ABSTRACT

Title of thesis:	HEXAVALENT CHROMIUM QUANTIFICATION AND REMEDIATION IN SOILS AND WASTE MATERIALS
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Hexavalent chromium (Cr(VI)) is a carcinogen and a pollutant of soils and natural waters. The standard method to extract and quantify total Cr(VI) in soils and waste materials was modified to prevent method-induced reduction of Cr(VI) by not heating (95°C) but shaking (100 cycles/min) at 23°C, followed by quantification using the 1,5-diphenylcarbazide method or ion chromatography. Forms of carbon and Cr(VI) (mineralogical vs. soluble) significantly influenced method-induced reduction. The proposed method should be used with samples containing ≥ 10 g/kg organic C. The new method was used to study the reduction of Cr(VI) in soils with Fe(II), Fe(III), and organic carbon, and the Cr in remediated soils was fractionated. Fe(II) in combination with Fe(III) was the most effective at reducing Cr(VI) and immobilizing newly-reduced Cr(III). The extraction and quantification refinements are relevant to accurate and precise metrics for Cr(VI) and its remediation in soils.

HEXAVALENT CHROMIUM QUANTIFICATION AND REMEDIATION IN
SOILS AND WASTE MATERIALS

By

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DEDICATION

I wish to dedicate this thesis work to my late father, Douglas DeSarle, who was my greatest proponent in everything I pursued.

ACKNOWLEDGEMENTS

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CHAPTER 1

**HEXAVALENT CHROMIUM QUANTIFICATION AND REMEDIATION IN
SOILS AND WASTE MATERIALS:
LITERATURE REVIEW**

Chromium Speciation and Analysis Overview

Chromium (Cr) is a transition element that exists by nature in the form of ores, and was first isolated from the mineral crocoite ($PbCrO_4$), by French chemist Nicolas Louis Vauquelin in 1797 (Enghag, 2004). Chromium is the 21st most abundant metal in the Earth's crust (Barnhart, 1997). Chromium is named after the Greek word *chromos* for color, and thus its first major applications were in the field of colored pigments (e.g. lead based paints), but eventually expanded to industrial processes such as leather tanning, chromium plating, timber preservation, and corrosion protection (Darrie, 2001; Enghag, 2004). For example, chromium sulfate ($Cr_2(SO_4)_3$) is used as a tanning agent for an estimated 90% of the global production of leather (Darrie, 2001; Foldi et al., 2013). Chromite ($FeO \bullet Cr_2O_3$) and chrome-magnesite ($MgO \bullet Cr_2O_3$) are used as refractories due to the high heat resistivity and high boiling point of chromite (Kotas and Stasicka, 2000).

Today, nearly all Cr for commercial use is mined and extracted from chromite ore ($FeO \bullet Cr_2O_3$). The insoluble trivalent Cr(III) is oxidized to soluble hexavalent Cr(VI) in a hot (1100-1150°C), alkaline (CaO is added to the ore) roast of the chromite ore; the chromate leachate is collected and used for commercial purposes (Burke et al., 1991; Darrie, 2001). The sodium chromate (Na_2CrO_4) and/or dichromate ($Na_2Cr_2O_7$) can be reacted to form potassium dichromate ($K_2Cr_2O_7$), ammonium dichromate (($NH_4)_2Cr_2O_7$), chromic acid (H_2CrO_4), chromic oxide (Cr_2O_3) and chromic sulfate ($Cr_2(SO_4)_3$) for a variety of Cr applications (Darrie, 2001).

Chromium waste generated and disposed of on land, wetlands and/or landfills has increased the concentration of Cr(VI) and Cr(III) in the soils, subjacent groundwater and nearby surface waters; the resulting global contamination is great cause for concern. The heavy metal can exist in oxidation states ranging from -2 to +6, but trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}) are the most commonly observed due to their stability in the pH and redox range of the environment (Losi et al., 1994; Fendorf et al., 2000). The speciation of Cr dictates the potential risk to the environment, as Cr(VI) is a carcinogen and Cr(III) is considered an essential nutrient with many health benefits (Anderson, 2000; NTP, 2008). Therefore, many remediation strategies are used to target reduction to Cr(III) with subsequent Cr(III) immobilization, since soluble Cr(III) salts and freshly-precipitated hydroxides can oxidize back to Cr(VI) in the presence of oxidants (e.g. Mn(III,IV)(hydr)oxides) in moist soils (Bartlett and James, 1979). In order to measure the success of a remediation, a reliable and robust method for total fractionated Cr(VI) and Cr(III) must be available. However, the potential oxidants and reductants that would cause inter-conversions of Cr(III) and Cr(VI) have proven to be problematic when attempting to extract Cr(VI) in soils and waste materials, followed by wet chemical analysis methods.

This research first identifies the issues with an Environmental Protection Agency's (EPA) extraction and analysis method (USEPA, 2014) and uses modifications to the method in order to include soils with highly reducing environments (Vitale et al., 1997). Once a reliable method was identified, a remediation by the reducing agents Fe(II), Fe(III), oxalic acid and compost was investigated and quantified with the established method. A literature review was conducted to determine all previous

knowledge within the method revision and remediation past and recent research, but first we must address the sources of Cr, the health effects and chemistry of Cr, and the characterization of chromite ore processing residue (COPR).

Sources of Cr

We encounter Cr on a daily basis. Chromium in soils is inherited from parent rock and tends to be higher in soils derived from volcanic and mafic parent materials (Kabata-Pendias and Pendias, 2001). An elevated amount of natural Cr concentrations (1,700-10,000 mg Cr/kg) was found by researchers in a 2009 study conducted on surface soils sampled from the Sierra Nevada and Coast Range geographic provinces in northern California, USA (Morrison et al., 2009). Serpentine rocks that are rich in Fe and Mg silicate minerals dominate the geochemical processes and mineralogy of this particular area. The ultramafic serpentine comprises Cr-rich minerals, i.e., chrome magnetite ($Fe^{2+}(Fe^{3+},Cr)_2O_4$) and chromite ($FeCr_2O_4$) (Morrison et al., 2009). Soils on serpentines typically contain from 2.0-4.0 g/kg Cr, which is much higher than the average worldwide surface soil content of 0.054 g/kg Cr (Kabata-Pendias and Pendias, 2001).

Through its presence in the soil, humans consume Cr in food and beverages, principally as Cr(III). The mean concentration of Cr ranged from 0.10 to 0.40 mg/L in canned beers sampled from Warri, Nigeria and included common brand names as Becks, Heineken, and Guinness Stout (Iwegbue, 2010). Food sources of Cr include broccoli, grape juice, mashed potatoes and turkey breast (Anderson et al., 1992). Trivalent Cr as an essential element and nutrient for plants, animals and humans is controversial and research results are contradictory, and will be addressed (Anderson, 2000; Vincent, 2010; Vincent et al., 2011).

Health Effects and Regulation of Chromium

Data on workers exposed to airborne Cr(VI) over an extensive period of time showed an increased risk of developing lung cancer (Langard, 1990), though the results were confounded by the high rate of smoking by such workers. Recent studies have shown Cr(VI) to cause cancer and certain mutagenic disorders via oral ingestion in drinking water over a lifetime. In July of 2008, the National Toxicology Program (a part of the NIH) released a report on the carcinogenic effects of sodium dichromate dihydrate ($Na_2Cr_2O_7 \cdot 2H_2O$), a common Cr(VI) containing-chemical. Dosages equivalent to 0, 5, 20, 60, or 180 mg Cr/L were given to 100 rats and dosages equivalent to 0, 5, 10, 30, or 90 mg Cr/L were given to 100 mice, both in their drinking water. The conclusion of the two-year drinking water study was that exposure to Cr(VI) caused cancer, based on increased incidences of tumors in the small intestine of mice (within the duodenum, jejunum, and/or ileum) (NTP, 2008). The researchers also saw a significant increase in the incidence of squamous cell carcinoma, a type of oral cancer, when experimenting with rats (NTP, 2008; Stout et al., 2009). Besides being mutagenic, Cr(VI) is also corrosive and allergenic (Burke et al., 1991).

Due to its high solubility, Cr(VI) readily enters and damages cells. The disorders caused by Cr(VI) have been studied thoroughly and a principal, proposed mechanism is during reduction of Cr(VI) to Cr(III) in cells, a reactive carbon-based radical species is formed from the oxidation of a carbon-based reductant, such as ascorbic acid (Vitamin C), which is regularly found in the body. It has been suggested that this unidentified and yet to be discovered carbon-based radical causes DNA strand breakage and other types of chromosomal changes (O'Brien et al., 2003). A second hypothesis suggests that a

hydroxyl radical (•OH), generated from Cr^{3+} and reactive intermediate species Cr^{5+} in the presence of elevated levels (mM) of H_2O_2, may also lead to oxidative DNA damage and strand breaks (O'Brien et al., 2003). Another hypothesis is that Cr(V) and Cr(IV) are reactive intermediates that are toxic as potent oxidants (Myers, 2012).

Conversely, Cr(III) is not toxic and is generally considered an essential trace nutrient for both humans and animals. Trivalent Cr is hypothesized to increase insulin sensitivity, which allows the assimilation of glucose, insulin and lipids and, when delivered as chromium picolinate ($Cr(C_6H_4NO_2)_3$), exhibits an overall antidepressant effect (Anderson, 2000; Davidson et al., 2003; Franklin and Odontiadis, 2003). The Institute of Medicine (IOM) advises a daily intake of 25 and 35 μg Cr(III) for females and males, respectively (IOM, 2001). Absorption of inorganic Cr(III) ranges from 0.4 to 2% of a daily intake of 40-240 μg, while organic Cr(III) is estimated to be greater than ten times more bioavailable (Lyons, 1994; Pechova and Pavlata, 2007). Chromium physiological demand in humans and animals increases during high stress periods due to increased glucose levels, thereby quickening the mobilization of the Cr reserves in the body, and eventually eliminating the Cr via urine excretion (Borel et al., 1984; Mertz, 1992; Pechova and Pavlata, 2007).

Chromium is not essential for plants, but growth is elevated at low to moderate concentrations of Cr(III) (Singh et al., 2013). For example, Cr(III) supplementation in nutrient solution at concentrations of 1 mM Cr(III) for 2 days stimulated growth in the aquatic plant, water hyacinth (*E. crassipes*), as well as increasing chlorophyll pigments and photosynthesis (Paiva et al., 2009; Singh et al., 2013).

Nevertheless, some authors today do not recognize Cr(III) as an essential nutrient for human health (Vincent, 2010; Vincent et al., 2011). Vincent (2010) completed a literature review of the biochemistry of Cr(III) over the past two decades and concluded that the data to this point in time does not definitively establish Cr(III) as an essential element, and agrees with the former head of the United States Department of Agriculture (USDA) Forrest Nielson, in that we need to identify a biomolecule that binds with Cr and subsequently results in a complex with a confirmed role in the body. Vincent et al. (2011) used a diet that contained as little Cr as possible (16 μg Cr/kg) that could reasonably be provided to rodents and the comparison of the low treatment to the Cr-supplemented treatments showed no effect on body mass, food intake, glucose metabolism or insulin sensitivity.

The federal drinking water standard in the United States (0.1 mg/L) is based on total Cr in solution, due to the possible reduction-oxidation inter-conversions of Cr(III) and Cr(VI) (USEPA, 2012). That way, 100% Cr(VI) is assumed and the greatest potential risk can be addressed. In comparison, the total Cr drinking water standards for Kazakhstan, Germany, and the United Kingdom are 0.0031, 0.05, and 0.05 mg/L, respectively. Japan has a drinking water standard for just Cr(VI) set at 0.05 mg Cr(VI)/L (ICDA, 2001).

In 2008, EPA began a comprehensive review of the health effects of Cr(VI) to determine whether this standard is low enough, but has yet to come to a decision. The maximum contaminant levels (MCL) are a set, enforceable regulation for total Cr, while maximum contaminant level goals (MCLG) are based on exposure over a lifetime and are not enforceable (USEPA, 2013). States may set lower (or more stringent) MCLGs and

MCLs for total Cr than EPA. The current MCL for California is set at 0.05 mg Cr/L, but a MCL specific to Cr(VI) of 0.01 mg Cr(VI)/L is under review, and anticipated to be enforced in 2014 (CDPH, 2014). New Jersey is considering lowering the MCL from 100 µg/L to 0.07 µg/L, but acknowledged that they do not have instrumentation with detection limits that low (NJDWQI, 2010). This was one of the primary reasons for the development of a new ultra-low LOD ion chromatography method/instrumentation for Cr(VI) in drinking water released in November 2011 (USEPA, 2011), which will be addressed after a review of Cr chemistry in the environment.

The Chemistry of Chromium in the Environment

Hexavalent Cr is a strong oxidizing agent and exists as a tetrahedral, oxyanion (Avudainayagam et al., 2003). Beginning with chromic acid occurring in the acidic range (pH 0), and progressing to highly alkaline conditions, the dominant species for Cr(VI) is as follows: H_2CrO_4 (pH <1), $Cr_2O_7^{2-}$ ($6 \geq pH \geq 2$ and at concentrations > 10 mM), $HCrO_4^-$ ($6 \geq pH \geq 2$ and at concentrations < 10 mM), and CrO_4^2 (pH $\geq$ 6) (Losi et al., 1994; Brito et al., 1997). In acid solution with concentrations of Cr(VI) greater than 10 mM, the anion $HCrO_4^-$ loses a water molecule and dimerizes to the orange-red dichromate ion $Cr_2O_7^{2-}$, represented by equation 1 (Brito et al., 1997; Avudainayagam et al., 2003).

$$2\ HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \qquad (1)$$

Sorption of Cr(VI) on mineral surfaces is another important phenomenon controlling the speciation of Cr in soils. Anion sorption reaches a maximum close to the pKa of its conjugate acid, and if it is polyprotic (e.g. H_2CrO_4) then its maximum is with the more acidic pKa (Sparks, 2003). Sorption can be as inner- or outer-sphere complexes.

Inner-sphere is through a ligand exchange mechanism between the metal and the surface and outer-sphere is by electrostatic attraction to positively charged surface sites, with a water molecule between the surface functional group and the bound ion. Inner-sphere complexation is generally slower, but often not reversible. The point of zero charge (PZC), or the pH at which a surface has a net charge of zero, is another important factor in sorption. If the pH < PZC, the surface has net positive charge, and therefore attracts and sorbs Cr(VI) anions. Iron and Al oxides have high PZC values, making them more likely as sorption sites in soils, compared to silica, soil organic matter and clay minerals with low or nonexistent PZCs (Sparks, 2003). The PZCs of pure Fe and Al oxides are approximately pH 8. Conversely, the PZCx of Si-OH (silanol), organic matter, and clay minerals (e.g. montmorillonite) are at or below pH 2 (Sollins et al., 1988; Sparks, 2003).

Sorption can proceed to precipitation if thermodynamically favorable. For example, a surface complex involving the coprecipitation of ions from both the bulk solution and the ions dissolved from the sorbent favors surface precipitation since the IAP at the surface of the precipitate is greater than that of the bulk solution (Sposito, 1986; Selim and Iskandar, 1999). Another reaction following sorption is reductive dissolution, where the sorbed species is capable of donating electrons to a chemical component of the oxide surface. For example if it is an Fe(III) oxide surface, once the electron transfer occurs from the reducing agent (e.g. oxalate), it induces the detachment of that newly reduced species (Fe^{2+}) (Schwertmann, 1991). Conversely, Deng et al. (1996) found Cr(VI) sorption onto the Fe(III) (hydr)oxide magnetite (Fe_3O_4) was followed by an electron transfer on the surface causing reduction of Cr(VI) to Cr(III) by structural Fe(II), as opposed to reduction of chromate by Fe(II) in solution. This

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processes is known as reductive precipitation. Although the structure of the Cr(III) product could not be identified, it was demonstrated that the chromium was immobilized, consistent with formation of a surface precipitate as opposed to the easily reversed adsorption of the chromate anion (Deng et al., 1996). Furthermore, soil surfaces (e.g. TiO_2, α-FeOOH, γ-Al_2O_3) can catalyze reduction of Cr(VI) in the presence of organic reductants via the formation of an activated *Cr(VI) species (Deng and Stone, 1996a; Deng and Stone, 1996b). Cr(VI) becomes adsorbed onto the surface area and then activated to *Cr(VI) either by transition from outer- to inner-sphere adsorption or the exchange of ligands at the Cr(VI) center or other similar phenomena that can change the stoichiometry, configuration, and reactivity of adsorbed Cr(VI) (Deng and Stone, 1996b). It is unknown whether or not the absorption of the organic compound is necessary for the Cr(VI) reduction to progress (Deng and Stone, 1996a; Deng and Stone, 1996b).

Sorbed Cr(VI) (released with added $H_2PO_4^-$ and operationally-defined as exchangeable Cr(VI)) has been compared to the sorption energy of $H_2PO_4^-$ because it is sorbed much more strongly than ions such as Cl^- or SO_4^{2-} (Fendorf, 1995). Sorption behavior of Cr(VI) onto Fe(III), Cr(III), and coprecipitated Fe(III)/Cr(III)(hydr)oxides has also been characterized and generally deceases with increasing pH, since there is more positive charges on pH-dependent sites at low pH. As previously mentioned, coprecipitation occurs when ions from the aqueous soil solution precipitate with the ions from the dissolution of a mineral (Sparks, 2003). Additionally, the coprecipitated Fe(III)/Cr(III)(hydr)oxides were retained more Cr(VI) than did pure Fe(III)(hydr)oxides, throughout the entire pH range (Tzou et al., 2003). They hypothesized that the higher retention by Fe(III)/Cr(III)(hydr)oxides could have been due to slow exchange of sorbed

Cr(VI) with OH⁻ on the Cr(III) surface, or due to complexes between Cr(VI) and Cr(III), or even that the sorbed Cr(VI) became entrapped in the (hydr)oxide structure. A study by Adhikari (2010) also showed Cr(VI) sorption to increase in the presence of heavy metal cations (Pb, Cd, Ni, and Zn) due to their role in neutralizing negative charges. Lastly, the maximum adsorption of Cr(VI) on a synthesized Fe(III) oxide (hematite (Fe_2O_3)) occurred at pH 2-3 with a plate-like morphological shape as opposed to hexagonal, rounded or spherical morphologies (Adegoke et al., 2014). The morphology was confirmed by use of a scanning electron microscope (SEM).

