276)
(1070)
(445)
Treatment (ppm)
500
200
50
1 day
21 day
50 day
100 day
200 day

Figure 2.2 Bioaccessibility of Cr(VI) treated soils. Aging and solid phase concentration effects for 4 soils treated with varying concentrations of Cr(VI) (1000, 250, and 50 ppm). (a.) Melton Valley A-horizon soil, (b.) Melton Valley B-horizon soil, (c.) Walker Branch A-horizon soil, and (d.) Walker Branch B-horizon soil.


a.
Chromium (VI) on MV-A
Solid phase conc. (mg/kg)
Cr_T % Bioaccessibility
80
60
40
20
0
(387)
(199)
(91)
Treatment (ppm)
1000
250
50
b.
Chromium (VI) on MV-B
Solid phase conc. (mg/kg)
Cr_T % Bioaccessibility
80
60
40
20
0
(269)
(220)
(150)
Treatment (ppm)
1000
250
50
c.
Chromium (VI) on WB-A
Solid phase conc. (mg/kg)
Cr_T % Bioaccessibility
80
60
40
20
0
(392)
(244)
(100)
Treatment (ppm)
1000
250
50
d.
Chromium (VI) on WB-B
Solid phase conc. (mg/kg)
Cr_T % Bioaccessibility
80
60
40
20
0
(433)
(331)
(218)
Treatment (ppm)
1000
250
50
1 day
21 day
50 day
100 day
200 day

at low surface coverage (< 20%) adsorption is the dominant process where Cr(III) forms inner-sphere complexes with the soil while at higher surface coverages (> 20%) surface precipitation occurs and becomes the dominant process (Fendorf et al., 1994; Fendorf and Sparks, 1994). The soils that were treated with 50 ppm Cr(III) have significantly lower Cr on the soil than the other soils treated with higher concentrations.

2.4.4 Influence of soil properties on Cr bioaccessibility

The bioaccessibility of Cr(III) and Cr(VI) varied significantly as a function of soil type and horizon, and the oxidation state of the contaminant. In general, A-horizon soils exhibited less Cr bioaccessibility relative to B-horizon soils. In the Cr(III) system, the higher organic matter content and higher pH of the A-horizon soils are probably the main factors responsible for this difference. The Walker Branch B-horizon (WB-B) soil is a good example of how soil properties effect the degree of bioaccessibility since it is the most acidic of the soils and has the lowest organic carbon content and consequently shows the highest percent of Cr(III) bioaccessibility (Fig. 2.1d). Both the Melton Valley A-horizon (MV-A) and Walker Branch A-horizon (WB-A) soils have a high pH and high organic carbon content and an equally low Cr(III) bioaccessibility. These results are consistent with observations in Chapter 3 of this thesis, which showed that Cr(III) bioaccessibility was limited in systems with high pH and high levels of inorganic and organic carbon.

In the Cr(VI) system, the two A-horizon soils and the Melton Valley B-horizon (MV-B) showed significantly lower Cr bioaccessibility than WB-B for all treatment concentrations and aging times. Although the WB-B soil adsorbed the most Cr(VI), its tendency to release Cr under the acidic conditions of the PBET is due to the soil's inability to maintain the weak bond between the Cr and the surface. The Cr(VI) ion is probably electrostatically bound to mineral oxides through outer sphere complexes, which are unstable during the conditions of the PBET. This leads to the question of why is it that both A-horizon soils and even the Melton Valley Inceptisol B horizon soils (MV-B) have such low Cr(VI) bioaccessibility when soil properties are such as to discourage strong sorption?

To address the above question both direct and indirect solid phase Cr speciation methods using X-ray Absorption Spectroscopy (XAS) and a chemical extraction technique, respectively, were employed. Analysis with XAS of the 250 and 1000 ppm Cr(VI) treated soils after 200 d aging suggested that all soils, except the WB-B soil, had Cr surface coverages that were > 95% Cr(III) (Table 2.3). The 250 and 1000 ppm Cr(VI) treated WB B-horizon soils contained only 30 and 53% surface bound Cr(III), respectively. Thus, the bioaccessibility of Cr(VI) was significantly influenced by the reduction of Cr(VI) to Cr(III). In order for reduction to occur there needs to be a source of electrons. Both organic matter and the Fe(II)-bearing minerals are able to supply electrons to catalyze the reduction of Cr(VI) to Cr(III). Since the soils used in this study were highly oxidized and most likely devoid of Fe(II)-bearing minerals, the reduction of Cr(VI) to Cr(III) was most likely catalyzed by soil organic matter or surface-bound organic carbon (Adriano, 1986; Sparks, 1995; Deng and Stone, 1996; Jardine et al., 1999). Thus, extensive reduction processes for the A-horizon soils and the MV B-

Table 2.3 Percentage of soil solid phase Cr(III) and Cr(VI) quantified by X-ray Adsorption Spectroscopy (XAS) on soils treated with two concentrations of Cr(VI)*

	Solid phase Cr(VI)	Solid phase Cr(III)
250 ppm Cr(VI)	%	
MV-A	< 5	> 95
MV-B	< 5	> 95
WB-A	< 5	> 95
WB-B	70	30
1000 ppm Cr(VI)		
MV-A	< 5	> 95
MV-B	< 5	> 95
WB-A	< 5	> 95
WB-B	47	53

* 200 d aged samples

horizon soils are most likely related to the ample supply of organic carbon in these soils (Table 2.1). Even the WB B-horizon soil showed Cr(VI) reduction to Cr(III) with a solid phase carbon mass of 0.1%. Jardine et al. (1999) showed that in acidic soils, the availability of even small amounts of surface-bound natural organic carbon (0.05% w/w on the solid) can result in significant reduction of Cr(VI) to Cr(III). Therefore, Cr(VI) reduction decreases Cr bioaccessibility since the Cr(III) product is more tightly bound to the solid phase. The Cr(III) probably adsorbs to the surface through strong covalent bonds or precipitates as hydroxide complexes on mineral surfaces. Thus, the percent of Cr that is bioaccessible will decrease during the PBET.

The XAS data is in agreement with aqueous Cr speciation measurements on the PBET solutions (Appendix 3). A significant portion of the total bioaccessible Cr was found to be Cr(III), with the WB B-horizon soil having the lowest total amount of extractable Cr(III) as indicated by the high Cr(VI) in Appendix 3. Using the 200 d aqueous speciation data coupled with the XAS solid speciation results (analyzed on 200 d aged soils), one can calculate the mass fraction of Cr(III) and Cr(VI) that are bioaccessible in each soil (Table 2.4). In all soils, the bioaccessibility of surface-bound Cr(VI) was significantly greater than that for Cr(III). Between 42 and 108% of the total adsorbed Cr(VI) was bioaccessible as compared with total adsorbed Cr(III), which was only 3 and 14% bioaccessible. Although Cr(III) may dominate total Cr in the PBET, surface bound Cr(VI) is significantly more bioaccessible. Thus, the reduction of Cr(VI) to Cr(III) by soil organic matter significantly decreases total Cr bioaccessibility. These results are important from a human health perspective since Cr(VI) is believed to be much more

Table 2.4 Percentage of total surface bound Cr(III) and Cr(VI) that was bioaccessible after 200 d aging

	MV-A		MV-B		WB-A		WB-B	
	Cr(VI) treatment conc. (ppm)							
	250	**1000**	**250**	**1000**	**250**	**1000**	**250**	**1000**
% Cr(III) bioaccessible	6.0	9.9	7.1	8.0	7.8	8.3	3.2	14.2
% Cr(VI) bioaccessible	101*	51.5	65.5	48.1	52.5	42.3	71.1	107.5*

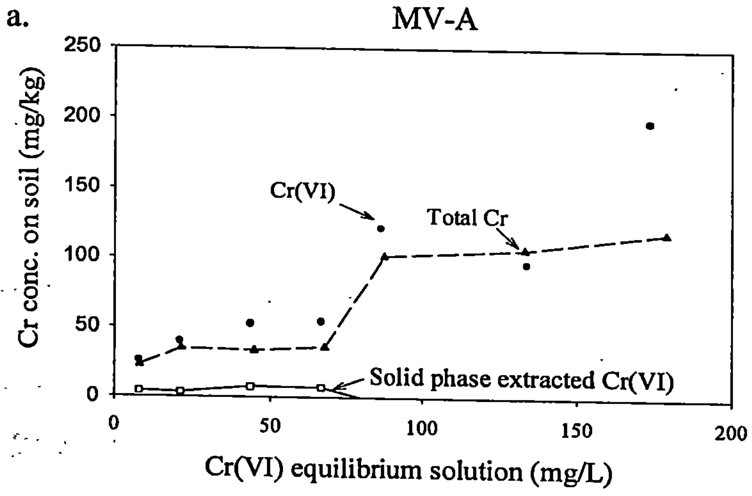
* values above 100% represent analytical error

toxic than Cr(III), with even sub-ppm levels considered lethal. Thus, under certain circumstances, soils that contain sufficient organic carbon or Fe-bearing minerals may be capable of decreasing Cr bioaccessibility through reduction of labile Cr(VI) to the more sparingly soluble Cr(III) species.

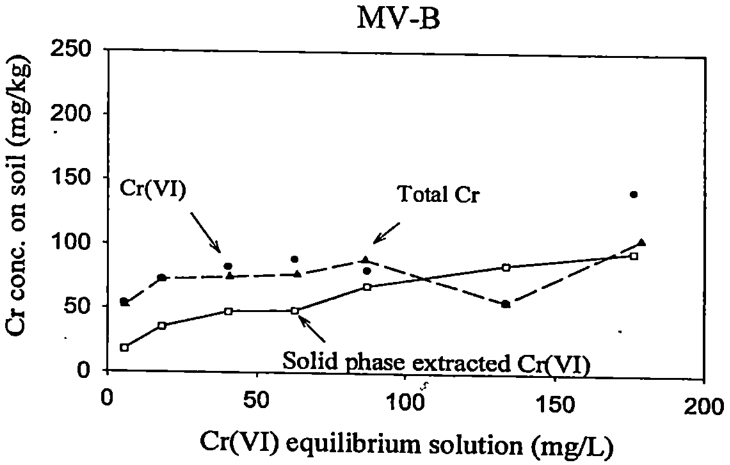
An indirect chemical extraction method was also used to show that Cr(VI) was being reduced to Cr(III). Chromium (VI) was adsorbed onto the soils using different treatment solution concentrations and then allowed to equilibrate for 2 d. Then the solid phase was treated with 0.05 M Na_2SO_4 to remove the Cr(VI) (Figure 2.3 a-d). The SO_4^{2-} anion should be a sufficient competitor for surface sites occupied by $HCrO_4^-$ since the latter is typically sorbed to the solid phase through weak outer-sphere electrostatic bonds. Thus, if Cr reduction processes are minimal, the SO_4^{2-} should be able to recover nearly all of the initial Cr(VI). In this study, the chemical extraction method can only be qualitatively compared to the XAS results since the latter technique was employed on 200 d aged samples, whereas the extraction method was employed on samples aged for 2 d. Jardine et al. (1999) previously measured a half-life of 85 hr. for Cr(VI) reduction by organic carbon so samples analyzed after 200 d of aging should have more Cr(III) product than samples analyzed after 2 d of aging. Nevertheless, the chemical extraction method agreed well with the XAS results and the quantity of organic C in the soils. With the exception of the WB B-horizon soil, the quantity of Cr(VI) extracted from the solid phase was significantly lower than the initial Cr(VI) sorbed, implying that Cr(III) is being formed and remains sorbed to the soil (Figure 2.3 a-d). A-horizon soils had significantly more Cr(III) production as compared to B-horizon soils which is consistent with the

Figure 2.3 Adsorption Isotherms. Indirect chemical extraction showing the amount of Cr(VI) on the solid phase as a function of concentration and the amount of Cr(VI) that was reduced to Cr(III). (a.) Melton Valley A-horizon soil, (b.) Melton Valley B-horizon soil, (c.) Walker Branch A-horizon soil, and (d.) Walker Branch B-horizon soil.

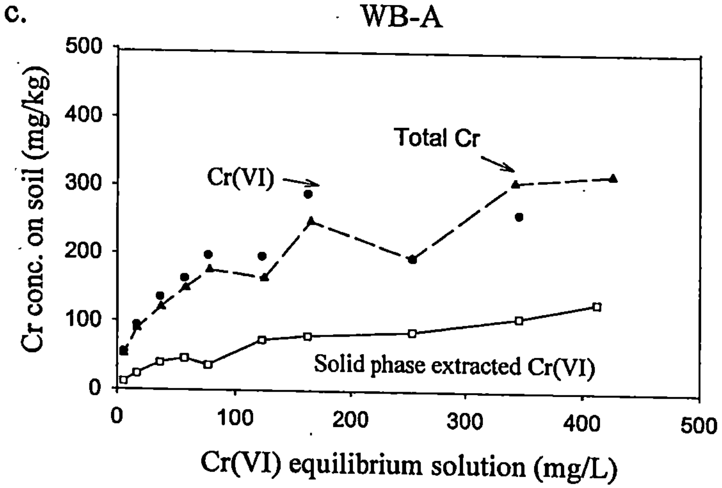
a.