Anionic Cr(VI) has greater mobility and bioavailability than Cr(III) in soils and surface waters (Fendorf et al., 2000). Trivalent Cr in the environment is principally in cationic species, instead of the Cr(VI) oxyanion, and the soluble cation Cr^{3+} exists at pH ≤ 4 while its hydrolysis products ($CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_4^-$) mostly dominate from pH 4-8 (Losi et al., 1994; Fendorf, 1995). At pHs greater than 5.5, the Cr(III) is likely to precipitate as insoluble Cr(III), $Cr(OH)_3$, which has a Ksp of 10^{-12} (mol/L) at pH 7 (James and Bartlett, 1983a; James and Brose, 2013). It can also coprecipitate with Fe(II) in aqueous environments with pH>5 and >3.6 μmol Cr/L concentrations (Jardine et al., 2011). However, if organic acids are present, Cr(III) may remain soluble, even in alkaline conditions (Avudainayagam et al., 2003). For example, Cr(III) in citric acid (Cr^{3+}-citrate) remained soluble up to pH 7-7.5 (James and Bartlett, 1983b).

Trivalent Cr can form precipitated minerals and be bound by organics, in addition to having strong sorption kinetics that are dependent on the geochemical parameters of soils, such as organic C content, type of clay mineral, and presence of complexing

ligands and inorganic cations (Avudainayagam et al., 2003). Similar to the Cr(VI) anion being attracted to positively charged surfaces, the cationic Cr(III) is most commonly associated with negatively charged ones. Due to the predominance of negative charges in soils, Cr(III) k_d values (adsorption parameter or partition coefficient) for different soil types have been shown to be orders of magnitude greater than for Cr(VI) (Hassan and Garrison, 1996). In a study conducted by Jardine et al. (2011) high Cr(III) retention in the forms of Cr^{3+} and $CrOH^{2+}$ was observed in two soils with high clay contents, high surface area aluminosilicates and low pH (pH 4). Chromium(III) outcompeted the counter ion Ca^{2+} on exchange sites. However, a third soil high in Mn(III,IV)(hydr)oxides exhibited significantly lower Cr(III) sorption; the authors attributed this to a lower concentration of Cr, which allowed the solid phase to takeover buffering, raising the pH to 7 where Cr either precipitated or was oxidized to Cr(VI). Hydrolysis of $CrOH^{2+}$ will make the sorption more "irreversible," due to the surface-induced hydrolysis and precipitation of $Cr(OH)_3$ (Jardine et al., 2011).

The most likely speciated form of Cr(III) and Cr(VI) is dependent on soil mineralogy and reduction-oxidation reactions. The incorporation of Cr(III) and Cr(VI) into interlayers of minerals is a topic closely related to chromite ore processing and will be discussed next. The reduction-oxidation reactions of Cr will then be discussed in relation to potential remediation arrangements used in this study.

Chromite Ore Processing Residue (COPR)

Chromite ore processing factories were run unregulated for decades. From 1905 to 1976, Hudson County, NJ, USA served as a chief center for chromate (CrO_4^{2-}) and

dichromate ($Cr_2O_7^{2-}$) chemical manufacturing, with two facilities in Jersey City and a third in Kearny, NJ (Burke et al., 1991). The chromite ore processing residues (COPRs) used in our studies are surface materials from Kearny, NJ and contain up to 6500 mg Cr(VI)/kg soil. COPR is the residual, soil-like material from two separate processes of roasting and leaching the chromite ore. These three facilities alone produced approximately 2.75 million tons of COPR, making the improper disposal of such an extraordinary amount of waste a lingering problem and legacy pollution, requiring cleanup (Chrysochoou et al., 2009). Many of the contaminated sites in NJ have been capped with asphalt and have resulted in the effective prevention of Cr(VI) from reaching the ground surface or further migration to groundwater, and thus direct human exposure (Henry et al., 2007). Other uses of the COPR waste include the recovery of the makings (Fe and Cr) for chrome steel, a valuable construction material. In order to extract the Fe, COPR must be thermally treated using techniques in steel manufacturing. In an anoxic environment with high temperatures (1450°C–1500°C for 1 hour) and sufficient graphite as a reducing agent, the separated metal had Fe/Cr ratio between 14% and 18%, a suitable range for stainless steel (Meegoda and Kamolpornwijit, 2011).

Further south in Baltimore, MD, USA, chromite ore was processed from the 1820s to the mid-1980s, and the residue was used as a fill material throughout the Baltimore Harbor waterfront (Graham et al., 2009). Sample collection of 22 sites in the harbor between 2005 and 2007 indicated a wide range of total Cr, from 2.5 to 1050 mg Cr/kg (Graham et al., 2009). Outside the United States, another prominent area of Cr contamination from chromite ore processing exists in Glasgow, Scotland. Of 27 soils sampled, the soil total Cr ranged from 65-3680 mg Cr/kg (Broadway et al., 2010).

Chromium(VI) ranged from 6 to 40% of the total Cr content. Hudson County, NJ, Baltimore County, MD and Glasgow, Scotland constitute the three most intensely studied areas for COPR deposition, characteristics, and possible remediation strategies.

COPR material is highly alkaline (at or above pH 8), therefore, it still contains an array of soluble Cr(VI) salts that can percolate with water down into the subjacent soil, and can also be precipitated at the surface via capillary action (Burke et al., 1991). Dermatas et al. (2006) compared the sampling and laboratory testing (e.g. mineralogy and metals) techniques of the NJ COPR to those of soil in order to determine whether or not it should be considered a hazardous contaminated soil or a hazardous soil waste. A solid waste, as defined by the Resource Conservation and Recovery Act (RCRA) is "any discarded, abandoned or recycled material," and soil, as defined by the United States Environmental Protection agency (USEPA), is "unconsolidated earth material overlying bedrock and composed of clay, silt, sand or gravel as classified by the U.S Natural Resources Conservation Service (NRCS), or a mixture of such materials that are inseparable from liquids, sludges and/or solids." The lawful requirement of excavation and subsequent off-site disposal (solid waste) vs. on-site treatment (soil) of the hazardous material strongly depends on the characterization between solid and soil. The authors ultimately concluded that COPR should be classified as a hazardous, contaminated soil. Some of the reasons given were the laboratory testing for physical and mechanical properties are the same as soil and yielded similar results, COPR is intermixed with soil and soil minerals that are inseparable by simple physical or mechanical means, and that COPR as a filling material was unsuccessful due to shrinking and swelling, similar to that of a soil (Dermatas et al., 2006).

The mineralogy of COPRs has been identified using X-Ray Powder Diffraction (XRPD), and largely depends on where the sample was taken. For example, some of the major mineral phases (crystalline and paracrystalline) identified in the COPR from Jersey City, NJ were brownmillerite ($Ca_4Al_2Fe_2O_{10}$), brucite ($Mg(OH)_2$), calcite ($CaCO_3$), quartz (SiO_2), hydrotalcite ($4MgO \cdot Al_2O_3 \cdot 10H_2O$), and katoite ($Ca_3Al_2(H_4O_4)_3$) (Wazne et al., 2008). In contrast, a study on the land where sodium chromate, chromium salts and chromium sulfate were previously manufactured in India, the authors observed the primary composition to be calcium chromate ($CaCrO_4$), calcium aluminochromate ($3CaO \cdot Al_2O_3 \cdot CaCrO_4$), tricalcium chromate ($Ca_3(CrO_4)_2$), basic ferric chromate ($Fe(OH)CrO_4$), and potassium iron chromates ($KFe_3(CrO_4)_2(OH)_6$ and $KFe(CrO4)_2 \cdot 2 H_2O$). According to Kanchinadham et al. (2013), the major constituents of COPR were Cr, Ca, Mg, Al, and Si.

Narrowing the scope of our investigation to COPR mineral phases, knowledge of Cr(VI)-bearing phases is valuable in order to target their dissolution, so that the resulting soluble Cr(VI) can be reduced by the added reductants in a remediation. The host phases of Cr have been identified as layered double hydroxides (LDH) that can substitute Ca, Mg, Al, and Fe in the octahedral sheet and Cl^-, CO_3^{2-} or CrO_4^{2-} in the interlayer (Chrysochoou et al., 2009). Katoite (a hydrogarnet) ($Ca_3Al_2(OH)_{12}$) has been shown to be a host phase for Cr(VI), and calculations based on its abundance as the crystalline phase in millions tons of COPR in Glasgow, indicated that as much as 50% of the Cr(VI) content of the COPR can be found in hydrogarnet (Hillier et al., 2007). Hydrogarnet is a common COPR mineral, identified in sample sites ranging from Glasgow, Scotland to Jersey City, USA and Baltimore, USA (Geelhoed et al., 2002; Chrysochoou et al., 2009;

Chrysochoou et al., 2010). The only known Cr(VI)-bearing mineral identified by Wazne et al. (2008) in their NJ samples was calcium aluminum oxide chromium hydrate (CAC) ($Ca_4Al_2(OH)_{12}CrO_4 \bullet nH_2O$), also known as Cr(VI)-hydrocalumite, and other studies have confirmed this phase as a primary Cr(VI)-bound mineral (Geelhoed et al., 2002; Hillier et al., 2003; Chrysochoou et al., 2009; Chrysochoou et al., 2010). The chromate anions (CrO_4^{2-} and $HCrO_4^-$) are held in the interlayers of CAC (Wazne et al., 2008). Brownmillerite ($Ca_2(Fe,Al)_2O_5$) is considered a "parent," mineral of COPR due to its formation during the roasting process, and may contain Cr^{3+} substituting for Fe and Al (Hillier et al., 2003; Chrysochoou et al., 2010). Hillier et al. (2003) showed brownmillerite to account nearly 15% of total Cr, representing a significant pool for Cr(III). Chromium(VI) has also been identified in ettringite ($Ca_6Al_2(OH)_{12}(CrO_4)_3 \bullet 26H_2O$), but in lower amounts and likely in the pH range of 9-11.2 (Geelhoed et al., 2002; Hillier et al., 2003).

The release of all forms of Cr(VI) from COPR is highly dependent on the Cr(VI)-containing solid phases (Geelhoed et al., 2002). Wazne et al. (2008) did a thorough study on the solubility of their NJ COPR sample and observed that at pH < 10, most of the Cr(VI) bearing minerals became unstable and their dissolution contributed to an increase in Cr(VI) concentration in solution. The authors suggested that hydrotalcite ($[Mg_3Al(OH)_8]_2CO_3 \bullet nH_2O$) controlled the solubility of Cr(VI) through anion substitution in the pH range 8-11. All Cr was released when 32eq H^+/kg of acid was added to the dried COPR, to achieve a pH of 1.5 (Wazne et al., 2008).

Non-COPR Hexavalent Chromium Contamination

Hexavalent Cr pollution extends beyond chromite ore processing. Leachate from leaking and unlined coal ash dumps has become a sizeable issue in the United States. Coal ash dumps are not federally regulated, and in a 2009 EPA report, coal ash waste taken from power plants in Michigan, Alabama, North Carolina, Florida and Wisconsin was used in a leaching test. The leachates measured over 11 to 35 times higher than 100 µg Cr/L or the current federal drinking water standard (Evans et al., 2011).

China is also struggling with both air and water Cr emissions from industrial sources that include, but are not limited to, fossil fuel combustion, waste incineration, chromium metal production, and leather tanning. There is a small amount of Cr in coal (estimated to be 10 mg/kg), but the large amounts of coal use increase the Cr concentrations by several orders of magnitudes; in 2009 the Cr emissions in China from coal combustion alone were 8,880 tons (NRC, 1974; Cheng et al., 2014). The amount of Cr(III) oxidized to Cr(VI) during the process of coal combustion depends on the heat, O_2 content, and type of fuel used (Cheng et al., 2014). The compiled data on anthropogenic Cr emissions from 1990 to 2009 in China indicate approximately 1.92×10^5 tons of Cr were discharged to the atmosphere, with coal and oil combustion as the leading sources. Leather production and metal fabrication were the leading contributors to water discharge, which was approximately 1.34×10^4 tons (Stam et al., 2011).

Chromium spills, leaks and/or emissions are an unfortunate occurrence in the world today. To replicate such incidences, this thesis investigates the behavior of previously uncontaminated soils, spiked with a soluble Cr(VI) solution.

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Methods of Measuring and Extracting Chromium(VI) in Environmental Samples

Measuring Cr(VI)

Total soluble Cr is quantified as the sum of all Cr species present. A common analytical technique to measure total Cr is inductively coupled plasma (ICP), paired with various detections such as mass spectrometry (MS) or atomic emission spectrometry (AES). A graphite furnace and flame atomic absorption (FAA) spectrophotometer can also be used (Parks et al., 2004; Rakhunde et al., 2012). These methods are applicable for prepared aqueous samples.

The speciation of Cr(III) and Cr(VI) is vital for assessing potential risk in any given environmental situation, as described above for human health, soil contamination, and environmental fates of the heavy metal. For aqueous samples (either collected in the field or extracted from soils), one of the most sensitive methods to obtain Cr(VI) and Cr(III) simultaneously is to separate the two oxidation states using high-performance liquid chromatography (HPLC) and then detect and quantify them with inductively coupled plasma (ICP) coupled with mass spectrometry (MS) (HPLC-ICP-MS) (Rakhunde et al., 2012). However, the more common approach is to use a speciation technique for Cr(VI), obtain total Cr separately, and through subtraction, calculate soluble Cr(III). A spectrophotometric method that follows a colorimetric reaction with diphenylcarbazide (DPC) in acid solution is a common way to measure Cr(VI) in solution. At the pH of the DPC solution (pH ≤ 2), Cr(VI) is rapidly reduced to Cr(III), followed by complexation of newly-reduced, unhydrated Cr^{3+} by diphenylcarbazone, the oxidized form of diphenylcarbazide (Bartlett and James, 1979; Huo et al., 1998). According to EPA protocol, when analyzed by a spectrophotometer this method is known

as Method 7196A, but when analyzed by an ion chromatograph using separation on an exchange column it is Method 7199 (USEPA, 2014). In this EPA-certified, ion chromatographic method, through interaction of charges with a solid, positively charged resin in a column, ions are separated based on charge, size, and molecular weight. As mentioned earlier, Method 7199 was modified to measure Cr(VI) at lower concentrations in Method 218.7. The differences between the two methods include an eluent flow rate decrease from 1.5 to 0.7 mL/min and a post-column flow rate decrease from 0.50 to 0.22 mL/min for the most recent method (USEPA, 2011). The published EPA method states the lowest concentration minimum reporting levels (LCMRLs) as a range from 0.012 to 0.036 μg/L. A LCMRL is the lowest spiking concentration that has a 99% probability of spike recovery in the 50% to 150% range. The method can qualitatively detect Cr(VI) as low as 0.005 μg/L (USEPA, 2011). There are two potential interferences for any method employing the DPC reaction and that is (1) solubilized reducing agents that are not oxidized or precipitated can compete with DPC to reduce Cr(VI) at the acidic pH of the reaction and (2) some soluble humic and fulvic compounds absorb light at the same wavelength as does the Cr(III)-DPC complex (540 nm) (Pettine and Capri, 2005a,b). Due to anion separation on the anion separator column, these interferences are less problematic in the ion chromatograph methods, but still possible, especially when used as in the EPA method 7199 and the newly-developed ones (USEPA, 2011; USEPA, 2014)

Extraction of Solid Samples

To extract Cr(VI) from a soil, waste, or other solid sample, one must use (1) an extraction method and (2) a post-extraction quantification procedure, discussed above. EPA's SW-846 Method 3060A is a widely accepted extraction that aims to solubilize all

forms of Cr(VI) in the samples, precipitate any solubilized Cr(III), and prevent oxidation of native Cr(III) to Cr(VI) or reduction of native Cr(VI) to Cr(III) (Pettine and Capri, 2005a). The samples are digested in an alkaline solution (0.28 M Na_2CO_3/0.5 M NaOH) and heated at 90-95°C for 1 hour (USEPA, 2014). Under the high temperature and pH of the extraction (≥11.5), solubilized reducing agents (e.g. iron(II), organic C, and sulfides) are favored to react with dissolved atmospheric O_2, instead of Cr(VI) (Pettine and Capri, 2005a). High carbonate soils also favor the oxidation of Fe(II) by O_2, which balances the diminished concentration of O_2 that comes with high temperatures (90-95°) (Pettine and Capri, 2005a). However, the reduction of Cr(VI) by Fe(II) remains theoretically possible in this pH range, and even more so when the method is used with soils and/or sediments that contain an excess of reducing agents relative to Cr(VI). Therefore, the solubilized Cr(VI) may be susceptible to method-induced reduction (MIR) during digestion or subsequent analysis by solubilized reducing agents (Vitale et al., 1997; Pettine and Capri, 2005a). Methods 7196A, 7199, or 218.7 (as described above) are the suggested EPA methods for subsequent quantification of Cr(VI) in the final Method 3060a digestates.