MV-A
Cr conc. on soil (mg/kg)
250
200
150
100
50
0
Cr(VI)
Total Cr
Solid phase extracted Cr(VI)
0
50
100
150
200
Cr(VI) equilibrium solution (mg/L)

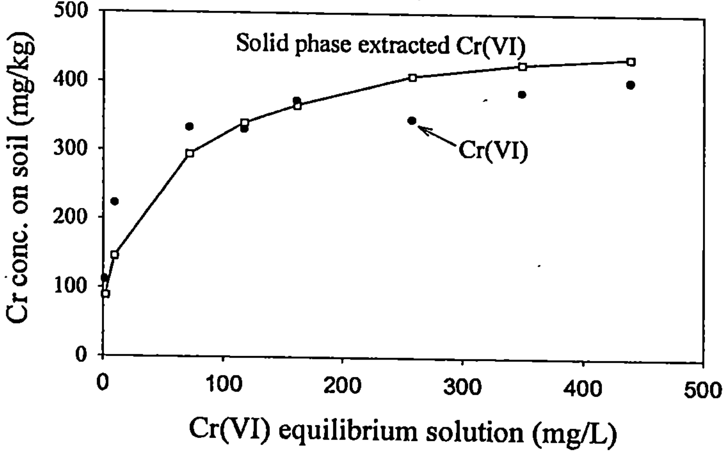
b.


MV-B
Cr conc. on soil (mg/kg)
250
200
150
100
50
0
Cr(VI)
Total Cr
Solid phase extracted Cr(VI)
0
50
100
150
200
Cr(VI) equilibrium solution (mg/L)

c.


WB-A
Cr conc. on soil (mg/kg)
500
400
300
200
100
0
Cr(VI)
Total Cr
Solid phase extracted Cr(VI)
0
100
200
300
400
500
Cr(VI) equilibrium solution (mg/L)

d.


WB-B
Cr conc. on soil (mg/kg)
500
400
300
200
100
0
Solid phase extracted Cr(VI)
Cr(VI)
0
100
200
300
400
500
Cr(VI) equilibrium solution (mg/L)

larger organic carbon content of the former. The WB B-horizon, which had as little as 0.1% organic carbon showed no Cr(VI) reduction after 2 d (Figure 2.3b). The low organic content of this soil does not lend itself to the rapid reduction of Cr(VI) nor is the source of iron, hematite (Fe_2O_3) and maghemite (γFe_2O_3) conducive to Cr(VI) reduction. The presence of Fe(III) suggests that the iron is already oxidized and therefore not in the correct state to facilitate the reduction of Cr(VI). This further explains why the percent of Cr that is bioaccessible in the WB-B soil remains so high compared to the other three soils examined. These results are consistent with the XAS findings that showed Cr(VI) reduction was nearly complete on all soils after 200 d with the exception of the WB-B-horizon soil.

2.5 Environmental Significance

This study has shown that the metal sequestering properties of soil significantly lower the percent of Cr(III) and Cr(VI) bioaccessible upon ingestion. The percent of bioaccessible Cr is largely independent of the initial solid phase concentration of Cr prior to the PBET simulated digestion. Sorption and bioaccessibility of Cr(III) and Cr(VI) vary significantly as a function of soil type and horizon, and the oxidation state of the contaminant. Soils with higher pH and abundant inorganic and organic carbon can often be expected to have higher solid phase concentrations of Cr(III) while for Cr(VI) the patterns are reversed, with Cr(VI) adsorption favored by lower soil pH and soil minerals with amphoteric charge. The aging tests show Cr bioaccessibility decreases after the first 50 d and this is related to the enhanced stability of Cr on the soil surface followed by stable bioaccessibility to 200 d. Bioaccessibility of Cr(III) can be significantly reduced by its ability to bind strongly to organic matter and also form Cr – hydroxide precipitates on the soil surface, even under the conditions present in the PBET. Soil sequestration of Cr(VI) significantly lowers its bioaccessibility. Organic rich soils and/or soils with Fe(II) – bearing minerals present enhance Cr(VI) reduction to Cr(III), with the latter being strongly adsorbed and less bioaccessible. This is important from a human health perspective since Cr(VI) is believed to be much more toxic than Cr(III).

Chapter 3

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

3.1 Abstract

There are numerous chromium (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 usual risk driver that 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-six 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. 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 day aging. The proportion of bioaccessible Cr that was Cr(VI) was always less than 1% suggesting that oxidation reactions were minimal or that oxidation products of Cr(VI) were tightly held by the soil. Statistical analysis revealed that Cr(III) sequestration by the soils was strongly correlated with the clay, total inorganic carbon (TIC), pH, and Mn-oxide content of the soils. Soils with higher quantities of clay, inorganic carbon (i.e. carbonates), higher pH and low Mn-oxide contents generally sequestered more Cr(III). Statistical analysis further showed that the

bioaccessibility of Cr(III) on soil was again related to the clay, TIC, and pH of the soil. Bioaccessibility decreased as the soil TIC content and pH increased and as the clay content decreased. The model was statistically rigorous, passing both a normality test and a constant variance test, with no indication of parameter collinearity. 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. Thus, the model should be useful for assessing Cr(III) bioaccessibility at contaminated sites so that the appropriate remediation criteria can be determined.

3.2 Introduction

The presence of chromium 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 chromium on a daily basis (Nriagu and Nieboer, 1988). Chromium itself is thermodynamically stable in two oxidative states: cationic chromium with a valence of three (Cr(III)) and anionic chromium with a valence of six (Cr(VI)). Cr(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: (1) strong adsorption onto the negatively charged soil surfaces, (2) the ability to form complex molecules with organics found in the soil, and (3) the formation of oxides and hydroxides and other insoluble minerals in soil (Fendorf and Zasoski, 1992; Dragun, 1998; Losi et al., 1994).

When assessing the risks posed by Cr(VI) and Cr(III), the exposure pathway of most concern is ingestion by children (Paustenbach, 1989). Cr(VI) is considered the most harmful of the oxidative states since it is considered both a mutagen and a carcinogen even al low sub-ppm levels (Levis and Bianchi, 1982). Although Cr(III) is generally considered less harmful to human health it is of concern to environmental regulators due to its potential to oxidize to Cr(VI) and its ability to accumulate to very high solid phase concentration 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 metals has received less attention. 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 chromium in soil need to consider specific soil properties instead of using generic guidelines (Proctor et al., 1997). Specific testing on chromium's actual potential to be a human health risk, that is, its *bioaccessibility*, needs to be performed where the bioaccessibility is defined as that amount of Cr which is soluble due to gastric functions and has the potential to cross the intestinal wall (Hamel et al., 1998).

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 National Resource Conservation Service (NRCS) database, can be used to assess Cr(III) bioaccessibility at contaminated sites.

3.3 Methods

3.3.1 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 United States were chosen for consideration based on the high concentration of chromium in their soils and the possible need for remediation (Table 3.1). 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 200 g of the A-horizon and the upper B-horizon soil was obtained for each soil series (Table 3.1). Two additional soils were obtained from the Oak Ridge Reservation in eastern Tennessee, which also had properties similar to DOD sites in the southeast U.S. Thirty six soils were acquired and these encompassed seven major soil orders (Table 3.1).

Table 3.1 U.S. Department of Defense Army bases with their associated soil series designations

Army bases by soil order	Facility location by state	Soil Series
Ultisol		
Holston AAP	Tennessee	Allen
Fort Gillem	Georgia	Cecil
ORNL*	Tennessee	Minvale
Alfisol		
Seneca AD	New York	Angola
Indiana AAP	Idiana	Crider
Bluegrass Facility	Kentucky	Lawrence
Ft. Knox	Kentucky	Lenberg
Lexington Facility - LBAD	Kentucky	Lenberg
Inceptisol		
Letterkenny AD	Pennsylvania	Berks
ARDEC (Picatinny Arsenal)	New Jersey	Rockaway
Letterkenny	Pennsylvania	Weikert
ORNL*	Tennessee	Montevello
Spodosol		
Stratford Army Engine Plant	Connecticut	Charlton

Table 3.1 Cont.

Army bases by **soil order**	Facility location by state	Soil Series
Mollisol		
Kansas AAP	Kansas	Dennis
Lake City AAP	Missouri	Sibley
Aridisol		
Ft. Wingate	New Mexico	Doakum
Toole Army Depot	Utah	Kzin
Desert Chem. Depot	Utah	Kzin
Dugway	Utah	Kzin
Hawthorne	Nevada	Oricto
Pueblo Chem. Depot	Colorado	Stoneham
Entisol		
Savanna Depot Activity	Illinois	Wakeland

* Department of Energy sites at the Oak Ridge National Laboratory

All soils were gently ground with a mortal and pestle to pass a 250 μm sieve since it is the smaller particle size material that is more commonly ingested by children (Rodriguez and Basta, 1999). Soil properties were obtained from the NRCS database and from repeated or additional measurements in the laboratory. Soil properties included pH, cation exchange capacity (CEC), Fe- and Mn-oxide content, particle size distribution, and total organic and inorganic carbon (Table 3.2). The NRCS database has many of these soil properties already measured. Soil CEC and soil particle size distribution was obtained directly from the NRCS database. Soil pH was determined using double dionized (DDI) water and 5mM $CaCl_2$ in a 2:1 solution to 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 total carbon analyzer.

3.3.2 Contaminant Addition to Soil

Ten grams of soil was placed in a 200 ml glass centrifuge vessel along with 100 ml of 500ppm Cr (III) as $CrCl_3$, pH 4.0. The slurry was agitated on a reciprocal shaker for 2 days, centrifuged and the supernatant decanted for analysis. This was repeated 3 more times. After the forth addition of Cr, the soils were washed 3 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 30% moisture. The soils were kept in a container out of

Table 3.2 Select soil chemical and physical properties

	TOC (%)	TIC (%)	Clay (%)	Silt (%)	Fe (g/kg)	Mn (mg/kg)	CEC ($cmol_c/kg$)	pH (5mM $CaCl_2$)	pH (DDI)
Ultisol									
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	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	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
Alfisol									
Lawrence Ap1	0.91	0.59	19.50	48.50	11.17	1.35	5.8	4.97	5.27
Lawrence Bt1	0.11	0.10	25.80	34.30	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
Angola B21	0.09	0.25	25.6	52.9	5.83	0.19	4.5	7.86	8.13
Crider Ap	0.55	0.39	22.5	75.8	13.34	0.72	5.6	6.57	6.84
Crider B21t	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 Bt1	0.36	0.25	64.7	29.5	15.69	0.12	5.5	4.35	4.77

Table 3.2 Cont.

	TOC (%)	TIC (%)	Clay (%)	Silt (%)	Fe (g/kg)	Mn (mg/kg)	CEC ($cmol_c/kg$)	pH (5mM $CaCl_2$)	pH (DDI)
Inceptisol									
Berks A	2.72	1.01	15.7	46.6	13.18	0.15	9.1	3.65	3.91
Rockaway A1	3.55	0.62	12.4	34.8	14.03	0.52	10.6	3.86	3.98
Rockaway B2t	0.42	0.26	12.6	32.1	17.34	0.16	3.7	4.10	4.41
Weikert Ap	3.54	1.49	24.4	56.2	21.41	6.47	13.3	4.44	4.70
Weikert Be	0.21	0.18	23.9	54.3	28.98	5.42	8.0	4.28	4.65
Montevello A	3.97	2.37	6.0	69.0	10.68	1.42	8.0	6.91	7.18
Montevello B	0.42	1.15	19.0	42.2	22.07	0.17	14.0	4.23	4.87
Spodosol									
Charlton A2	2.30	0.40	2.9	26.5	1.33	0.00	11.7	3.15	3.57
Mollisol									
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	9.11	0.59	6.8	6.36	6.76
Aridisol									
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	6.86	0.16	7.0	6.87	7.39
Kzin A2	3.27	1.35	22.20	44.20	4.07	0.29	13.3	7.74	7.87
Kzin Bk	3.40	1.88	27.00	38.50	3.26	0.18	10.0	7.80	7.88

Table 3.2 Cont.

	TOC (%)	TIC (%)	Clay (%)	Silt (%)	Fe (g/kg)	Mn (mg/kg)	CEC ($cmol_c$/kg)	pH (5mM $CaCl_2$)	pH (DDI)
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
Entisol									
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

direct light and maintained at 30% water content in a moisture saturated environment (Appendix 1). The total chromium on the soil surface was determined based on the amount of chromium that was removed from the spiking solutions. This method of estimating solid phase bound Cr(III) agreed well with a more rigorous microwave assisted acid digestion (EPA Method 3052).

3.3.3. In Vitro Bioaccessibility

A physiologically based extraction test (PBET) was adapted from Ruby et al. (1996; 1999; Ruby, 2000, personal communication) to assess the in vitro bioaccessibility of Cr(III) from contaminated soils in humans. The PBET method has been found to agree with in vivo studies involving Pb contaminated soils (Ruby et al., 1996) and As contaminated soils (Rodriguez and Basta, 1999). Triplicate 0.39 g moist samples (0.3 g dry weight) 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 and agitated at 30±2 rpm for 1 hour. The method is designed to simulate the stomach digestive system in humans. Supernatant was separated from the solid via centrifugation (Appendix 1). The pH of the supernatant was measured to ensure that the final pH was within ±0.5 pH units of the initial pH. This scenario held for all cases. Thus, bioaccessibility is calculated as:

$$\%\ \text{Bioaccessibility} = \left(\frac{\text{Cr in PBET supernatant (mg/L)} \times 0.03\text{L} \div 0.3\text{g dry soil}}{\text{Cr on soil surface (mg/kg)}}\right) \times 100$$

3.3.4 Chromium Analysis

The PBET supernatant, soil spiking solution, and equilibrium solution were measured for Cr (VI) and Cr total (Cr_T). Cr(VI) was measured using a modified *s*-diphenylcarbohydrazide colormetric method (Bartlett and James, 1979) using a UV-VIS spectrophotometer at wavelength 540 μm (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 hr was insignificant. Total chromium was measured on a Perkin Elmer AAnalysist 800 atomic absorption spectrophotometer (Wellseley, PA). All standards used were made using an atomic absorption chromium standard (EM Industries, Hawthorne, NY). Cr(III) was calculated as the difference between Cr_T and Cr(VI).