The flaws in Method 3060a have previously been identified and modifications proposed by researchers. In one proposed method, the authors use speciated isotopic-dilution mass spectrometry (SIDMS) (Huo and Kingston, 2000; Rahman et al., 2005). Before and after microwave-assisted extraction, the authors double spike the samples with the isotopes ^{50}Cr(III) and ^{53}Cr(VI). This is paired with the analysis by ion-exchange chromatography, inductively coupled plasma mass spectrometry (IC-ICP-MS) in order to track and correct for the bidirectional inter-conversions of Cr(III) and Cr(VI). This method is complex and uses proprietary software and laboratory equipment unavailable

to most laboratories without paying licensing fees or other charges to the inventors of this patented method.

In a presentation given by Christopher Mills at the Geological Society of America (GSA) annual conference, he and his fellow researchers proposed a slight adjustment to the procedure, which was "intensive-grinding," of COPR soils prior to extraction. The authors found this extra step resulted in a marked increase of 1.6 times the Cr(VI) recovered (Mills et al., 2013). Giuriati et al. (2005) altered the extraction procedure by using an accelerated solvent extractor (ASE), which works by extracting solid samples under high heat (200°C) and high pressure (1500 psi). Ammonium sulfate (pH 9-9.5) had to be used because bases with pH > 11 would damage the ASE (Giuriati et al., 2005). The extracted Cr(VI) was analyzed with the ion chromatograph (spectrophotometric detector), as in Method 7199. The automated extraction in this method saves time, but it requires specific equipment, sufficient knowledge to operate it, and further validation on diverse soil samples. Grabarczyk et al. (2006) extracted total Cr(VI) in certified reference material (soil) with 10 mL of 0.05 M $(NH_4)_2SO_4/NH_4OH$ buffer amended with 0.02 M of the complexing agent diethylenetriaminepentaacetic acid (DTPA) in order to thoroughly dissolve Cr(VI) and simultaneously prevent the oxidation of Cr(III) to Cr(VI). The extraction solution was stirred at 40°C for 10 min. The authors further tested their method by spiking sampled soil collected next to a cement plant with 25 mg/L of both humic and fulvic acids to test the robustness of the method, and they recovered 97% of the Cr(VI) in these samples. The authors determined Cr(VI) by adsorptive stripping voltammetry (AdSV), but any Cr(VI) specific detector can be used.

Malherbe et al. (2011) replaced the extraction step all together by using X-ray absorption near edge structure (XANES) spectroscopy, an element-specific technique that can measure Cr(VI) directly in the solid state. The method operates based on electron transition energies that are sensitive to oxidation state and geometry, making the quantification of both Cr(VI) and Cr(III) possible. Similarly, time-resolved XANES is becoming more important for analysis of *in situ* remediation techniques, due to its rapid Cr analysis and ability to track the speciation and form of Cr non-invasively. For example, one study employed this methodology on a soil sample spiked with $K_2Cr_2O_7$ and with a time resolution of 30-45 minutes. The authors were able to identify Cr in sparingly soluble Cr species (e.g. $PbCrO_4$, $Cr(OH)_3$, Cr_2O_3), soluble Cr salts (e.g. $K_2Cr_2O_7$) and organically bound Cr (Cr-acetylacetonate or $Cr–(O_2C_5H_7)_3$) (Kappen et al., 2008). However, the limitations of the XANES approach is one must have access to a synchrotron facility with analysts who are formally trained in this technology.

Remediation-by-Reduction Strategies

The remediation strategies to cleanup Cr(VI) in soils have been innovative and wide-ranging in design. An *in situ* remediation method refers to the cleanup of the soil without physically removing it from the field or its position in the profile, while an *ex situ* remediation method removes the contaminated waste and remediates the excavated soil material on- or off-site in batches. With or without remediation *ex situ*, the material may be transported to a hazardous materials landfill for storage or off-site disposal. Advantages of *in situ* managements include treatment without excavation and obviated costs for excavation and transport. Disadvantages include a more time consuming

remediation than *ex situ* and uncertainty about the uniformity and completeness of the *in situ* process. Remediation strategies can involve chemical and/or biological processes. Chemical remediation takes many forms, e.g. batch reactors, packed bed columns, Na-dithionite injections and permeable reactive barriers, and involves a mixture of chemicals (e.g. reducing agents) in varying combinations (Dhal et al., 2013).

Bioremediation is among the more cost-effective approaches, though. One example of the applicability of microbial remediation and its large scale-implications is an *in situ* field experiment along the Columbia River, west of Hanford, Washington. The collaborators (Faybishenko et al., 2008) periodically injected the groundwater with a hydrogen release compound (HRC) that caused the microbial density increase from a less than 10^4-10^6 cell count to over 10^8 cell count. HRC is mainly comprised of slow release glycerol polylactate ($C_{39}H_{56}O_{27}$) and when hydrated, HRC releases lactic acid, which provides carbon and energy sources for both aerobic and anaerobic microbes (Faybishenko et al., 2008). The Cr(VI) concentration went from greater than 2.0 mg/L to below the detection limit of groundwater, approximately 0.01 mg/L, and has been maintained at that concentration. The mechanism of reduction is the depletion of electron acceptors (O_2, NO_3^-, SO_4^{2-} and Fe^{3+}), which then allows iron reducers (*Geobacter metallireducens*) and sulfate reducers (*Desulfovibrio vulgaris*) to generate ferrous iron (Fe^{2+}) and hydrogen sulfide (H_2S), capable of reducing Cr(VI) (Faybishenko et al., 2008).

Theoretical Redox Concepts of Cr, Fe, and Organic C Compounds

This thesis explores the chemistry of remediation and is applicable work to an *in situ* or on-site *ex situ* remediation design in COPR-amended soils and for soils that may

have been contaminated by an industrial leak or spill. The latter was simulated by spiking

soils from Maryland, USA with a soluble Cr(VI) spike prior to remediation. The extent of

Cr(VI) reduction by organic acids, e.g. oxalic acid and compost, and/or Fe(II) and Fe(III)

has previously been studied and is reviewed below.

Thermodynamics of Cr(VI) Reduction

An overview of pH will be covered in the literature review below, but the

thermodynamic redox potentials were calculated using specifics of our designed

experiment (Table 1-1). The values are calculated for given proton and electron

conditions and are an estimate for the potential for an electron to do electrical work. Log

K values for the reduction half-reactions can be compared to predict which species would

be oxidizing and which species would be reducing (James and Brose, 2012). Take for

example the pe values for $HCrO_4^-$ and $Fe(OH)_3$ at pH 5. Since the pe of Cr(VI) reduction

>> pe of Fe(III) reduction, $HCrO_4^-$ will be reduced to $Cr(OH)_3$ and Fe(II) will be oxidized

to $Fe(OH)_3$.

Divalent Iron

The species of Fe(II) that have the ability to reduce Cr(VI) are the Fe(II) in the

aqueous form as an ion as well as Fe(II)-bearing minerals (Buerge and Hug, 1998;

Fendorf et al., 2000). According to Richard and Bourg (1991), Fe(II)(hydr)oxides such as

biotite $(KMg_{2.5}Fe^{2+}_{0.5}AlSi_3O_{10}(OH)_{1.75}F_{0.25})$, react as shown below:

$$3\ FeO\ +\ 6H^+ +\ Cr(VI)_{(aq)}\ \leftrightarrow\ Cr(III)_{(aq)}\ +\ 3\ Fe(III)_{(aq)}\ +\ 3\ H_2O \quad\quad (2)$$
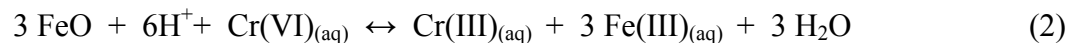
The stoichiometry of this reaction of 3 mol Fe: 1 mol Cr corresponds with the aqueous

balanced equations as seen here from Buerge and Hug (1997) for the pH range of 4 to 6:

$$3Fe^{2+}\ +\ HCrO_4^-\ +\ 3H_2O\ \rightarrow\ 3Fe(OH)_2^+\ +\ CrOH^{2+} \quad\quad (3)$$

Table 1-1. Thermodynamic log K values for reducing agents used in remediation scheme.

Reduction Half-Reaction	Log K[a] (pe at pH 0)	pe[b] pH 5	pH 7
$1/3\ HCrO_4^- + e^- + 4/3H^+ \rightarrow 1/3\ Cr(OH)_3 + 1/3\ H_2O$	18.5	11.9	9.2
$1/4\ O_2 + e^- + H^+ \rightarrow 1/2\ H_2O$	20.8[c]	15.6[c]	13.6[c]
$Fe(OH)_3 + e^- + 3H^+ \rightarrow Fe^{2+} + 3\ H_2O$	16.7	1.7	-4.3
$FeOOH + e^- + 3H^+ \rightarrow Fe^{2+} + 2\ H_2O$	14.0	-1.0	-7.0
$CO_2 + e^- + H^+ \rightarrow 1/2\ H_2C_2O_4$	-10.1	-15.1	-17.1

[a]Calculated using free energy of formation data from Lindsay (1979), Garrels and Christ (1965), and Loach (1976), except for oxalic acid, which was taken from Bourdoiseau et al. (2012). Values calculated using 25°C and 1 atm pressure.
[b]Calculated using tabulated log K values, and (red) and (ox) activities for all soluble ions and molecules used in the remediation scheme in Chapter 3. The activities of solid phases=1 and for trace gases, 0.21 atm for O_2 and 0.00032 for CO_2. The slight differences in the activities for 6500 COPR did not notably affect the final log K or pe, thus the activities for the MD soils and MES COPR were used (see Table C-1 for activity calculations). Note: pe x 59.2 =Eh(mV) at the specified pH.
[c]Values taken from James and Brose (2012).

The reaction mechanism of the reduction of Cr(VI) by Fe(II) is well understood as three separate one electron transfers (Buerge and Hug, 1997). The authors claim that in acidic pH ranges, Cr(VI) species react with H^+ to form soluble Cr(III) and Fe(III) species, while in alkaline conditions the Cr(VI) reacts with Fe(II) and water to form a precipitated Fe(III)-Cr(III) hydroxide, but the stoichiometry remains the same (Buerge and Hug, 1997). However, Schlautman and Han (2001) found that for pH value 9, the expected molar ratio of Fe(II) oxidized to Cr(VI) reduced, increased slightly from 3 to 3.5 under oxic conditions.

The rate of reduction of Cr(VI) (0.95µM) by Fe(II) (39.2µM) in an anoxic aqueous solution decreases as pH increases from 1.5-4.5, remains constant from pH 4.5-5, and increases from 5-8.7 (Pettine et al., 1998). Conversely, for oxic conditions, Pettine et al. (1998) calculated the reaction of Fe(II) with O_2 at the same conditions (25°C and pH 8) to be 20 times faster than that with Cr(VI) at 0.01 M ionic strength, while the rates were similar at pH 7, and 7 times lower at pH 6. Additionally, under highly acidic conditions (pH<2) the oxidation of Fe(II) by O_2 is very slow with a half life of days to weeks, making Cr(VI) the favorable oxidant (Fendorf, 1995; Pettine and Capri, 2005a).

Singh and Singh (2002) also measured the removal rates of Cr(VI) by Fe(II). Their research design comprised a 1:3 ratio (0.001 M Cr(VI) and 0.003 M Fe(II)) at pH 3-7, in oxygenated and deoxygenated solutions, after 30 minutes of mixing. At pH 3, the Cr(VI) removal rate was 98.2% with O_2 and 99.5% without; at pH 7 the rate decreased to 88.2% with O_2 and 98.0% without. The magnitude of the transition from oxygenated pH 6, which had a 95.2% Cr(VI) removal, to pH 7 was surprisingly high. The authors

concluded that incomplete Cr(VI) reduction in oxygenated solutions begins around pH 4, but becomes significant at pH 7 (Singh and Singh, 2002).

More recently, the Cr(VI) (100 μg/L) and Fe(II) (0.5 mg/L) reaction rate at 25°C was measured in the environmentally relevant pH range 6-8 and under oxic conditions (Mitrakas et al., 2011). The authors determined that dissolved oxygen strongly competes with Cr(VI) in Fe(II) oxidation beginning at a pH higher than 6.5. Furthermore, the batch experiments showed an increase of the reaction ratio Fe(II)/Cr(VI) from the nearly stoichiometric value 3.1 at pH 6 to 25 at pH 8 (Mitrakas et al., 2011). Based on these results, the authors went on to determine the optimum Fe(II)/Cr(VI) ratio to ensure a complete Cr(VI) removal at sub-ppb level (Cr(VI)<1μg/L and Fe(II)<1μg/L), which was 10, 15 and 20 at pH 7, 7.5 and 8. Temperature also strongly influenced the total reaction time, occurring in 5 minutes at 40°C as opposed to 60 minutes at 10°C (Mitrakas et al., 2011). Although results can be contradictory, overall, the oxidation of Fe(II) has proven to be sensitive to pH, temperature, Cr and Fe concentrations, and presence of dissolved oxygen.

The reduction of Cr(VI) by Fe(II) is favorable in remediation strategies because it often results in a very insoluble Cr(III) hydroxide, decreasing the reversibility of the reaction (Fendorf, 1995). In the case of COPRs, the SO_4^{2-} within $FeSO_4$ is capable of exchanging with the chromate in Cr(VI)-bearing minerals, and has been shown to dramatically increase the amount of Cr(VI) in solution (Geelhoed et al., 2003). The authors, however, found that due to the high pH of COPR (pH 11-12), Fe(II) was not effective in reducing Cr(VI), but instead precipitated as $Fe(OH)_2$. Only at the inlet of their

column studies (where the pH was below 8) did they observe Cr(VI) reduction by Fe(II), resulting in the precipitation of an iron (III)/chromium(III) hydroxide:

$$3Fe^{2+} \; + \; CrO_4^{2-} \; + \; 8H_2O \; \rightarrow \; 4Fe_{0.75}Cr_{0.25}(OH)_3 \; + \; 4H^+ \quad\quad (4)$$
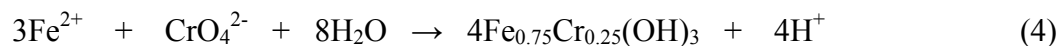
We used $FeCl_2$ in our experiment, for which there is a lack of previous literature, but since it is a soluble salt, eqn. 2-4 should be applicable. In fact, $FeCl_2$ is a better choice for this thesis work, considering that in a pilot-scale remediation treatment where ferrous sulfate heptahydrate ($FeSO_4 \bullet 7H_2O$) was added to COPR as a reducing agent, X-ray powder diffraction (XRPD) identified ettringite formation ($Ca_6Al_2(SO_4)_3 \bullet 32H_2O$), which resulted in swelling and upheaving in the soils (Dermatas et al., 2006).

Trivalent Fe

Trivalent Fe alone cannot reduce Cr(VI), as it is the highest, stable oxidation state of Fe in soils and natural waters. However, there are very important sorption reactions involving Fe(III) and Fe(III)(hydr)oxides. According to Buerge and Hug (1999), Cr(VI) reduction by Fe(II) was extremely fast in the presence of goethite (α-FeOOH) and lepidocrocite (γ- FeOOH), two Fe(III)(hydr)oxides. The fractionation of adsorbed Cr(VI) after 30-60 min was between 15 and 100%, depending on initial concentration. Buerge and Hug (1999) suggest that this Cr(VI) sorption is coupled to its reduction, followed by precipitation of paracrystalline Fe(III)/Cr(III) on the surface at pH 5.

Additionally, the reductive dissolution of Fe(III)(hydr)oxide minerals within a soil can potentially enhance reduction of Cr(VI) through an indirect route. In a study by Banwart et al. (1989), the monoanion ascorbate ($C_6H_7O_6^-$) was investigated as the role of reductant in the reductive dissolution of hematite (α-Fe_2O_3). At pH 3 and $1x10^{-4}$ mol L^{-1} initial ascorbate, the rate of dissolution was 1.48×10^{-7} mol m^{-2} h^{-1}. The mechanism

responsible for this dissolution is that ascorbate becomes adsorbed to the hematite surface, probably as an inner-sphere complex, donates electrons to the Fe(III), and the subsequent Fe(II) formed on the surface becomes detached. The authors also found that reductive dissolution rates increased to 5.97×10^{-7} mol m^{-2} h^{-1} when the chelating ligand oxalate $(C_2O_4^{2-})$ was added (Banwart et al., 1989). There are two proposed explanations for their results: (1) the oxalate formed a surface complex with Fe(II), enhancing the detachment into solution or (2) oxalate weakened the Fe^{3+}-O bond at the oxide surface and induced non-reductive dissolution. Once the Fe(III) was in solution, oxalate was capable of reducing it to Fe(II) (Banwart et al., 1989; Schwertmann, 1991).