3.3.5 Modeling

A multiple regression technique in the statistical software package SigmaStat 2.0 (Jandel Scientific, San Rafael, CA) 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.

3.4 Results and Discussion

3.4.1 Influence of Soil Properties on Cr Sorption

Chromium sorption and sequestration by the thirty six soils varied markedly with values ranging from 1276 mg/kg to 19982 mg/kg (Table 3.3). 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 ~3000 mg/kg to ~6000 mg/kg with four soils as high as ~20000 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 from the Desert Chemical Depot contained 27,000 mg Cr/ kg soil. Artificially contaminated Kzin soils in this study contained ~20,000 mg Cr/kg soil.

The large contrast in Cr(III) sequestration can be explained by the differences in soil properties. Multiple linear regression showed that four soil properties were important in determining the amount of chromium adsorbed by the soils: pH, TIC, clay content, and Mn-oxide content. The relationship describing chromium adsorption was: Cr(III) (mg/kg on soil) = -9737.481 - (1602.597 * mg/kg Mn) + (95.925 * % clay) + (6890.348 * % TIC) + (1764.116 * soil pH in DDI). Cr(III) sequestration by the soils was strongly correlated with these soil properties ($r^2 = 0.747$) suggesting that 75% of the variability in Cr(III) sorption could be described by pH, TIC, clay, and soil Mn-oxides. Incorporating the other measured soil properties from Table 3.2 (e.g. CEC, TOC, etc.) did not improve the model fit. The model was statistically rigorous at the 95% confidence level since P

Table 3.3 Cr(III) solid phase concentrations on the various soils and their corresponding bioaccessibility after 1 and 100 d aging

	C_T on Soil (mg/kg)	1 day % Cr(III) Bio.	100 day % Cr(III) Bio.
Ultisol			
Allen A	4275.20	3.60	1.79
Allen Ba	2284.54	10.03	5.79
Cecil Ap	2662.09	9.50	4.99
Cecil Bt1	3520.63	27.69	18.79
Minvale Ap	2421.67	14.83	7.98
Minvale Bt1	1276.05	55.42	36.02
Alfisol			
Lawrence Ap1	4333.51	15.54	6.94
Lawrence Bt1	3788.49	25.83	17.50
Angola Ap	10656.86	28.60	14.64
Angola B21	13001.64	2.48	1.26
Crider Ap	2867.27	43.97	26.68
Crider B21t	3270.95	65.32	42.00
Lenberg A	9104.17	27.16	18.20
Lenberg Bt1	8169.19	45.20	36.98
Inceptisol			
Berks A	6720.55	3.35	2.60
Rockaway A1	3017.54	9.56	5.31
Rockaway B2t	2153.95	23.34	15.84
Weikert Ap	5750.00	11.81	5.44
Weikert Be	3164.61	20.14	10.57
Montevello A	6012.57	18.76	6.93
Montevello B	2837.44	46.26	25.44
Spodosol			
Charlton A2	3497.60	13.61	10.47
Mollisol			
Dennis Ap	4137.37	16.80	11.82
Dennis Ba	3580.08	33.06	26.25

Table 3.3 Cont.

	C_T on Soil (mg/kg)	1 day % Cr(III) Bio.	100 day % Cr(III) Bio.
Mollisol cont.			
Sibley A	3821.46	34.57	23.79
Sibley B1	3884.45	43.89	30.63
Aridisol			
Doakum Ab	3151.92	24.81	13.21
Doakum Bt	5484.32	42.85	35.64
Kzin A2	19982.05	14.05	11.42
Kzin Bk	19912.63	15.03	12.39
Oricto A2	19641.46	12.14	9.12
Oricto Bt	19658.81	14.98	13.35
Stoneham A	3306.36	38.75	25.12
Stoneham Bt1	3746.82	41.37	30.47
Entisol			
Wakeland Ap	3376.64	40.81	26.61
Wakeland Cg1	2781.74	51.50	33.88

values for the independent variables were all below 0.05 (Table 3.4). Thus it can be concluded that the independent variables, the soil properties, significantly contribute to predicting the dependent variable, Cr sequestration. The Variance Inflation Factor (VIF) also suggested that collinearity between independent variables was not significant (Table 3.4). 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, although the Constant Variance Test failed, suggesting that the variance of the dependent variables was not 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) sequestration is enhanced by higher soil pH, more TIC (i.e. carbonates), more clay, and less Mn-oxides. 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 chromium on the soil increases. At low pH Cr(III) is adsorbed or complexed on soil negative charges while at a higher soil pH values, above 5.5, Cr precipitates 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) precipitit consisted of macromolecules with Cr ions in six coordination with water and hydroxy groups. A study 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.

Table 3.4 **Parameter estimates, standard errors, and statistics obtained from a multiple linear regression analysis that related soil properties to Cr(III) sorption.**

	value	std error	P	VIF
intercept	-9737.481	2316.804	<0.001	—
g/kg Mn	-1602.597	465.97	0.002	1.627
% clay	95.925	39.775	0.022	1.01
% TIC	6890.348	1157.925	<0.001	1.630
pH in DDI	1764.116	352.482	<0.001	1.122
r^2	0.747		<0.001	

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) sequestration. The mechanism of increased sequestration is most likely a localized pH effect at the carbonate surface, which promotes the formation of $Cr(OH)_3$ 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.

The model also shows a positive correlation between clay content and amount of chromium adsorbed. This was expected since clay minerals tend to be dominated by negatively charged sites on the surface due to isomorphic substitution (Klein and Hurlbert, 1993). These negatively charged sites attract the cation Cr^{3+} and a weak, electrostatic bond is formed. Further, clay minerals typically have a large surface area which is capable of accommodating large quantities of $Cr^{3+}$and $Cr(OH)_3$ precipitated phases. The more surface area a soil has, the more reactive sites the soil has, and consequently the more chromium that will adsorb to the soil.

The last factor controlling the amount of chromium the soils adsorbed were extractable manganese. The model indicated that soils with higher quantities of manganese oxides exhibited less tendency to sorb Cr. While manganese oxides can adsorb Cr(III), they also are extremely effective at oxidizing Cr(III) to Cr(VI) (Bartlett and Kimble, 1976; Bartlett and James, 1979; and Fendorf et al., 1992). The Cr(VI) anion is more mobile and less likely to adsorb onto the soil particles

3.4.2 Influences of Soil Properties on Cr Bioaccessibility

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 aging (Table 3.3). Bioaccessibility values were consistently higher for 1 d aging versus 100 d aging. For all soils the percent bioaccessibility ranges from 3.6% to 65.3% at day 1 and 1.8% to 42.00% bioaccessible at 100 days (Table 3.3). 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. Previous studies, discussed in Chapter 2, 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 versus the B horizons (Table 3.3). Bioaccessibility did not appear to be a function of soil order, suggesting that more detailed soil series data, as is used in the current study, was necessary for predictive purposes (Table 3.3). Cr(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 less than 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 in Chapter 2 of this thesis which showed limited bioaccessibility of Cr(VI) in several soils.

As demonstrated in Chapter 2 bioaccessibility values leveled off and reached near equilibrium after the first 50 to 100 days. 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: (1) % clay, % TIC, and pH and (2) % clay, % TOC and % silt. Using the independent variables from Table 3.2, the most significant model revealed that the bioaccessibility of Cr(III) on the soils was correlated with clay, TIC, and pH of the soil (Table 3.5). The relationship describing Cr(III) bioaccessibility was: % Cr(III) bioaccessible = 17.640 + (0.417 * % clay) – (10.152 * % TIC) – (429.329 * exp(-pH) with an r^2 value of 0.587 which indicated that as much as 59% of the variability in Cr bioaccessibility was explained by the model (Figure 3.1). The model was statistically rigorous at the 95% confidence level since P values for the independent variables were all below 0.05 indicating that they all contribute to predicting the % Cr(III) bioaccessibility (Table 3.5). 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 an issue 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 3.5). 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 and soil pH increase and the clay content decreases. As shown with the Cr sorption data,

Table 3.5 Parameter estimates, standard errors, and statistics obtained from a multiple linear regression analysis that related soil properties (clay, TIC, and pH) to percent Cr(III) bioaccessibility

	value	std error	P	VIF
intercept	17.64	3.475	<0.001	—
% clay	0.417	0.106	<0.001	1.038
% TIC	-10.152	2.383	<0.001	1.003
exp(-pH)	-429.329	204.554	0.045	1.036
r^2	0.587		<0.001	

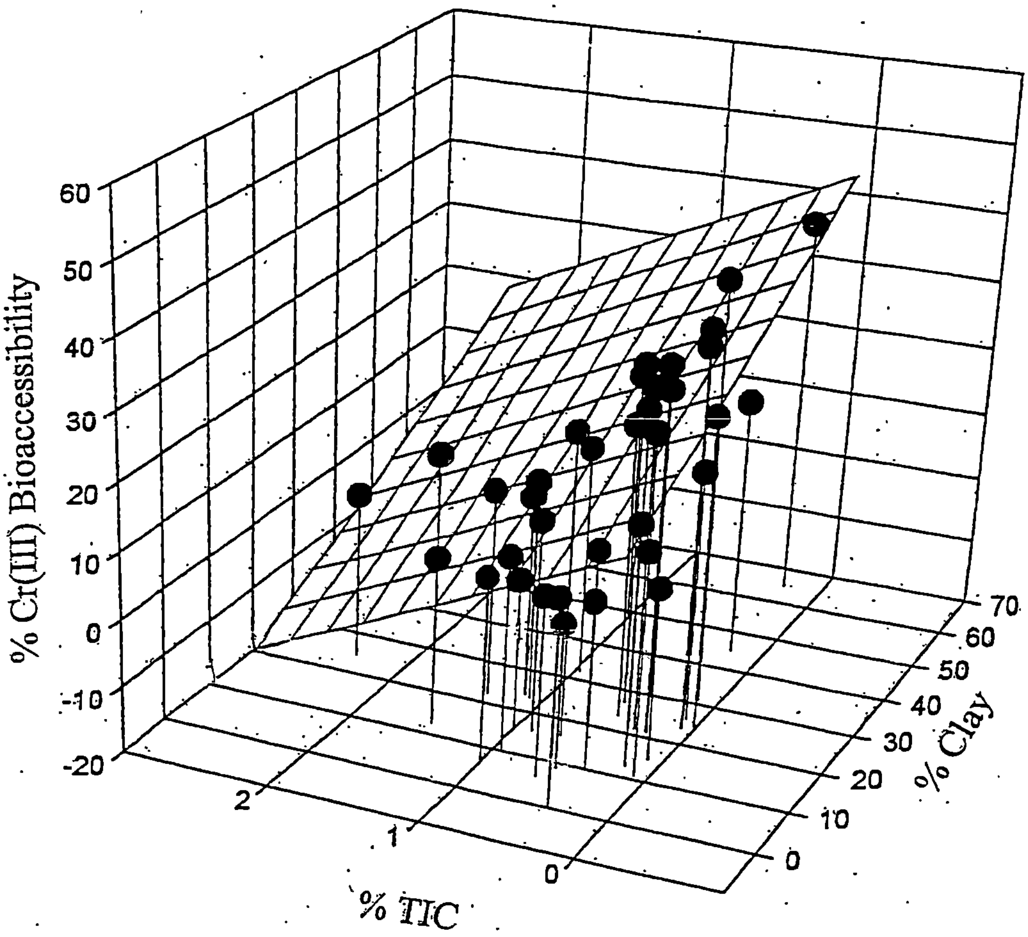


Figure 3.1 Model generated 3D representation relating the two most significant independent variables (% clay and % TIC) to the percent Cr(III)bioaccessibility. The observed (data points) and model fitted (grid surface) relationship between the two most significant independent variables (% clay and TIC) and % Cr(III) bioaccessibility using the model: % Cr(III) bioaccessible = 17.640 + (0.417 * % clay) – (10.152 * % TIC) – (429.329 * exp(-pH) with an r^2 value of 0.587.

Cr(III) sequestration is enhanced by soils with high levels of TIC and high pH. These conditions promote the formation of solid phase Cr(III) – hydroxides that are sparingly soluble, even under acidic conditions. These hydroxides (i.e. $Cr(OH)_3$) 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. Consequently as the TIC content and soil pH increase 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 chromium 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 chromium 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, silt, and TOC content of the soil (Table 3.6). The addition of pH and TIC did not improve the model fit when TOC was in the model. The relationship describing Cr(III) bioaccessibility was: % Cr(III) bioaccessible = 5.826 + (0.442 * % clay) + (0.195 * % silt) – (4.648 * % TOC) with an r^2 value of 0.595. Again this model was statistically rigorous at the 95% confidence level since P values for the estimated parameters were < 0.05 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. A P value of 0.197 for

Table 3.6 **Parameter estimates, standard errors, and statistics obtained from a multiple linear regression analysis that related soil properties (clay, silt, and TOC) to percent Cr(III) bioaccessibility**

	value	std error	P	VIF
intercept	5.826	4.421	0.197	—
% clay	0.442	0.103	<0.001	1.011
% silt	0.195	0.076	0.015	1.036
% TOC	-4.648	1.025	<0.001	1.045
r^2	0.595		<0.001	

the intercept simply suggests that the estimated value is not statistically different than zero. This model also passed the Normality Test and the Constant Variance Test. The model suggested that as the clay and silt content decreased and the TOC content increased and the % Cr(III) bioaccessible decreased (Figure 3.2). The trends regarding clay and silt content are consistent with the previous model and the limited bioaccessibility of Cr in the presence of higher system organic carbon 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 60% of the variability in Cr(III) bioaccessibility and should be useful for soils devoid of carbonates (TIC).