It is important to note that Fe(III)-reducing bacteria such as *Schewanella alga* BrY in the presence of Fe(III) can potentially lead to extensive Cr(VI) reduction. The reduction of Fe(III) by the strain BrY to Fe(II) with successive re-oxidation to Fe(III) by reaction with Cr(VI) reveals a catalytic role of Fe in this system (Fendorf et al., 2000). Electron transfer cycles such as this are important to consider while evaluating results of any such system containing Cr(VI) and Fe species. Also relevant is the possibility of bioreduction of Fe(III) oxides in water saturated soils containing organic matter (Whittleston et al., 2011). This reduction results in coprecipitation as Cr(III) within a stable Fe(III)(hydr)oxide phase (Whittleston et al., 2011). Similarly, green rust (GR) is a mixed Fe(II)-Fe(III) double layered hydroxides built upon Fe(OH)$_2$-like sheets that forms in reduced soils by microbial processes (Fendorf et al., 2000; Loyaux-Lawniczak et al., 2000). Recent studies have shown this green rust to not only serve as a reductant for Cr(VI), but as a catalyst for the reduction reactions in the solution (Fendorf et al., 2000; Loyaux-Lawniczak et al., 2000). Loyaux-Lawniczak et al. (2000) observed GR reduce

Cr(VI) in such a way that resulted in the formation of Cr(III)-substituted ferrihdrite, as

shown in equation 5 (structural water molecules omitted and stoichiometry is 3 Fe: 1 Cr):

$$15Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 + 20CrO_4^{2-} \rightarrow 22Fe_{45/11}Cr_{10/11}HO_8 + 15SO_4 + 10OH^- + 74H_2O \quad (5)$$
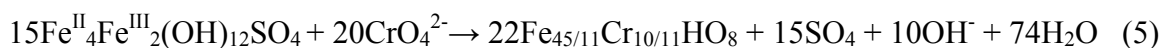
The Cr(III) substitution involved the removal of the interlayer anions, the insertion of Cr

atoms, and the consequent rearrangement of the hydroxide sheets; the magnitude of such

a physical change resulted in a "disordered form," of an Fe(III) oxyhydroxide with an

undefined stacking of $Fe(O)_6$ octahedra sheets, where oxygen atoms can be found in O^{2-},

OH^-, or even H_2O species (Loyaux-Lawniczak et al., 2000).

Organic Carbon

Soluble and insoluble organic C compounds and organic matter in soils have can

reduce Cr(VI) (James and Bartlett, 1983c; Fendorf et al., 2000). According to Wittbrodt

and Palmer (1996), the reduction of Cr(VI) by soil humic substances in aqueous solutions

is enhanced by Fe(III). It is hypothesized that this occurs because the Fe(III) is reduced

by the humic substances in solution, and oxidized by the Cr(VI), which can start the

redox cycling over; it was also determined that this reduction reaction occurs faster with

fulvic acids than with humic acids (Wittbrodt and Palmer, 1996). The effect of varying

the background electrolyte and ionic strength had little effect on the reactions.

Brose and James (2010) found that AQDS (a surrogate for soluble humic acids)

behaved as an electron shuttle under aerobic conditions, field moist conditions in soils.

AQDS is the highly reactive intermediate semiquinone. The AQDS was reduced by lactic

organic acid ($C_3O_3H_6$), and the reduced form was capable of then reducing soil Cr(VI).

This thesis replaces AQDS with Fe(III), and applies the same theory.

Chromium (VI) remediation studies with organic C amendments delivered as compost are few, but very diverse. The final composting product varies with many factors, including biodegradable inputs and conditions (aeration, moisture, time, etc.) (Shi et al., 1999). This presents a challenge in comparing compost studies and their effectiveness in removal of Cr(VI) from solution, but a literature review was completed on studies that bear a close resemblance to a commercially available Prince George's County, MD, USA leaf compost, derived from windrow composting, that was chosen for this thesis work.

Two common remediation research designs are either (1) batch equilibrations containing the contaminated soil and the sorbing and/or reducing material, or (2) permeable reactive barriers (PRB) that consist of a zone of reactive material intended to retain, reduce or precipitate contaminants in groundwater or liquid phases. A compost-based biobarrier is essentially a PRB targeting biological removal through the medium compost, whether it is direct microbial reduction via enzymatic reduction or indirect reduction through production of reducing agents, such as hydrogen sulfide (H_2S) (Cheung and Gu, 2007; Boni and Sbaffoni, 2009). In compost-based biobarriers, 10 mg Cr(VI)/L solutions effectively reduced with a combination of green compost and gravel (Boni and Sbaffoni, 2009). The green compost was comprised of yard and wood cellulose waste with pH 8.5 and a 320 mg organic C/kg content, while the gravel was characterized as siliceous with pH 8.7 and rich in cationic zeolites. The two main processes of removal were adsorption of Cr(VI) onto the organic surface and cabasite and phillipsite zeolites, followed by reduction to Cr(III) by microbial metabolism of the bacteria residing in the green compost (Boni and Sbaffoni, 2009). The authors were able to link such microbial

activity to reduction via altering the organic C and N within the contaminated solution. Without the higher electron donor source, the reduction was lessened. Throughout the experiment, pH increased from pH 6.6 until it stabilized around 7.5. The authors hypothesized that the pH increase was due to sulfate-reducing bacteria (SRB) reducing Cr(VI) indirectly by H_2S, according to the following reaction:

$$2HCrO_4^- \ + \ 3H_2S \ + \ 2H^+ \ \leftrightarrow \ 2Cr(OH)_{3(s)} \ + \ 3S_{(s)} \ + \ 2H_2O \qquad\qquad (6)$$

A common flaw of the studies discussed is not explicitly defining what is meant by "sorption." Therefore, the operationally defined terms necessary to understand the fractionation scheme for this thesis are described next.

Fractionation of Hexavalent Chromium

The fate of Cr includes sorption, precipitation, and solubility processes that are governed by reduction-oxidation potentials. In order to understand the speciation of Cr as the end-products of these reactions, a fractionation method was used in this thesis similar to that of James (1994). Chromium(VI) was operationally defined in soluble, exchangeable and nonexchangeable fractions. Chromium(III) could only be measured as soluble, due to the limits of the methodology with FAA. More specifically, the operationally defined Cr(VI) fractions are as follows: "soluble" in a 10 mM $NaNO_3$ extraction, "exchangeable" in a 10 mM KH_2PO_4-K_2HPO_4 phosphate buffer extraction, and "nonexchangeable" as the modified Method 3060a extraction, determined in Chapter 2. As for analytical measurements, soluble and exchangeable divisions were analyzed with the IC and conductivity detection; total soluble Cr was measured with a FAAS; finally, nonexchangeable Cr(VI) was analyzed with the IC/conductivity detection post-

digestion and extraction. The nonexchangeable fraction could include precipitated and sparingly soluble Cr(VI) salts, and Cr(VI) that was incorporated into the interlayers of mineral phases.

Novel Research Goals

The following two chapters present my thesis research and implications, with the last chapter containing concluding remarks and ideas for future researchers. This research stands alone from previous investigations and has developed new method modifications and remediation protocols as related to the diverse and complex chemistry of Cr. More specifically, this work addressed the following research questions in Chapter 2:

- Can the amount of method-induced reduction (MIR) in soils and waste materials be eliminated or minimized by removing heat from EPA's Method 3060a?
- Does analysis with an anion exchange column/IC conductivity detector over the DPC reaction/spectrophotometer influence the results?
- Is there a difference in MIR between contaminated soils and COPR-amended soils?

The flaws of EPA's Method 3060a have long been identified and each author in the literature review has taken a unique approach to address the issues. However, this thesis is novel in the sense that we use a range of C (0-500 g C/kg of soil) added in the form of compost to assess exactly when the C begins to affect the method, both with heat (90ºC) and without heat (23ºC). To further address the problem of MIR for Cr(VI), the methods were compared with both uncontaminated soils collected from sites in Maryland, USA, as well as anthropogenic COPR-amended soils collected from disposal areas in New Jersey, USA. Lastly, the samples were analyzed with both the IC and DPC method to investigate if there were any reduction-oxidation interferences post-digestion caused by the

analytical technique. Based on the literature, we hypothesized that the removal of heat would decrease MIR for MD soils, but not the COPR-amended soils. Another hypothesis was that the IC would be preferential over the DPC, based on pH-influenced reduction-oxidation interferences with organic C.

This work addressed the following research questions in Chapter 3:

- How does the different combination of Fe(II,III) and sources of reducing organic acids (oxalate and compost) affect the reduction of Cr(VI)without adjusting the pH?
- What is the final fate of Cr after the remediation?

The quantification of soluble, adsorbed, and nonexchangeable Cr(VI) post-remediation addresses these research questions, and especially sheds light on the importance of Fe(III) in a remediation scheme that raises interesting questions for the future of Cr(VI) reduction. Because the soil contamination ranged from 1,040 to 6,500 mg Cr(VI)/kg, the results are applicable to a large-scale contamination of high Cr(VI) concentrations in soils and waste materials. We hypothesized that the combination of two reducing agents would reduce the highest amount of Cr(VI), based on enhanced reduction from redox cycling of electrons.

CHAPTER 2

TOTAL HEXAVALENT CHROMIUM QUANTIFICATION IN HIGH ORGANIC CARBON SOILS: MINIMIZING REDUCTION DURING EXTRACTION AND ANALYSIS

Introduction

Chromium (Cr) is a transition metal that can exist in a variety of chemical species, with oxidation states ranging from -II to +VI, but only Cr(III) and Cr(VI) are stable enough to persist in near-surface environments, such as soils, sediments, and natural waters (Fendorf et al., 2000). There is a stark difference between the oxidation states of Cr(VI) and Cr(III): Cr(VI) is a carcinogen, damaging lungs and tissue via inhalation, while Cr(III) is widely acknowledged as an essential nutrient, considered tremendously beneficial for diabetes patients (Lim et al., 1983; Langard, 1990; Burke et al., 1991). The Institute of Medicine (IOM) suggested daily intake of Cr is 25 and 35 μg for females and males, respectively (IOM, 2001). In addition to inhalation, a recent 2-year study has shown Cr(VI) to cause mutagenic disorders in the small intestine and liver of mice via daily oral ingestion of water containing sodium dichromate dihydrate ($Na_2Cr_2O_7 \cdot 2H_2O$), a common Cr(VI) containing-chemical. A significant rise in abnormal growths began for concentrations ~30 mg Cr(VI)/L (NTP, 2008). Due to its history of improper industrial disposal, and alarming toxicity levels in the resulting contaminated lands (> 6500 mg Cr(VI)/kg), the importance of a reliable extraction method for accurate quantification of total Cr(VI) in soils and solid wastes cannot be overstated. This paper will attempt to address and correct for the reduction-oxidation inter-conversions of Cr that the current measurement of Cr(VI) exhibits.

To determine the Cr(VI) in a solid sample, one must use (1) an extraction method and (2) a quantification procedure. The widely accepted standard method for the

extraction of Cr(VI) in soils and solid waste is the Environmental Protection Agency's SW-846 Method 3060A, followed by either Method 7196A or 7199 for the measurement (USEPA, 2014).

In Method 3060a, samples are digested in an alkaline solution (0.28 M Na_2CO_3/0.5 M NaOH) and heated at 90-95°C for 1 hour (USEPA, 2014). These conditions are designed to solubilize all forms of Cr(VI) in the samples, precipitate any solubilized Cr(III), and prevent oxidation of native Cr(III) to Cr(VI) or reduction of native Cr(VI) to Cr(III). Even though the alkaline pH (11-12) inhibits reduction of Cr(VI) (Singh and Singh, 2002; Pettine and Capri, 2005a; Mitrakas et al., 2011), when the method is used with soils and/or sediments that contain strong reducing potential (e.g., Fe(II), organic matter, and sulfides) or are in excess of the stoichiometric ratio of 3:1 Fe(II)/Cr(VI), the solubilized Cr(VI) may be susceptible to method-induced reduction (MIR) during the hot, alkaline digestion or subsequent analysis of the solubilized Cr(VI) (Vitale et al., 1994;Vitale et al., 1997).

For the subsequent quantification of Cr(VI) in the final Method 3060a digestates, EPA suggests using either Method 7196A or Method 7199. Both methods ultimately use colorimetric detection to quantify the extracted Cr(VI) in the alkaline digestates by reaction with diphenylcarbazide (DPC) in acid solution; the difference being that Method 7196A is analyzed by a spectrophotometer, and Method 7199, by an ion chromatograph using separation on an exchange column (USEPA, 2014). The chemistry behind the methods is that at the pH of the DPC solution (pH ≤ 2), Cr(VI) is rapidly reduced to Cr(III), followed by complexation of newly-reduced, unhydrated Cr^{3+} by diphenylcarbazone, the oxidized form of diphenylcarbazide (Huo et al., 1998; Vitale et

al., 2000). A potential interference in Method 7196A is solubilized reducing agents that are not oxidized or precipitated can compete with DPC to reduce Cr(VI) (Pettine and Capri, 2005a; Pettine and Capri, 2005b). Additionally, humic compounds absorb light at the same wavelength as does the Cr(III)-DPC complex (540 nm) (Pettine and Capri, 2005a; Pettine and Capri, 2005b). Due to the ion chromatographic anion separation in Method 7199, these two interferences are less so for the ion chromatograph method, but still possible since the DPC-Cr(VI) reaction quantifies the Cr(VI) concentration.

In one proposed method to replace Method 3060a, the authors use speciated isotopic-dilution mass spectrometry (SIDMS) in order to track and correct for the bidirectional inter-conversions of Cr(III) and Cr(VI) (Huo and Kingston, 2000; Rahman et al., 2005). Their method includes double spiking with the isotopes $^{50}Cr^{3+}$ and $^{53}Cr^{6+}$ before and after microwave-assisted extraction, paired with the analysis by ion-exchange chromatography, inductively coupled plasma mass spectrometry (IC-ICP-MS). This method is complex and uses proprietary software and laboratory equipment unavailable to most laboratories.

Similarly, other slight adjustments have been proposed to improve the accuracy and precision of the USEPA methods. In a presentation given by Christopher Mills at the Geological Society of America annual conference, he and his fellow researchers found that "intensive-grinding," of COPR soils prior to extraction resulted in a marked increase of 1.6 times the Cr(VI) recovered (Mills et al., 2013). Malherbe et al. (2011) replaced the sensitive extraction all together by using X-ray absorption near edge structure (XANES) spectroscopy, a technique that can measure Cr(VI) directly in the solid state. It is

element-specific and operates based on electron transition energies that are sensitive to oxidation state and geometry, making the quantification of both Cr^{6+} and Cr^{3+} possible.

The objective of this study was to compare and refine conditions to minimize method-induced reduction during the alkaline extraction and subsequent analysis of Cr(VI) in soils and waste materials. Two heat conditions (95°C and 23°C) during the digestion and extraction were tested, as well as two analytical methods of determining Cr(VI) post-digestion: the manual DPC colorimetric method (Bartlett and James, 1979) and a new ion chromatographic method. Our ion chromatographic method uses anion separation and conductivity detection, and there is no addition of reagents, preventing method-induced conversions of Cr species during the analysis steps. Instead, diluted alkaline extraction centrifugate solutions are placed on the autosampler and injected into the carbonate-bicarbonate eluent (minimizing reduction of Cr(VI) at the high pH).

We tested the robustness of the proposed extraction and detection methods by adding organic C to the soils (with a range of native levels of organic C) in the form of leaf compost. Soil horizons were sampled from Maryland in areas with no known sources of Cr contamination, along with two chromite-ore processing residue (COPR)-amended soils from New Jersey, all with a wide range in organic C. These samples were chosen and used to determine the method that can withstand a range of redox potential (Eh) and pH for a variety of soils. Method 3060a was developed for industrial waste materials, such as COPR, but in addition, the method must be able to quantify Cr(VI) over a range of contamination and soil conditions, such as a chemical spill on previously undisturbed land, or the disposal of soluble Cr(VI)-containing wastes.

We hypothesized that three factors would singly or combined lead to underestimations of Cr(VI) concentrations: high heat, high C content, and the analysis method for extracted Cr(VI). More specifically, we hypothesized that a combination of the 23°C method temperature and the new ion chromatography analytical method would yield the most accurate and reliable results on soils with native organic C. We also hypothesized that the increase in the C-amended treatments would have a greater effect on the Cr(VI) recoveries from the Maryland soils than in the COPR-amended soils.

Methods

We studied five soil materials from horizons collected from three soils that were not known to be contaminated by Cr or other contaminants, which were sampled from the Coastal Plain and Piedmont physiographic provinces in the State of Maryland, USA. The two waste materials used were COPR-enriched soil materials from Hudson County New Jersey, USA, located in the Piedmont province. The Prince George's County, MD compost product, Leafgro®, was used as a medium for organic C amendments. These soils and materials were used in order to compare the total Cr(VI) extraction method with and without heat, followed by quantification by (1) the manual diphenylcarbazide method and (2) our new ion chromatogram method.

Uncontaminated Soils

Two locations were sampled on the Piedmont of Maryland and one on the Coastal Plain (Delmarva Peninsula). The Maryland samples were taken from profiles located in delineations of the three mapping units Conestoga, Askecksy, and Glenelg (see Appendix B for complete sampling details and soil characterization data). Since the description of

the Conestoga unit (coordinates: 39.54805, -77.17803) did not match any known soil series, it will be referred to as Flickinger, the name of the farmer using the land for crop production (Bourgault, 2008). Flickinger is a manganiferous soil, high in both Fe(III) and Mn(III,IV)(hydr)oxides. In particular, the Mn(III,IV) (hydr)oxides content influences subsoil horizons to be very black (value ≤ 2). Bourgault and Rabenhorst (2011) hypothesized that the Mn-rich soil formed in residuum, from the "dissolution of marble bedrock and accumulation of silicate residues plus Mn and Fe from within the rock." The horizons sampled from the profile in the Askecksy unit (coordinates: 38.214475, -75.522236) were similar to the Atsion series (sandy, siliceous, mesic, Aeric Alaquod). The spodic horizon collected from this profile is classified as a Bhs horizon because of the illuvial Al (3.0 g/kg) (Condron, 1990) and organic matter (29 g/kg), in addition to having a moist value and chroma < 3 (Table 2-1). The horizons sampled from the profile in the Glenelg unit (coordinates: 39.2618294, -76.9260483) were similar to the Glenelg series (fine-loamy, mixed, semiactive, mesic Typic Hapludults).

The soil samples were chosen for their range of characteristics in texture, Fe and Mn contents, but mostly the range in organic C content (Table 2-1). The Piedmont soils (Flickinger and Glenelg) are rich in dithionite-extractable Fe (9.0-31.0 g Fe/kg), with Flickinger also having an unusually high amount of extractable Mn (2.7-8.8 g Mn/kg) (Table 2-1). The Fe and Mn data, operationally defined by the citrate-bicarbonate-dithionite (CBD) method, are the free Fe(III) and Mn (III,IV)(hydr)oxides, not including structural forms within soil minerals (Loeppert and Inskeep, 1996). The Delmarva soil (Atsion) was chosen because it is a sandy Aquod with a spodic horizon containing a high organic C content (29 g/kg soil) with a notable difference in texture, compared to the

Table 2-1. Soil Characterization Data.

Soil Horizon[a]	Sample Depth (cm)	Color[b]	Texture[c] (% sand, silt, clay)	CBD Fe[d][e] ----------------	CBD Mn ----- (g/kg)----	Organic C[f] ----------------	Taxonomic Great Group[g]
Flickinger A1	27-43	7.5 YR 3/4	clay loam (31, 35, 34)	22 ± 2	2.7 ± 0.1	3.7 ± 0.1	Hapludalf?
Flickinger Bt1	43-87	5 YR 2.5/2	clay (29, 29, 42)	31 ± 0.9	8.8 ± 0.2	2.9 ± 0.1	Hapludalf?
Glenelg A1	11-23	10 YR 3/3	silt loam (39, 54, 7)	9.0 ± 0.7	0.12 ± 0.005	24 ± 0.2	Hapludult
Glenelg Bt1	23-39	7.5 YR 4/6	clay loam (40, 28, 32)	18 ± 0.3	0.036 ± 0.001	4.6 ± 1.1	Hapludult
Atsion Bhs	27-45	5 YR 2.5/2	sand (89, 8, 3)	0.15 ± 0.002	0.0010 ± 0.0	29 ± 1.1	Alaquod
MES COPR	0-30	10YR 5/3	sandy loam (67, 30, 3)	8.3 ± 0.8	0.15 ± 0.008	18 ± 0.80	Anthrosol
6500 COPR	0-30	7.5YR 2/2	sandy loam (61, 38, 1)	16 ± 1	0.16 ± 0.006	17 ± 0.07	Anthrosol
Leafgro® Compost	N/A[h]	Gley 1 2.5/N	N/A	4.5 ± 0	0.73 ± 0.006	395 ± 30	N/A

[a]Soil horizons are designated by their series name (USDA-NRCS), except for MES, 6500 and compost, which are named for their original use (James et al., 1995), contamination level, and product name, respectively.

[b]Color is field-moist and designated by the Munsell color system.

[c]Texture was determined using particle size analysis by pipette method (Gee and Bauder, 1986).

[d]CBD refers to a citrate-bicarbonate-dithionite extraction (Loeppert and Inskeep, 1996).

[e]Values are means and one SEM (n=3).

[f]Determined with LECO after destroying carbonates (Piper, 1942; Nelson and Sommers, 1996).

[g]Natural Resources Conservation Service (NRCS) official series description (Soil Survey Staff, 2014).

[h]Not Applicable.

Piedmont soils (Table 2-1). Total C and N were determined by combustion with a LECO CHN Analyzer at 950°C. For organic C determination, $CaCO_3$ was destroyed by reacting samples (1 g) with 1-5 mL of 5% sulfurous acid (H_2SO_3), depending on the continuation of bubbling with additional H_2SO_3. Once the reaction ceased, the soils were dried in a vacuum desiccator (20 h), followed by an oven (105°C, 20 hours), reground, and then analyzed by LECO (Piper, 1942; Nelson and Sommers, 1996).

Contaminated Waste Materials

From 1905-1976, Hudson County was a center for chromite ore refineries, producing an estimated 2-3 million tons of COPR (Burke et al., 1991). The two COPR surface horizons used in this study were sampled in Kearny, NJ (Hudson County) at the Diamond Shamrock field site, which was named after the chromate-manufacturing chemical facility that was once located there (Brose, 2012). It is thought that the COPRs were mixed with other fill material and disposed of as surface materials (James et al., 1995). MES (Method Evaluation Study) (sampled November 22, 1993) is named after its original use and contains approximately 1200 mg Cr(VI)/kg of soluble and insoluble Cr (James et al., 1995). 6500 COPR (sampled October 1, 1997) is named for its contamination level, or 6500 mg Cr(VI)/kg soil. Although there isn't any available data for the exact sample location (coordinates: 40.751469, -74.098697), nearby soils are from the delineation of the Transquaking mapping unit, and are similar to the Transquaking series (euic, mesic Typic Sulfihemists) (Soil Survey Staff, 2014) The Cr-enriched disposal sites are in the floodplain of the Hackensack river and such filling of wetlands formed an anthropogenic soil material enhanced with COPR underneath them.

All of the sampled soil horizons (uncontaminated and contaminated) were transported to the laboratory in College Park, MD, and then were sieved field-moist (approximately -10 kPa matric water potential) to 4-mm using a polyethylene sieve. The samples are stored in covered plastic buckets at room temperature (22-24°C), and kept at field-moist water content. Storing air- or oven-dried soils increases reduced Mn^{2+} as well as the solubility and oxidizability of organic matter (e.g. fulvic acids) (Bartlett and James, 1980). Field-moist, sieved soils maintain field soil chemical conditions far better than after drying.

Organic C Amendments

The soil horizons used were incubated for 1 week (168 ± 5 hours) with a range of added C as leaf compost from the compost product, Leafgro®; Leafgro® is a commercially-available, Prince George's County leaf compost, rich in C, N, and Mn (395, 17.9, and 0.727 g/kg, respectively). This compost may be high in Mn due to the cycling of tree leaves, as well as the role of Mn^{2+} in cation exchange reactions in response to H^+ inputs and buffering mechanisms in soil organic horizons (James and Riha, 1986). Since the compost is a complex, heterogeneous medium derived from tree leaves and microbial waste products, it contains a wide range of C-based reducing agents, and we hypothesized that it is a realistic material to investigate method-induced reduction of Cr(VI) in the soils and COPR samples. It also represents the type of material that might be used in the *in situ* remediation of Cr(VI)-contaminated soils. We tested the Leafgro® for Cr(VI) and the results were <LOD.

For each soil, the field-moist equivalent of 100 g of oven-dried material (105^oC for 24 h) was combined with four C treatments (0, 10, 100 and 500 g C/kg) in a one liter,

zip-lock freezer bag. Each treatment bag was kneaded and mixed until the soil and compost were thoroughly homogenized. The bag was placed into another freezer bag with moist paper towels between the bags to maintain 100% relative humidity during incubation. The treatment bags were incubated in a dry bucket at room temperature ($22 \pm 2°C$) for 1 week (168 ± 5 hours).

Extraction Procedure

Preliminary results demonstrated that heating spiked Cr(VI) soils (100 mg Cr(VI)/kg) with high organic C (9-29 g C/kg) increased their reducing conditions, lowering the accuracy of the test results (Table 2-2); this led us to explore the modification of EPA's Method 3060a by replacing the 1 hour of heating at 95-100°C with 1 hour of shaking at 100 cycles/min on an orbital shaker (USEPA, 2014). The shaking time was also determined by preliminary experiments that indicated only 4-25% more Cr(VI) was recovered after shaking longer than 1 hour (e.g. 24 hours or 1 week) (Table 2-3). Without considering the unspiked COPRs, the range decreases to only 4-5% more Cr(VI) recovered over the longer equilibration times. We also tested the effects of grinding the COPR samples with a mortar and pestle prior to a 1 hour, unheated method extraction, as a means of recovering more sparingly soluble Cr(VI). However, we found inconsistent results. The Cr(VI) recovery for MES decreased (4%), but increased for 6500 (7%), relative to the non-grinded samples. We decided this wasn't a significant change, and that preserving the sample at its natural mineralogy was more realistic (results not shown). The samples remained homogenized, though, through sieving to 4 mm as described earlier.

Table 2-2. Preliminary Results: Interference of organic C with Method 3060a extraction for soils spiked with soluble Cr(VI).

Soil Horizon[a]	Organic C[b] (g/kg)	Cr(VI) spike recovery[c] (%)
Jackland A/AB	9.0 ± 0.09	81 ± 3
Jackland Bt1	4.0 ± 0.07	102 ± 0.5
Flickinger A1	3.7 ± 0.1	103 ± 0.8
Flickinger Bt1	2.9 ± 0.1	104 ± 0.5
Glenelg A1	24 ± 0.2	1.0 ± 1
Glenelg Bt1	4.6 ± 1.1	97 ± 2
Atsion Bhs	29 ± 1.1	9.0 ± 0.6

[a]Abbreviations as in Table 2-1.

[b]Abbreviations as in Table 2-1.

[c]Soils subjected to a 100 mg Cr(VI)/kg soluble spike prior to running Method 3060a with heat (95°C) for 1 hour, and analyzed by DPC. Values are means and one SEM (n=3).

Table 2-3. Preliminary Results: Percentage of recovered Cr(VI) extracted by Method 3060A with and without heat, over a range of equilibration times.

% Total Cr(VI) Extracted[a]				
Soil Horizon[b]	Method with Heat[c] --------- (h) -----------	Method without Heat[d] ------------(h)--------------------------------		
	1	1	24	168
6500	100 ± 0.7	68 ± 0.3	81 ± 0.3	93 ± 2
MES	106 ± 0.7	88 ± 0.7	97 ± 0.4	98 ± 2
Inc Jackland Bt1[e]	43 ± 4	75 ± 1	76 ± 1	80 ± 0.3
Inc Flickinger Bt1	109 ± 0.8	101 ± 0.8	103 ± 0.7	106 ± 1
Inc Russett Bt1	99 ± 2	94 ± 0.2	95 ± 2	98 ± 1

[a]Percentages assume MES is 1200, 6500 is 6500 and Jackland, Flickinger, and Russett are 100 mg Cr(VI)/kg. Values are means and one SEM (n=3). MES and 6500 did not receive pre-digestion spikes.

[b]Abbreviations as in Table 2-1.

[c]The original Method 3060a was run with heat (95°C) for 1 hour and analyzed by DPC.

[d]The extraction was run at 23°C on rotary shakers (100 cycles/min), with varying equilibration times, and analyzed by DPC.

[e]Incubated (Inc) soils stored at 23°C with 100 mg Cr(VI)/kg spike for 1-2 months before analysis. Therefore, soil-induced reduction could be influencing the results.

The Method 3060a extraction method is represented in Fig. 2-1. The basic digestion method (both that of SW-846 Method 3060a and our modification) includes the following: 2.5 g oven-dried equivalent of field-moist soil weighed into triplicate 250-mL, Pyrex® heavy-duty graduated beakers, to which 50 mL digestion solution is added. The digestion solution is 0.28 M Na_2CO_3 and 0.5 M NaOH (pH >11.5). The beakers were covered with watch glasses and subjected to the two heating conditions: 60 ± 5 min of heating at 90-95°C or swirling (100 cycles/min) at 22°C (room temperature) for 60 ± 5 minutes. After the digestion period, the beakers were brought to a total solution volume of 100 mL based on weight (knowing the beaker and soil masses) with 18 MΩ nanopure water. The suspensions were swirled, an aliquot was poured into a 15-mL polyethylene centrifuge tubes, and they were centrifuged (4,000 x g, 15 min, 22°C).

Spiking Protocols

Chromium treatments comprised three Cr(VI) matrix spikes: 0 and 100 mg Cr(VI)/kg pre-digestion spike, and 1 mg Cr(VI)/L post-digestion spike. The 100 mg Cr(VI)/kg pre-digestion spike was delivered as 2.5 mL of a 100 mg Cr(VI)/L to the 250-mL digestion beaker containing both the soil and the extracting solution, prior to the respective heating treatments. Pre-digestion spikes were designed to quantify method-induced reduction during the alkaline extraction. The post-digestion spike was delivered after the soil solutions were centrifuged and sample aliquots were diluted prior to analysis by DPC or the IC method. That is, the post-digestion spike was delivered straight to the test tube that was to be ultimately analyzed. Post-digestion spikes are used for testing the analytical method effects on Cr(VI) post-extraction. Serial dilutions were then made, as needed, to bring the analyte concentration into the linear range of quantitation of the DPC
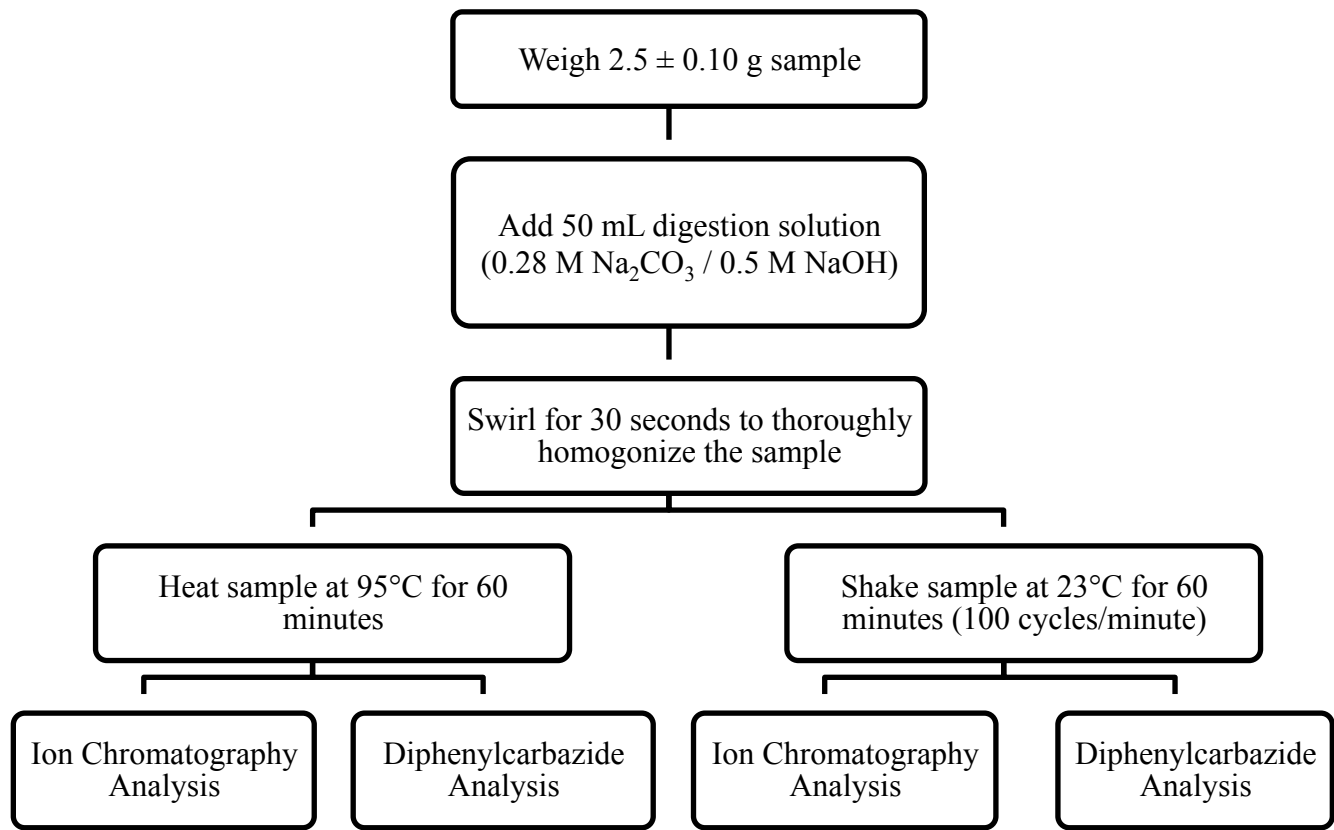
Figure 2-1. Method Flow Chart.

and IC methods.

Diphenylcarbazide Analysis for Cr(VI)

An amended version of the 1,5-diphenylcarbazide method (DPC) was used in this

study (Bartlett and James, 1979). DPC reagent was prepared by dissolving 0.35 ± 0.01 g

1,5-diphenylcarbazide in 100 mL 95% ethanol, 280 mL 18 MΩ nanopure water, and

bringing the final volume to 500 mL with 120 mL 85% H_3PO_4. DPC reagent was pipetted

into sample dilutions (at least 1:10 in nanopure water) and vortexed for 15 sec. The DPC

reaction occurs at pH 1.7-2. The diphenylcarbazide is oxidized to diphenylcarbazone

after behaving as a reducing agent for $HCrO_4^-$. The oxidized form of DPC,

diphenylcarbazone, then complexes with the newly reduced, unhydrated Cr^{3+} to form a

magenta complex with a maximum molar absorptivity at 540 nm. A typical molar

absorptivity from a standard curve, calculated in change in absorbance units (1.0) per

change in concentration (mg/L) over the range of 0-2.0 mg/L is 0.713 (Fig. 2-2). When

calculated using molarity (mol/L), the molar absorptivity changes to 37,000. The color

was allowed to develop for 20 min to ensure that the DPC-Cr(VI) reaction was complete.