3.5 Environmental Significance

This study has shown that site assessments of soil metal bioaccessibility based solely on total soil metal concentrations do not accurately reflect the risk posed by the soils. The sequestering properties of soil significantly lower the percent of chromium bioaccessible upon ingestion of the otherwise labile chromium. Cr(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

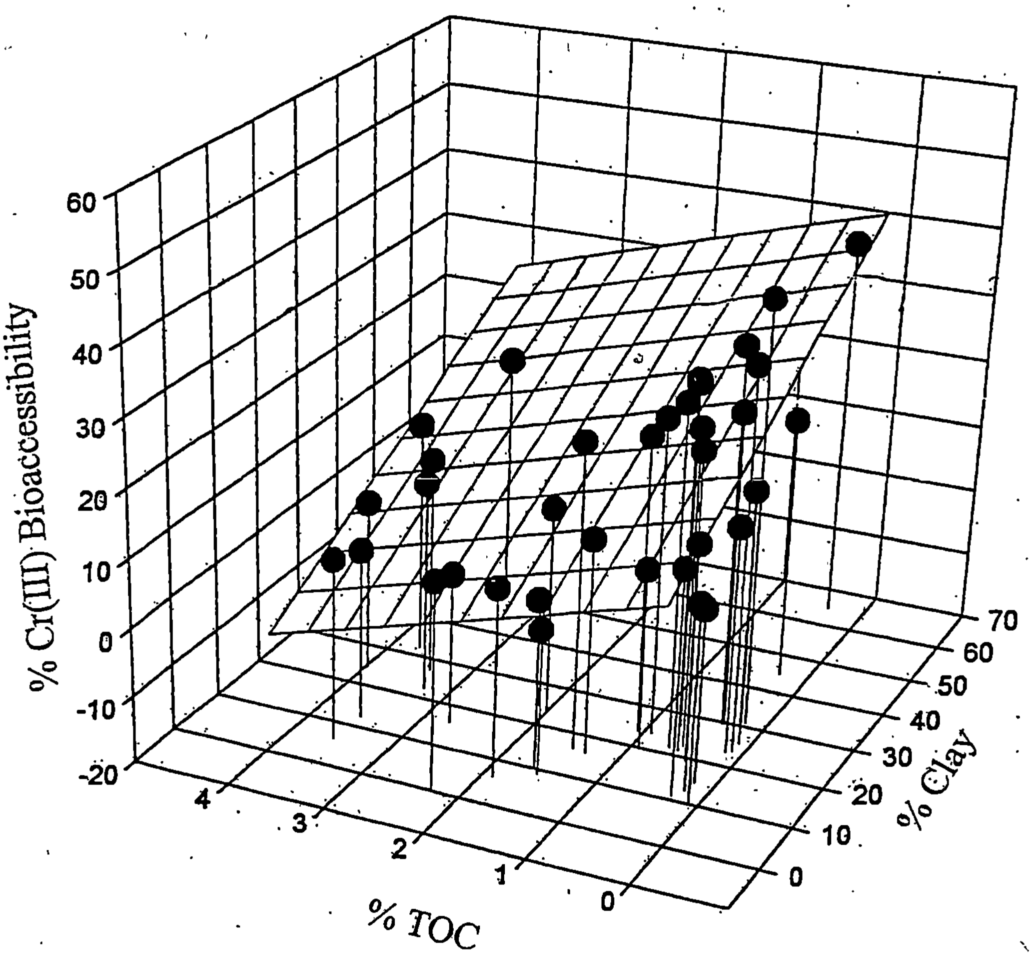


Figure 3.2 Model generated 3D representation relating the two most significant independent variables (% clay and % TOC) to the percent Cr(III)bioaccessibility. The observed (data points) and model fitted (grid surface) relationship between the two most significant independent variables (% clay and TOC) and % Cr(III) bioaccessibility using the model: % Cr(III) bioaccessible = 5.826 + (0.442 * % clay) + (0.195 * % silt) – (4.648 * % TOC) with an r^2 value of 0.595.

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 clean-up of contaminated DOD sites and others to a level safe for human use.

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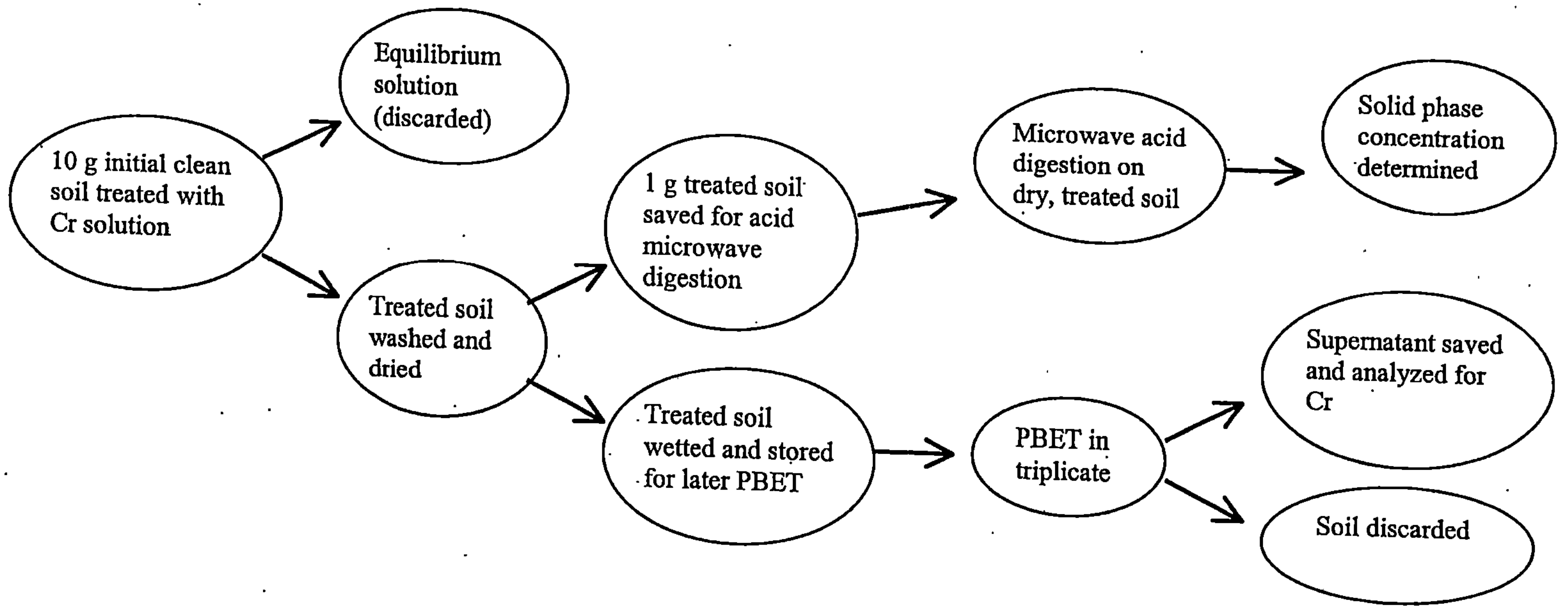
Appendices