The solution color was quantified for Cr(VI) concentrations using a Genesys 10S UV-

VIS spectrophotometer (LOD = 0.01 mg Cr(VI)/L) with a 1-cm flow cell at 540 nm

wavelength. Five Cr(VI) standards ranging from 0.01 mg/L to 2.0 m/L were made via a

series of dilutions of a 1000 mg Cr(VI)/L stock solution. The stock was made from oven-

dried K_2CrO_4. All standards were made in nanopure water. A "blank reagent" was used to

eliminate any possible organic C interference, since the colored organic solutions (e.g.,

humic and fulvic acids) can absorb light at 540 nm, causing false positive results. The
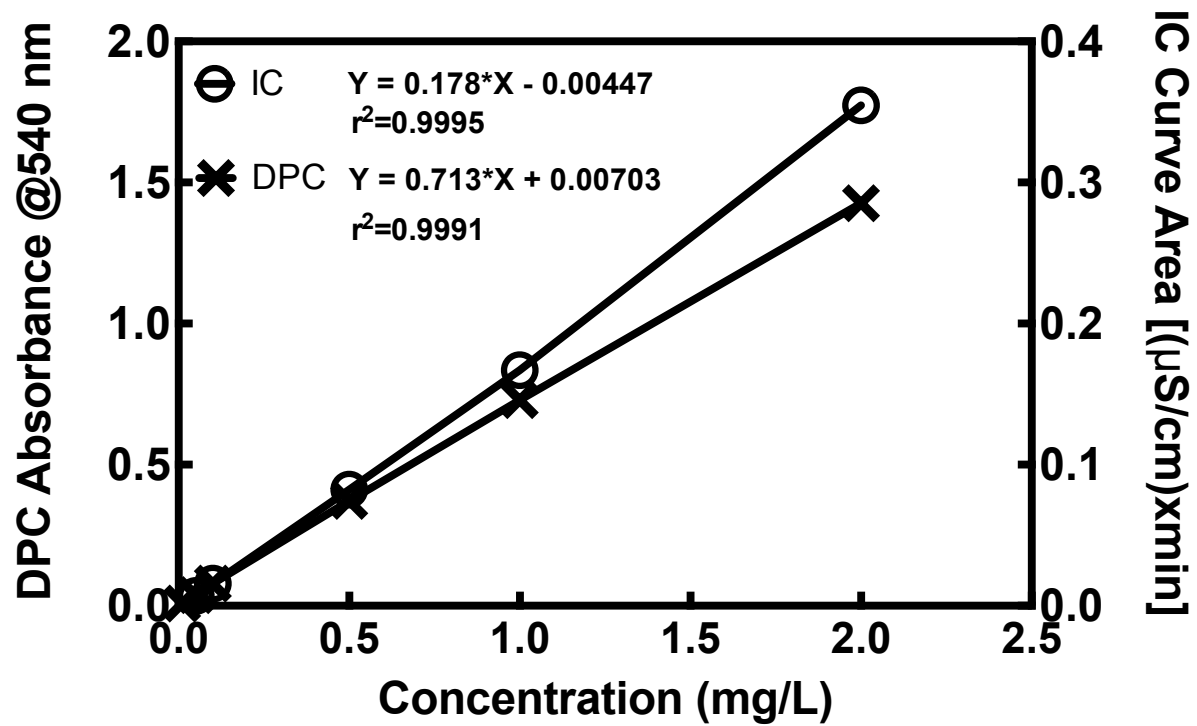
Figure 2-2. Standard curves for IC and DPC. This graph illustrates a typical calibration curve of concentration (mg/L) vs absorbance for DPC and concentration (mg/L) vs area for IC. DPC was measured at λ_{540} nm. The error bars represent one SEM (n=3).

blank reagent solution contained ethanol, water and phosphoric acid only. Due to the low

pH of both the DPC and blank reagent, we saw flocculation of organics in the test tubes

of some samples, which will be further addressed later in this chapter (Fig. 2-3). In these

cases, the samples were not analyzed due to the potential damage to the

spectrophotometer, and due to light scattering by the suspended humic acid floccules.

Ion Chromatographic Analysis for Cr(VI)

A Metrohm 850 Professional Ion Chromatograph was used for our ion

chromatographic method, with model 858 Sample Processer and 872 Extension Module.

Sample dilutions were made similar to the DPC method (ranging 1:10-1:100 in nanopure

water), except there was no addition of reagents; instead, sample dilutions were placed on

the model 858 autosampler and injected into the carbonate-bicarbonate eluent, 3.2 mM

Na_2CO_3 / 1.0 mM $NaHCO_3$. The IC was set to operate at a flow rate of 0.7 mL/min and

use a sample injection of 20 μL. The Cr(VI) and alkaline eluent were drawn up through

peristaltic onto the anion exchange column (150x4.0mm). The pressure of the column

ranges from 8-10 MPa. There, the negatively charged anions in solution are attracted to

the positively charged solid support, or anion exchange resin of the column, on which

they are retarded in accordance with anion size and charge (Claudia et al., 2002). The

higher the anion charge, the greater the strength of the interaction with the column, and

the longer the retention time will be on the column. Similarly, larger ions are retained

more strongly than are smaller ones, and retention times are longer. Once leached out of

the anion separation column, a Digital Signal Processing (DSP) conductivity detector

analyzed the electrical conduction of the anion after the eluent background conductivity

is suppressed by injection of 0.1 M H_2SO_4. The detector generated a measurable signal
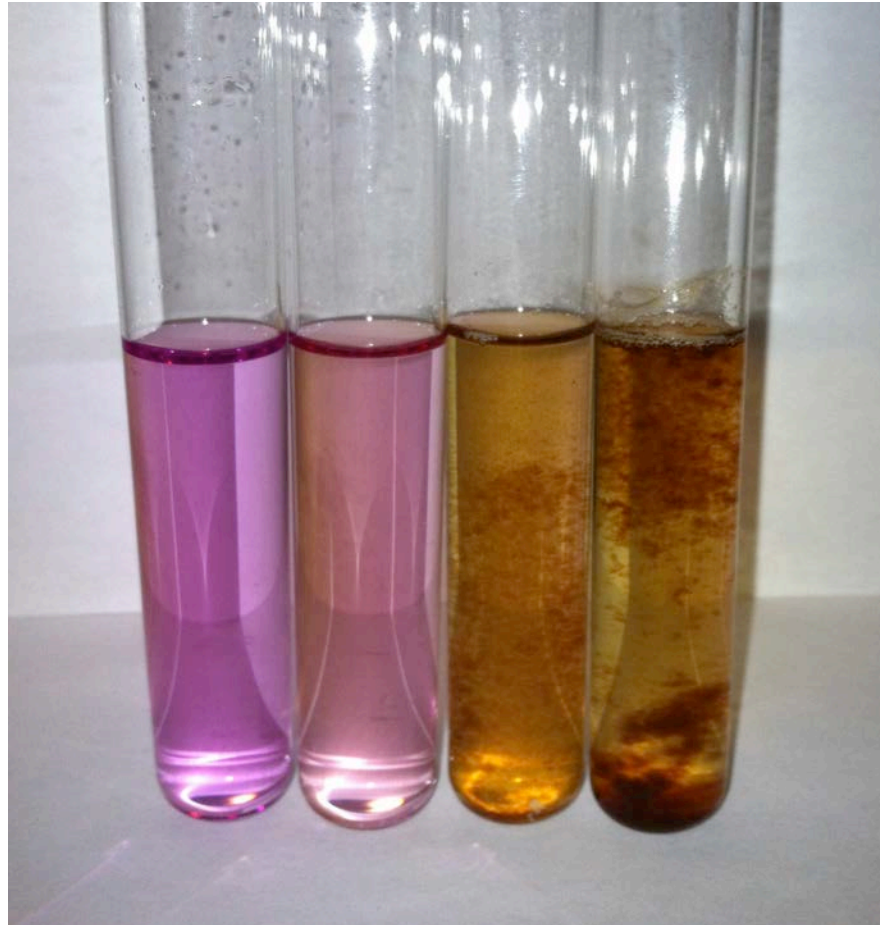
Figure 2-3. Test tubes for heated-DPC analyses (from left to right: 0, 10, 100, and 500 g C/kg additions). This picture represents how all MD soils behaved after being heated at 95°C for 1 hour and analyzed by DPC. Flocculation occurred for the 100 and 500 g C/kg additions.

for conductivity only associated with Cr(VI) after 16 min, and a chromatogram was developed, where the x-axis is retention time, and y-axis is the conductivity response, measured in μS/cm. There was a clear separation between Cr(VI) and other anions such as chloride, nitrate, phosphate and sulfate, which elute after 5, 8, 11 and 12 min, respectively (Fig. 2-4).

The concentrations were calculated using the area under the peaks, and also by comparison to the standards. The limit of detection (LOD) is 0.01 mg Cr(VI)/L and a typical regression equation was:

$$C = [0.543777 + (112.052)(A)] / (V) \tag{7}$$

where C is the concentration of Cr(VI) in the final solution before dilution (mg/L), A is the area under the chromatogram peak, and V is the sample volume injected (20 μL). A typical coefficient of determination (r^2) was ≥ 0.999 (Fig. 2-2).

Results and Discussion

a. Uncontaminated Maryland Soils Spiked with Cr(VI)

i. 0 g C/kg Addition

The heated treatments for Glenelg A1 and Atsion Bhs were significantly different from the unheated ($p \leq 0.05$), regardless of analytical method, recovering only 0-3% Cr(VI). Since these treatments were unamended with C, native reducing agents were responsible for the MIR (Fig. 2-5, Tables A-1 to 2). The remaining heated treatments (Flickinger A1, Bt1 and Glenelg Bt1) and all unheated treatments recovered $\geq 100\%$ Cr(VI) (Fig. 2-5, Tables A-3 to 5).

With such a complex matrix as soil, it is hard to single out one reducing agent
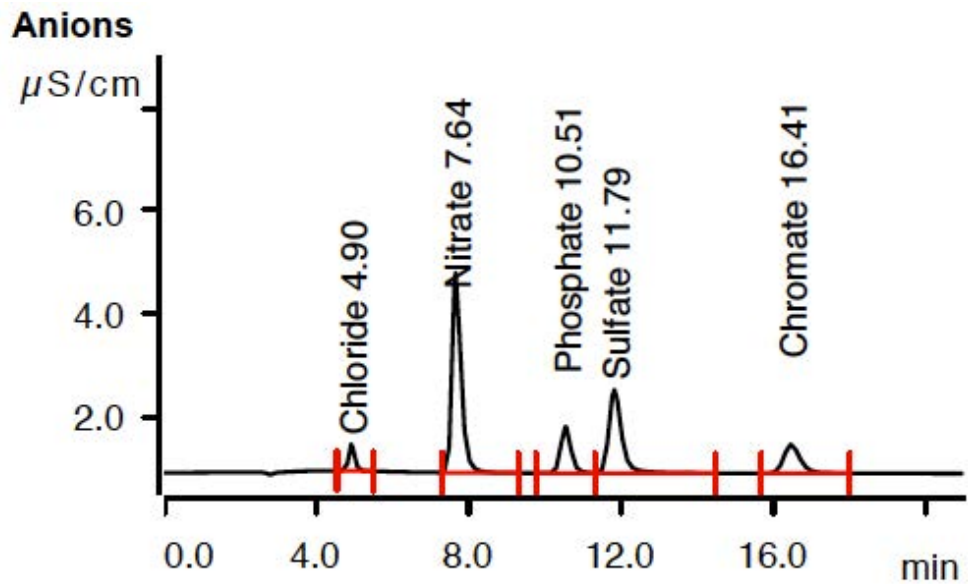
Figure 2-4. Sample Metrohm IC Chromatogram. This chromatogram illustrates a typical sample output of electrical conductivity (μS/cm) vs time (min). The anions are separated based on their charge and size. The anion with the greatest charge and size will be retained the longest, thus the Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, CrO_4^{2-} peak order. The red line represents Metrohm's automated peak integration.
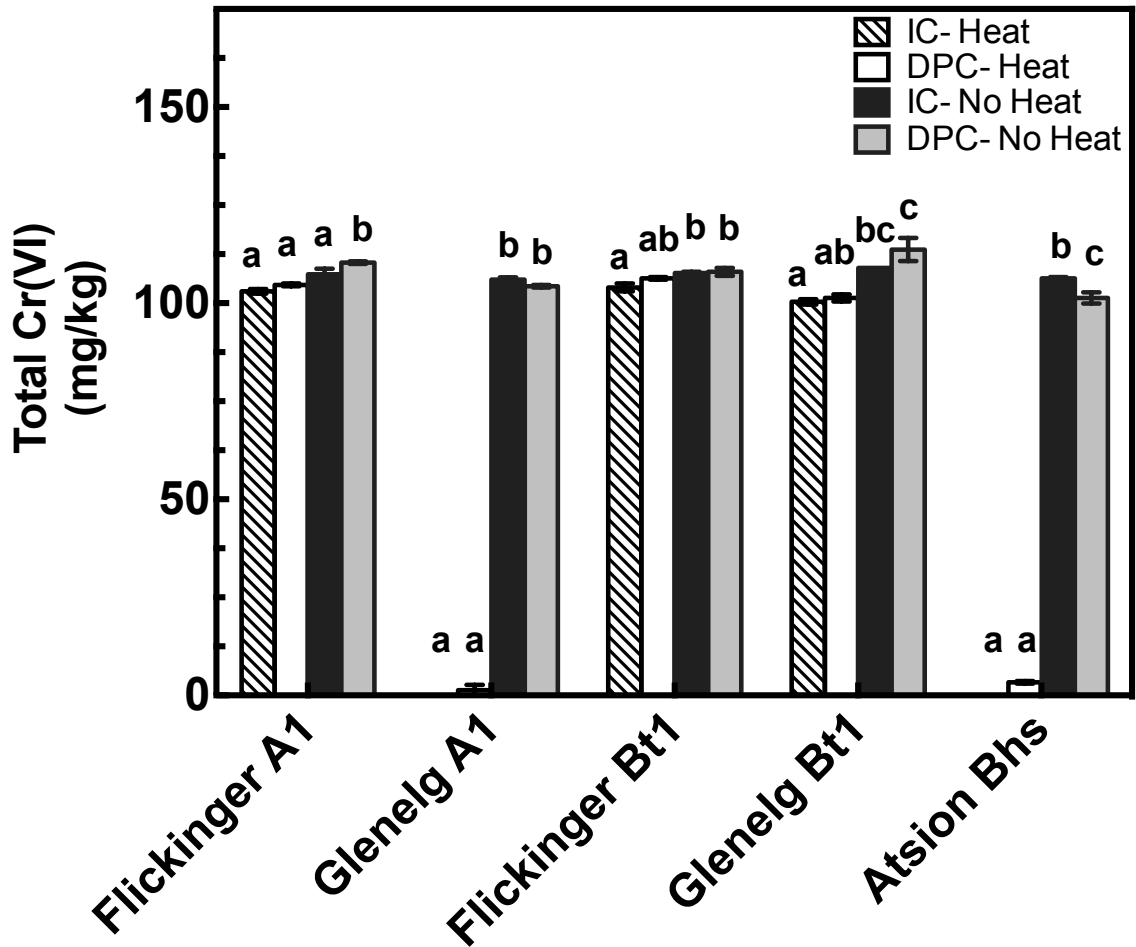
Figure 2-5. Pre-digestion Cr(VI) spikes of Maryland A and B horizons with 0 g C/kg additions. The A and B horizons were incubated for 1 week with 0 g C/kg equivalent additions of compost. The soils were subjected to a 100 mg Cr(VI)/kg spike prior to running Method 3060a with and without heat, and analyzed by IC and DPC. Two-way ANOVAs were performed for each soil, comparing both method temperatures and analytical method ($p \leq 0.05$). The error bars represent one SEM (n=3).

responsible for the entirety of the Cr(VI) reduction observed, but our results strongly indicate that organic C has a dominant role. Under the highly alkaline conditions of the extraction for Cr(VI), the rates of dissolved O_2 (DO) oxidizing Fe(II) are faster than they are for the reduction of Cr(VI) by Fe(II) (Pettine and Capri, 2005a; Pettine and Capri, 2005b). The lack of evidence for Fe(III) reductive dissolution surface reactions is indicated within our results as well. Flickinger A1 has the highest amount of free Fe(II,III)(hydr)oxides Fe (22 ± 2 g Fe/kg) (Table 2-1), and yet this soil showed no MIR (Fig. 2-5), proving that Fe had little effect on Cr(VI) reduction during the extraction. Furthermore, Atsion Bhs has the lowest amount of free Fe(II,III)(hydr)oxides (0.15 ± 0.002 g Fe/kg) (Table 2-1), and has the highest MIR (100% Cr(VI) reduction) (Fig. 2-5). Atsion has high organic matter content (29 ± 1.1 g org. C/kg) (Table 2-1), indicating a likely cause of the MIR was due to the native organic C solubilized by the alkaline extraction in this soil.

Soil organic matter (SOM), synonymous with humus, comprises the total mass of organic compounds in a soil, including the decomposition products of plants and animals, as well as soil biomass and their synthesized substances (Sparks, 2003). Soil organic matter can be divided into humic substances and nonhumic substances. Humic substances can be further divided into humic acids, fulvic acids and humin. Humic acids are soluble in base, but not in acidic conditions, while fulvic acids are soluble in both acid and base, and they are lower in molecular aggregate weight than humic acids. They also have a lower C content than humic acids (Wittbrodt and Palmer, 1995). Humin is the alkali and acid insoluble fraction of SOM. Nonhumic substances are biochemical compounds and

include the re-synthesis products of the soil microbes (e.g. amino acids, carbohydrates, organic acids) (Sparks, 2003).

The nature of SOM is not well understood, due to its structural variability and complex chemistry. Among others, organic compounds such as phenols, quinones, alcohols, and organic acids (e.g. citrate, oxalate, gallate) have been identified as successful reducing agents for Cr(VI) (James and Bartlett, 1983c; Elovitz and Fish, 1995; Brose and James, 2010). Our results showing that soils with higher organic matter are capable of reducing Cr(VI) (Fig. 2-5, Table 2-1), regardless of pH, are supported by previous reports (Bartlett and Kimble, 1976; Vitale et al., 1997; Xiao et al., 2012). However, the previous findings lack evidence for fast reduction rates, especially under the highly alkaline conditions and at the high temperatures of the extraction for Cr(VI). Xiao et al. (2012) used seven soils with a range of properties that included organic matter (OM), dissolved organic matter (DOM), and Fe(II) in order to study their influences on reduction kinetics of Cr(VI). Reduction of Cr(VI) was positively correlated with total OM and DOM contents. After 28 days of incubation at 25°C, the Calcaric Regosol soil, which had the highest OM content and the highest pH of the seven soils tested by Xiao et al. (2012) (21.80 g/kg and 8.25, respectively), reduced 63% of the initial 100 mg Cr(VI)/kg. Similarly, Wittbrodt and Palmer (1995) found that the half-life of Cr(VI) reduction by humic acid was days to weeks for the pH range 4-7. Conversely, in two of the soils in our study, 97-100% of an initial 100 mg Cr(VI)/kg spike was reduced in 60 min under the conditions of pH 12 and 95°C (Fig. 2-5, Tables A-1 to 2). Therefore, we conclude that the combination of high organic matter and heat is the most likely cause of the swift MIR.

In a similar experiment to the one we conducted, Vitale et al. (1997) compared Method 3060A with and without heat, and observed a darker organic C color in the alkaline extract when used with heat, which supported their hypothesis that the heat may have released S- and C-containing compounds within their anoxic sediment sample, causing reduction of Cr(VI), despite the high pH conditions. Our results support their conclusion that heat accelerates dissolution reactions, which at 22°C, would be much slower.

Comparing IC and DPC analysis of extracts from the same soil, the two methods were not significantly different for any of the heated treatments (Fig. 2-5, Tables A-1 to 5). The soils Flickinger A1 and Atsion Bhs showed statistical difference between IC and DPC for the unheated treatments ($p \leq 0.05$), but scientifically the difference was small enough that it has little meaning compared to the spike amount. The mean difference was only 3 mg Cr(VI)/kg for Flickinger A1 and 5 mg Cr(VI)/kg for Atsion Bhs, out of a total 100 mg Cr(VI)/kg spike (Fig. 2-5, Tables A-1 to 5). In addition to the small mean differences, the method discrepancy is considered non-problematic since there was $\geq$ 100% Cr(VI) recovery.

ii. 10 g C/kg Addition

The percent increase over native soil C levels due to the addition of 10 g of compost C/kg soil is tabulated in Table 2-4. The most affected treatments were the Flickinger Bt1 (345%), Flickinger A1 (270%), and Glenelg Bt1 (217%). Even with this large percent increase, the total amount of C for each of these soils was still less than the native C in Glenelg A1 (24 g/kg) and Atsion Bhs (29 g/kg). Despite the carbon increase,

Table 2-4. Total organic C and C-to-Cr(VI) ratios for each C amendment (0, 10, 100 and 500 g C/kg soil).

| | Carbon Amendment (g/kg) | | | | | | | |
| | 0 | | 10 | | 100 | | 500 | |
Soils	Native C^a	C:Cr(VI)[b]	Total C^c	C:Cr(VI)	Total C	C:Cr(VI)	Total C	C:Cr(VI)
Flickinger A1	3.7	160	13.7	594	104	4494	504	21827
Flickinger Bt1	2.9	126	12.9	559	103	4459	503	21792
Glenelg A1	24	1040	34	1473	124	5373	524	22707
Glenelg Bt1	4.6	199	14.6	633	105	4533	505	21866
Atsion Bhs	29	1257	39	1690	129	5590	529	22923
MES COPR	18	65	32	101	122	426	522	1871
6500 COPR	17	11	28	18	118	78	518	345

[a]Organic C (g/kg) determined with LECO after destroying carbonates (Piper, 1942; Nelson and Sommers, 1996).

[b]The C:Cr(VI) exhibits the total initial organic C (mol) to total initial Cr(VI) (mol) in the soil. For Maryland soils, $Cr(VI)_0$ was 4.8×10^{-6} mol Cr(VI); MES was 5.8×10^{-5} mol Cr(VI) and 6500 was 3.1×10^{-4} mol Cr(VI).

[c]Determined by adding the compost C to the native organic C of the soil.

the unheated treatments maintained a high Cr(VI) recovery rate of 95-116%, which includes both analytical treatments.

The heated Glenelg A1 and Atsion Bhs remained at 0-3% Cr(VI) recovery for this lowest compost addition, indicating that the compost C had no further effect on these soils (Fig. 2-6, Tables A-1 to 2). The average of the remaining three heated soils exhibited 82±5% recovery of Cr(VI) for IC and 76±5% recovery for DPC (Fig. 2-6, Tables A-3 to 5). The degree of reduction corresponds to an increasing initial C/Cr(VI) ratio. For example, when Glenelg A1 and Atsion Bhs showed 100% reduction, their averaged ratio of C/Cr(VI) was 1149±109, which in our experiment ($5x10^{-6}$ mol $[Cr^{6+}]_0$), corresponds to an organic C content of ≤ 27 g/kg. A 20-25% reduction occurred in the remaining three soils at an average C/Cr(VI) ratio of 595 ± 21. If we assume a fixed ratio, we expect to see 100% reduction of the Cr(VI) spike at approximately a C/Cr(VI) of 2380 for Flickinger A1 and Bt1, and Glenelg Bt1. In our experiment, this ratio corresponds to an organic C content of ≤ 55 g C/kg soil. That is, it takes nearly twice the organic C content to fully reduce the Cr(VI) spiked Flickinger and Glenelg Bt1 soils. This led us to consider not only the C/Cr(VI) ratio, but the fractionation of the carbon within the soils.

In order to assess the relative proportion of fulvic and humic acids in the method extract, we measured the absorbances at 465 and 665 nm, commonly known as the E_4/E_6 ratio (Table 2-5). In soils, a visible spectrum of humic substances has little value, but a ratio of $\lambda_{465}/\lambda_{665}$ has been correlated with particle size and therefore molecular weight of the dissolved organic compounds (Chen et al., 1977; Thurman, 1985). Humic acids from soils fall in the range of 2-5 and soil fulvic acids from 6.5-10 (Chen et al., 1977;
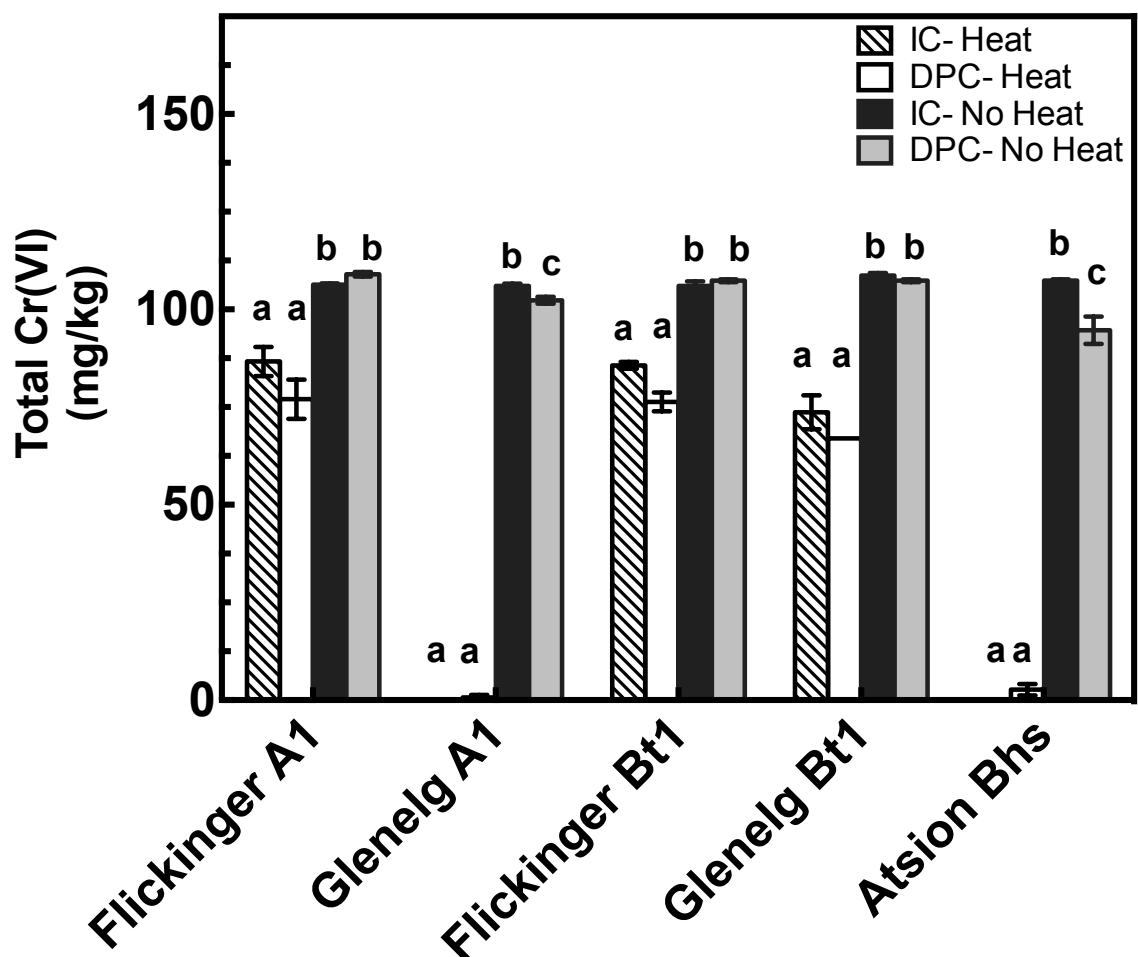
Figure 2-6. Pre-digestion Cr(VI) spikes of Maryland A and B horizons with 10 g C/kg additions. The A and B horizons were incubated for 1 week with 1 g C equivalent additions of compost to 100 g soil. The compost-amended soils were subjected to a 100 mg Cr(VI)/kg spike prior to running Method 3060a with and without heat, and analyzed by IC and DPC. Two-way ANOVAs were performed for each soil, comparing both method temperatures and analytical method ($p \leq 0.05$). The error bars represent one SEM (n=3).

Table 2-5. Absorbances measured at 465 nm (E_4) and 665 nm (E_6) for digestate extracts adjusted to pH 12 and 1.7.

Soil[b]	pH 12[a]		pH 1.7[a]	
	Abs$_{465}$	Abs$_{665}$	Abs$_{465}$	Abs$_{665}$
Flickinger A1	0.007 ± 0.001	0.001 ± 0.000	0.003 ± 0.000	nd[c]
Flickinger Bt1	0.007 ± 0.000	nd	0.002 ± 0.000	nd
Glenelg A1	0.121 ± 0.002	0.014 ± 0.000	0.015 ± 0.001	0.001 ± 0.000
Glenelg Bt1	0.011 ± 0.001	nd	0.006 ± 0.001	nd
Atsion Bhs	0.421 ± 0.002	0.059 ± 0.001	0.095 ± 0.003	0.006 ± 0.000
Compost	0.396 ± 0.012	0.057 ± 0.012	0.091 ± 0.004	0.006 ± 0.001
MES	0.002 ± 0.000	nd	nd	nd
6500	0.003 ± 0.000	nd	0.004 ± 0.001	nd

[a]Errors are one SEM (n=3).

[b]Abbreviations as in Table 2-1.

[c]nd is not detected (zero absorbance), as measured by the UV-VIS spectrophotometer.

Schnitzer and Khan, 1978; Thurman, 1985). Therefore, a lower ratio corresponds to humification (Thurman, 1985).

This experiment was performed on the unamended soils and compost alone, to understand the effects of native organic matter. To better relate this ratio to our study, we measured the absorbances at the pH of the extraction (11-12), and then acidified the extracts to pH 1.7, and measured the absorbances again (Table 2-5). We hypothesized that by comparing the two ratios at the separate pHs, we could qualitatively determine the relative amounts of humic vs. fulvic acids. We will begin our discussion with the soils containing the highest amount of organic C. (Table 2-1). The E_4/E_6 ratios at pH 12 for Glenelg A1, Atsion Bhs and compost were 8.6, 7.1 and 6.9, respectively (Table 2-5). These large values of E_4/E_6 suggest that there are smaller, highly aliphatic compounds present associated within the FA fraction, which is known to be the more reactive part of SOM, largely due to its solubility (Rivero et al., 2004). It is hard to say whether or not these soils contain a higher fulvic acid fraction, or the high heat, alkaline extraction favors the release of fulvic acids over humic acids. During acidification to pH 1.7, flocculation occurred and the samples had to be centrifuged prior to measurement, which qualitatively informs us that there is indeed a portion of humic acids in the high organic C soils. At pH 1.7 the ratios increased to 15, 16 and 15, respectively (Table 2-5). We expected the ratio to increase at pH 1.7 because humic acids are insoluble at low pH; a higher E_4/E_6 ratio corresponds with low molecular weight compounds that contain less C but more O, carboxyl groups and total acidity, consistent with our knowledge of fulvic acids (Chen et al., 1977).

It should be noted that if future researchers are looking to mimic soils' organic C

reactivity, then Leafgro® would be a practicable option. It is remarkable how comparable the two soil horizons Glenelg A1 and Atsion Bhs were to compost, with the greatest difference being 1 ratio unit at pH 1.7, and 1.7 units at pH 12. Since the weight of dissolved organics and, thus, the presence of O, C, and COOH functional groups govern the magnitude of the ratio, the results from this study show that compost would be a suitable surrogate for a high organic C soil horizon for research purposes (Chen et al., 1977). This is a similar conclusion to that of researchers studying peat, who found that the elemental composition, functional group types, and NMR spectral characterization of peat-derived humic acids were comparable to those from mineral soils (Wittbrodt and Palmer, 1997).

As for the remaining three MD soils, very low absorbances (≤ 0.011) were measured for λ_{465} and zero absorbance for λ_{665}, at both pH 12 and 1.7 (Table 2-5). In comparison, Glenelg A1, Atsion Bhs and compost all had ≥ 0.100 for absorbance measurements at λ_{465} and ≥ 0.014 for λ_{665}. Due to zero in the denominator, E_4/E_6 could not be determined for Flickinger A1 and Bt1 and Glenelg Bt1. Despite the lack of quantitative data, our analysis remains informative. Humic acids have a higher absorbance at λ_{665} due to their greater reddish color (Thurman, 1985). This also explains why humic acids have a lower E_4/E_6. This qualitatively informs us that the Flickinger soils and Glenelg Bt1 have little-to-no humic acids extracted during Method 3060a. Additionally, there was no flocculation after acidification, supporting our hypothesis of low humic acids. Therefore any MIR occurring with these soils can be attributed to native fulvic acids, similar to our conclusion above regarding the higher organic C soils. It is logical that the lower organic C soils would have a smaller fraction of fulvic acids,

considering the lower absorbances at λ_{465} as compared to the soil samples Atsion Bhs, Glenelg A1 and compost. From this investigation, we now understand that low molecular weight, aliphatic compounds (we assume to be fulvic acids) attribute to the majority of MIR seen in the extraction, as they are dominant in the extracted solution.

At 10 g C/kg, for many soils and treatments (heat and/or no heat), DPC consistently recovered less Cr(VI), showing the most MIR (Fig. 2-6). This suggests that ≥10 g C/kg is a threshold above which the IC method for extracted Cr(VI) is more reliable than is the DPC method. Our first hypothesis as to why this is occurring is specific to the Flickinger horizons. Flickinger is a manganiferous soil with high Fe(III) and Mn(II,III,IV) contents. A similar method redox interference involving Fe was identified by Huo et al. (1998) where the Fe(III) appeared to be a reducing agent, but was in fact just oxidizing the DPC, underestimating the total Cr(VI) value. Another hypothesis is that electron shuttling is occurring between the DOC and Cr(VI). Brose and James (2010) found that electron shuttling between organic acids and soil organic matter moieties may be capable of indirectly reducing Cr(VI). In their work, AQDS (a surrogate for soluble humic acids) was reduced by lactic organic acid, and the reduced form of AQDS was capable of then reducing soil Cr(VI). This pathway of electron shuttling by metals and organic acids is a plausible explanation for our results, considering the combined compost and soil humic materials present in our experimental treatments. In summary, the MIR in the DPC method was likely due some combination of these soil processes: (1) low pH being conducive to reduction reactions (2) DPC behaving as reagent with reactants other than Cr(VI) and (3) organic shuttling reductive pathways.

ii. 100-500 g C/kg Addition

As the organic C input as compost increased to 100 and 500 g/kg (10 and 20 mmol C), the DPC method could no longer be used for analyzing the heated extracts; this was supported by an absence of the DPC-with-heat bar (Fig. 2-7). The dark brown precipitated floccules in the DPC-treated test tubes would have caused erroneous measurements in the colorimetric method and also would have caused damage to the spectrophotometer (Fig. 2-3). The low pH of the DPC method (< 2) caused solubilized humic acids to flocculate and precipitate. This is a significant finding of this study, considering that a heated method followed by DPC analysis is the standard, recommended EPA extraction method, at least for COPR materials, and presumably for soils (USEPA, 2014).

We can compare IC vs. DPC for the unheated treatments, though, and IC consistently had higher results for Cr(VI). The range for IC across the five soils amended with 100-500 g/kg C amendments was 105±0.18%, while DPC only recovered 87±1%, differing significantly at $p \leq 0.05$. These results are consistent with our earlier threshold of ≥ 10 g C/kg above which IC method for extracted Cr(VI) is more reliable than the DPC method, even without heat in the alkaline extraction. Since we eliminated the interference of colored organic complexes absorbing light at 540 nm by using a blank reagent and subtracting the absorbance value, we are confident that the cause is reduction. We maintain the same hypotheses from the "10 g C/kg addition," section regarding this issue.