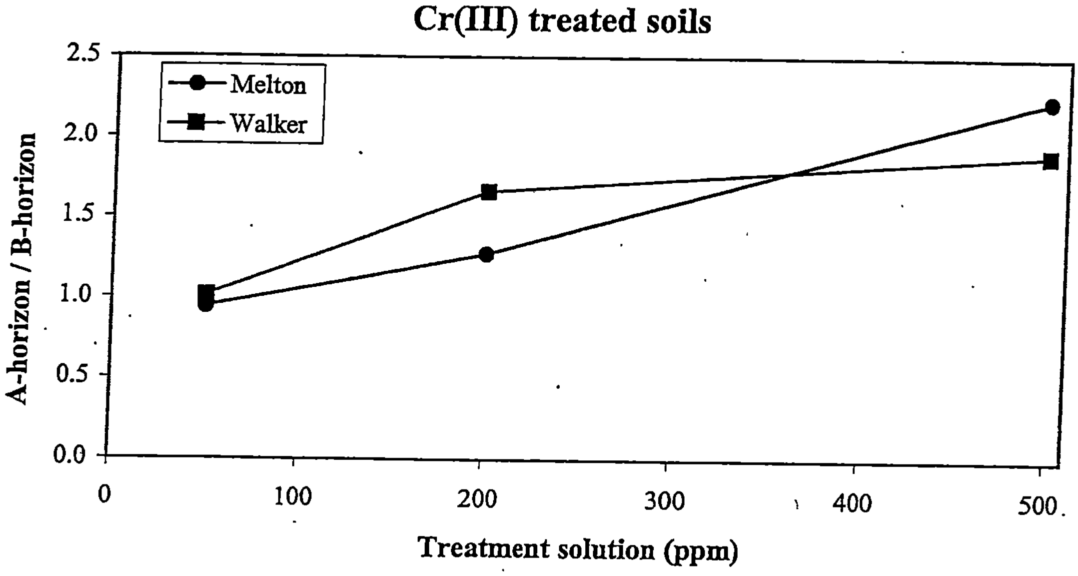
Appendix 1


10 g initial clean soil treated with Cr solution
Equilibrium solution (discarded)
Treated soil washed and dried
1 g treated soil saved for acid microwave digestion
Treated soil wetted and stored for later PBET
Microwave acid digestion on dry, treated soil
Solid phase concentration determined
PBET in triplicate
Supernatant saved and analyzed for Cr
Soil discarded

Appendix 2

Ratio of solid phase concentration of Cr on the A-horizon to the B-horizon at different treatment solution concentrations (ppm) of Cr(III) and Cr(VI)

a.



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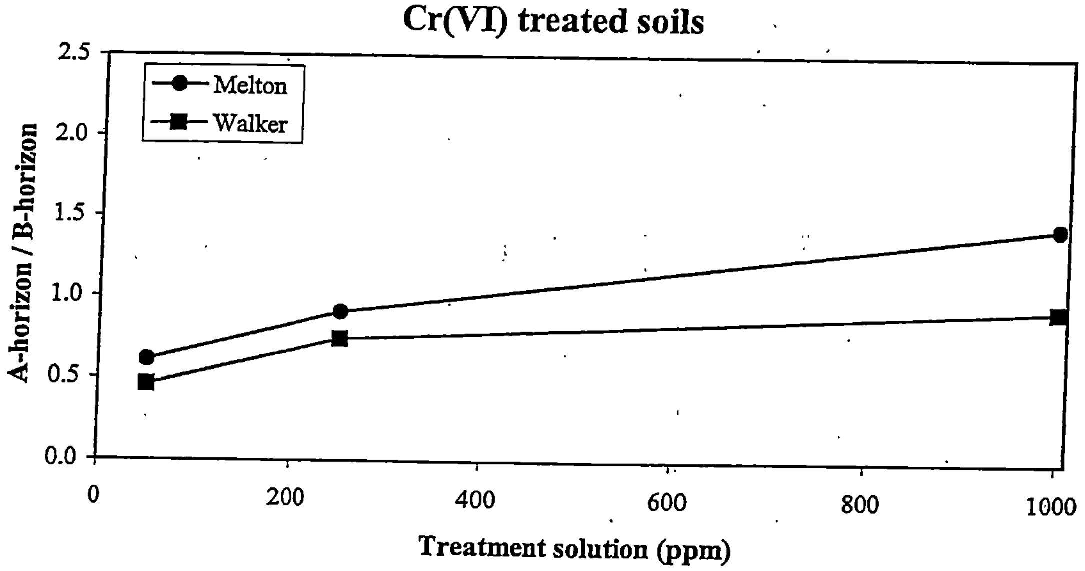

Appendix 3 Percentage of total Cr bioaccessibility desorbed from the solid phase as Cr(VI) as a function of time for soils treated with 250 and 1000 ppm Cr(VI)

	1 day	21 day	50 day	100 day	200 day
250 ppm	~~~~~~~~~~~~~~	~~~~~~~~~~~~~~	%	~~~~~~~~~~~~~~	~~~~~~~~~~~~~~
MV-A	28.73	61.90	78.02	64.91	46.26
MV-B	21.64	59.09	71.92	67.75	32.88
WB-A	16.54	22.86	57.28	28.61	26.38
WB-B	76.92	81.16	99.10	76.07	94.27
1000 ppm					
MV-A	3.81	15.29	6.31	44.09	21.89
MV-B	14.59	13.26	22.09	90.46	24.07
WB-A	4.23	8.15	4.31	31.53	21.25
WB-B	60.28	84.72	63.57	73.00	78.91

Vita

Melanie A. Stewart was born in Peoria, Illinois. After graduation from Farragut High School in Knoxville TN she attended the University of Tennessee at Knoxville minus the year that she was an exchange student at the University of Manchester, in England. While getting her B.A. in Environmental Studies at UT with a minor in Geology in 1998 she had the opportunity to work at Oak Ridge National Laboratory where she realized her love of scientific research. This experience gave her the opportunity to understand that she enjoyed the research aspect of science, and combined with her interest in geology she decided to obtain a Master's in the field of geology. In 1999 she started a Master's in Geological Sciences at the University of Tennessee under Dr. Larry McKay. She conducted her research at the Oak Ridge National Laboratory and was co-supervised by Dr. Philip Jardine.