Heating during the alkaline extraction is not advisable with soils uncontaminated with Cr(VI), with MIR problems arising between 5 and 13 g C/kg content (Table 2-4).

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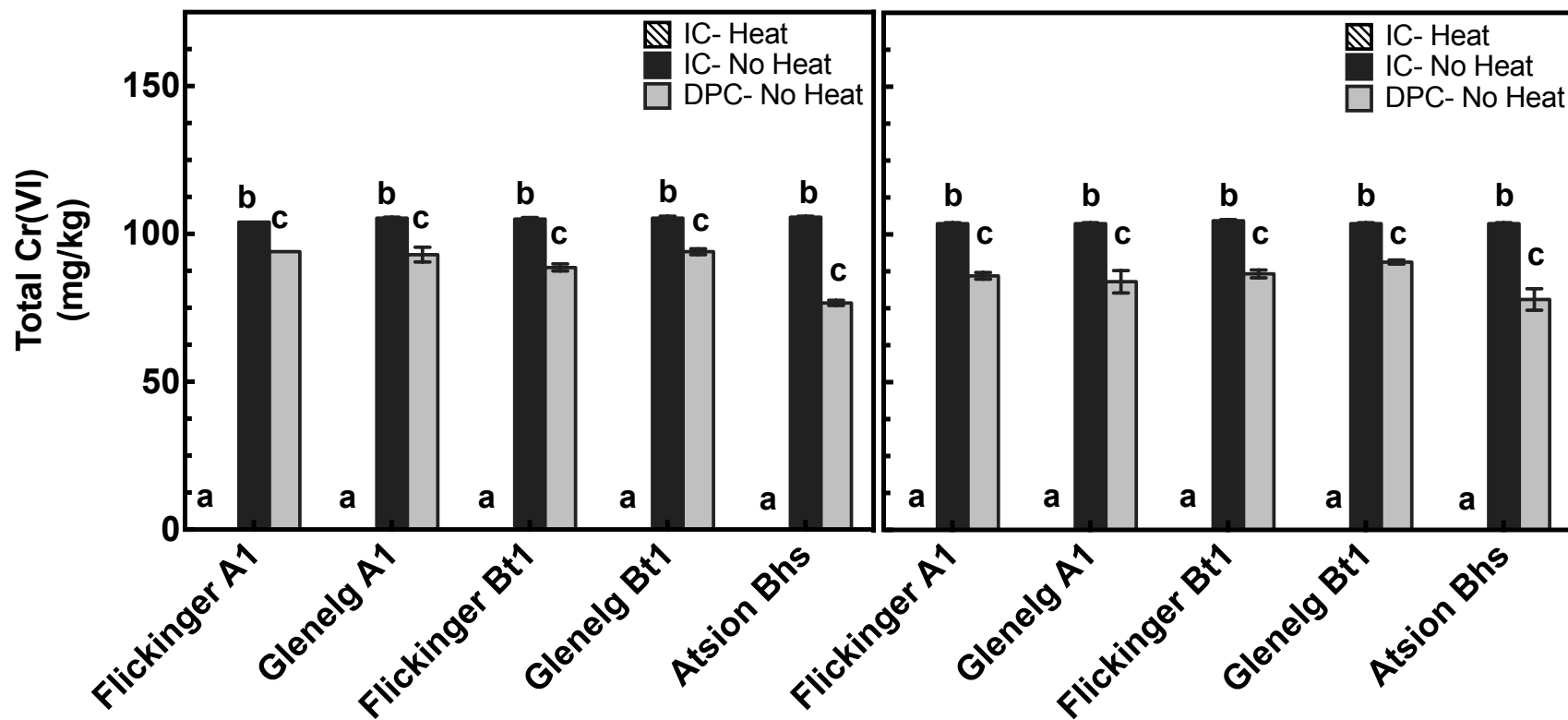
Figure 2-7. Pre-digestion spikes Cr(VI) of Maryland A and B horizons with 100 (left graph) and 500 g C/kg additions (right graph). The A and B horizons were incubated for 1 week with 10 and 50 g C equivalent additions of compost in 100 g soil. The compost-amended soils were subjected to a 100 mg Cr(VI)/kg spike prior to running Method 3060a with and without heat, and analyzed by IC and DPC. One-way ANOVA was conducted due to the absence of results for Heat-DPC ($p \leq 0.05$). The error bars represent one SEM (n=3).

The heat causes inconsistent, inaccurate results by the IC and DPC methods in these soils. The bar that represents our proposed method of an unheated extraction followed by the new IC method is consistent and highly accurate in terms of recovering total Cr(VI) (Fig. 2-5 to 7). We conclude that heating the alkaline solution predominantly dissolves organic carbon in the form of fulvic acids from soils, which causes method-induced reduction, and interference in subsequent Cr(VI) analyses.

We originally hypothesized that the low pH of DPC would enhance the reduction of the Cr(VI), but, instead, we found good recoveries of post-digestion spikes, at or above a 100% recovery rate (results not shown). This indicated that there was no reduction in the post-digestion solutions for any of the method temperatures and analytical methods.

b. High Cr(VI) Waste Materials

The high Cr(VI) COPRs did not exhibit interference due to flocculated humic acids during the analysis of the alkaline extracts with the DPC method, regardless of the C amendment. We originally hypothesized that this was due to the majority of COPR native C existing as carbonate-C, or humin that is insoluble in alkaline solutions, and therefore not capable of reducing Cr(VI) during extraction. High carbonate content in COPRs can be attributed to carbonate phases forming when the original waste materials were exposed to atmospheric CO_2 upon land filling (Wazne et al., 2008). This carbonated formation from CaO and $Ca(OH)_2$ was only possible because of the high alkalinity of the COPRs. The carbonate content depends on the degree of atmospheric exposure and the manner of exposure, therefore the deposition and/or mixture into indigenous soils will influence the carbonate content. Other discrepancies result from the various ways the chromite ore was processed. For example, 6500 was a high lime process COPR with a

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high purity product, but less chromate salt recovery; conversely, MES was a low lime, low purity product, with a higher yield. Color, pH, and soluble Cr(VI) are other diagnostic factors. Wazne et al. (2008) reports that the carbonate content comprises approximately 11.5% of total mass of COPR at the same Hudson County, NJ site from where our soils were sampled, particularly in the high lime process COPRs.

However, after removing the carbonates before CHN analysis, the organic C content was still high for MES and 6500, at 18 and 17 g C/kg, respectively (Table 2-1). The high organic C content was not completely unexpected, though, and has been observed in other COPR studies, ranging from 9-25% organic C by weight (Weng et al., 1994; Elzinga and Cirmo, 2010). Our particular COPR samples spent decades as fill of Histosol wetland soils along the Hackensack River in Hudson County, NJ, where a cool climate, wet conditions and vegetation input provided for organic C accumulation in peaty formations. In the case of COPRs, and presumably other similar waste soils, it is valuable to discuss how the organic C exists within the soil, more than just focusing on total organic C. For COPRs, the native organic C is likely tightly bound by Cr(III) and associated oxides and hydroxides of Fe(III) and Al(III), and therefore is not easily solubilized in the alkaline extraction, preventing flocculation from proceeding in the DPC acidic solutions. Elzinga and Cirmo (2010) estimated the organically complexed Cr(III)-DOM contribution from 8 to 56% of total Cr, depending on the soil. The authors attributed the rather broad range to differences in organic inputs, climate, and sedimentary deposition rates among samples. The excess Cr(III) is from residual, unreacted chromite ore in the roasting process. MES and 6500 measured low absorbances (≤ 0.004) for λ_{465} and zero absorbance for λ_{665}, at both pH 12 and 1.7 (Table 2-5). Thus,

at the pH of the extraction there is little to no dissolved organic carbon in the form of fulvic or humic acids. This corroborates Elzinga and Cirmo's findings of Cr(III) bound by organics. James and Bartlett (1983a) found that fulvic acid effectively complexes Cr(III) and prevents its precipitation, but only up to pH 7.5. We hypothesize that at the pH of the extraction, any soluble DOM has most likely been bound by Cr(III), precipitated, and removed by centrifugation. Similarly, we speculate that the added carbon from compost could also be absorbed or bound by Fe oxides and/or organic matter in the COPRs, preventing solubilization in the alkaline extract. Thus, we add yet another deciding parameter that must be considered in deciding which analytical method for Cr(VI) to use when extracting and quantifying Cr(VI) in waste-amended soils: the availability of the C within the soil.

Furthermore, the discussion of C/Cr(VI) as related to COPRs becomes less important for two reasons: (1) if the C is not solubilizing, it will not influence the triggering of MIR, and (2) the denominator is so large that we will actually see MES and 6500 becoming more affected at lower C/Cr(VI). In fact, MIR (for the heated extractions) begins occurring at approximately 100 C/Cr(VI) (mol units) for MES and C/Cr(VI) 78 for 6500 (Table 2-4, 6 and 7).

i. 0 g C/kg Addition to COPRs

The heated, alkaline extraction for both unspiked (0 mg Cr(VI)/kg addition) and unamended (0 g C/kg addition) COPRs differed significantly from the unheated treatments ($p \leq 0.05$), and the heated extraction recovered an average of 10% more Cr(VI) from the MES and 34% from the 6500 COPR (Tables 2-6 to 7). This result is

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Table 2-6. Cr(VI) extraction and analysis comparison with heat (95°C) or without (23°C) and analyzed by IC or DPC: MES COPR results.

Carbon Addition (g C/kg)	Heat Treatment[a]			
	Unheated[b]		Heated[b]	
	IC	DPC	IC	DPC
0	1092±12 a	1058±7 a	1349±11 b	1278±8 c
10	1096±12 a	1046±9 b	1126 ± 14 a	1024±4 b
100	873±7 a	713±12 b	nd[c] c	8±2 c
500	1089±10 a	712±26 b	nd c	11±7 c

[a]Statistically significant differences were identified within the same C addition treatment (in each row) with two-way ANOVA ($p \leq 0.05$).

[b]Means are given in mg Cr(VI)/kg COPR and errors are SEM (n=3).

[c]nd is <LOD. LODs are 0.01 mg Cr(VI)/L for both the IC and DPC methods.

Table 2-7. Cr(VI) extraction and analysis comparison with heat (95°C) or without (23°C) and analyzed by IC or DPC: 6500 COPR results.

Carbon Addition (g C/kg)	Heat Treatment[a]			
	Unheated[b]		Heated[b]	
	IC	DPC	IC	DPC
0	4023 ± 41 a	3742 ± 52 a	6245 ± 104 b	6020 ± 50 b
10	3485 ± 6 a	3599 ± 26 a	5957 ± 60 b	5803 ± 71 b
100	4075 ± 70 a	4326 ± 6 a	2393 ± 184 b	2336 ± 250 b
500	6486 ± 85 a	6845 ± 77 b	7.5 ± 8 b c	184 ± 14 c

[a]Abbreviations as in Table 2-6.

[b]Abbreviations as in Table 2-6.

consistent with previous findings and attests to the original purpose of Method 3060a, which was to solubilize the sparingly-soluble, adsorbed, and freely-soluble forms of Cr(VI), requiring the more aggressive, heated approach (Vitale et al., 1994; James et al., 1995). Some of the major mineral phases (crystalline and paracrystalline) identified in the COPR using X-Ray powder diffraction (XRPD) were brownmillerite ($Ca_4Al_2Fe_2O_{10}$), brucite ($Mg(OH)_2$), calcite ($CaCO_3$), quartz (SiO_2), hydrotalcite ($4MgO \cdot Al_2O_3 \cdot 10H_2O$), and katoite ($Ca_3Al_2(H_4O_4)_3$) (Wazne et al., 2008). Katoite (a hydrogarnet) has been shown to be a host phase for Cr(VI), and calculations based on its abundance as the crystalline phase in millions tons of COPR in Glasgow, indicated that as much as 50% of the Cr(VI) content of the COPR can be found in hydrogarnet (Hillier et al., 2007). The only known Cr(VI)-bearing mineral identified by Wazne et al. (2008) in their NJ samples was calcium aluminum oxide chromium hydrate (CAC) ($Ca_4Al_2(OH)_{12}CrO_4 \bullet nH_2O$), also known as Cr(VI)-hydrocalumite. The chromate anions (CrO_4^{2-} and $HCrO_4^{-}$) are held in the interlayers of CAC. The hydroxide was present as 0.87% at pH 12, indicating a concentration of approximately 667 mg Cr(VI)/kg, which was 13% of the total Cr(VI) identified in the soils of this paper. The amount of Cr(VI) held in mineral phases varies among samples depending on the history of industrial processing, deposition location, pH, time spent in the landfill, etc., but earlier research found that the release of total Cr(VI) from COPR is highly dependent on the Cr(VI)-containing solid phases (Geelhoed et al., 2002). This helps to explain why the conditions of high heat and alkalinity are required to extract the Cr(VI) more aggressively.

There was only one analytical difference at 0 g C/kg addition among the same heat treatment, and it was for the heated MES (Table 2-6). The IC method recovered 71

mg Cr(VI)/kg or ~6% more Cr(VI) than DPC, for a statistical difference of p=0.033. However, we are not considering this a scientifically significant result, since both methods were capable of recovering $\geq$ 1200 mg Cr(VI)/kg, the approximate total Cr(VI).

i. 10 g C/kg Addition

It is important to note that from here on, these results account for the dilution that occurred when mixing COPR together with compost, as described in the Methods section. For example, at 500 g C/kg addition of compost C, the soil:compost ratio was nearly 1:1 (127 g compost and 100 g COPR oven-dry equivalents), and therefore, we multiplied the extracted results by 2.27, or the dilution factor, and those final numbers are indicated in Tables 2-6 and 7. We used compost-amended COPR, but after accounting for the Cr(VI) dilution brought on by the compost, the units are presented in mg Cr(VI)/kg COPR.

At 10 g C/kg addition for MES, the IC-unheated treatment was not statistically significantly different from the IC-heated one, and the DPC-heated treatment was not different from the DPC-unheated treatment (p$\leq$0.05) (Table 2-6). Therefore, with organic C contents 0$\leq$x$\leq$10 g C/kg, heat or no heat could be used for the MES COPR, but both treatments exhibit roughly 10% MIR (Table 2-6). Although the analytical results between the same heat treatments were much greater for the heat treatment (p=0.0006) than for the unheated (p=0.038), for both, IC recovered more Cr(VI) than did DPC (Table 2-6).

As for 6500, at 10 g C/kg, the heated, alkaline extraction remained preferable over the unheated (p$\leq$0.05) (Table 2-7). Processes that are responsible for the release of Cr(VI) include (1) desorption of exchangeable Cr(VI) (2) oxidation of Cr(III) to Cr(VI) and (3)

dissolution of Cr(VI)-bearing minerals (Foldi et al., 2013). The extraction method is designed to solubilize all forms of Cr(VI) and prevent the oxidization of Cr(III) to Cr(VI), thus we can eliminate the first two from our consideration (USEPA, 2014). In fact the oxidation of Cr(III) at an alkaline pH is extremely rare, due to the likely precipitation of $Cr(OH)_3$. James (1994) found that only 0.3% of a soluble 600 mg Cr(III)/kg spike resulted in oxidation in COPR-bearing, alkaline soils. Therefore, we are left to focus on the mineralogical composition to explain the difference in dissolution between MES and 6500. Although previous research has suggested that the moderately soluble salts $CaCrO_4$ (K_{sp} $7.1x10^{-4}$) and $CaSO_4$ (K_{sp} $3.1x10^{-5}$) may control the soluble fraction of COPRs, we are more concerned with explaining the dissolution of the insoluble fraction of COPR, since it is the limiting factor in the determination of how much Cr(VI) will be released (James, 1994; Geelhoed et al., 2002). Recall, 6500 was made through a high lime process, while MES was a low lime process; samples with a relatively high content of Ca and Cr as seen in 6500 generally have low fractions of carbonate bound Ca, signifying there are other Ca-rich phases (Foldi et al., 2013). Geelhoed et al. (2002) determined through batch and speciation experiments that the presence of calcium aluminate phases, e.g. Cr(VI)-hydrocalumite (CAC) ($Ca_4Al_2(OH)_{12}CrO_4 \bullet 6$ H_2O, log k=68.3), Cr(VI)-bearing hydrogarnet ($Ca_3Al_2((Cr/Si/H_4)O_4)_3$, log k=65.4), and Cr(VI)-ettringite ($Ca_6Al_2(OH)_{12}(CrO_4)_3 \bullet 26$ H_2O, log k=55.8) dominate the solubility chemistry of COPR (log K values are thermodynamic solubility constants). The Cr(VI) contained in the CAC mineral, a layered double hydroxide (LDH), is in the interlayer space (Geelhoed et al., 2002). The LDHs have a metal hydroxide layer located in the top and bottom layers, while the anion

layer is located in the middle; the exchangeable anions compensate for positive charge, e.g. brucite type layers (Nalawade et al., 2009). As for hydrogarnet minerals, the chromate anion (CrO_4^{2-}) is substituted for hydroxyl tetrahedra (Hillier et al., 2007). Ettringite incorporates CrO_4^{2-} through substitution for SO_4^{2-} (Hillier et al., 2003). We hypothesize that the difference seen between COPRs is due to the higher degree of Ca mineral phases, capable of bearing chromate in the interlayers of the structure. Although the confirmation of such minerals is beyond the scope of this research, our results indicate a more robust heating treatment is required to extract such forms.

No differences were seen between analytical methods, for the same heat treatment ($p \leq 0.05$) (Table 2-7). Our hypothesis, supported by previous researchers, attributes these results to the decreased influence of soil reducing agents in 6500, as compared to the magnitude of Cr(VI) content. For example, the ratio of sample (kg) to Cr(VI) (mg) for 6500 is 1:6500, and therefore the influence of the soil properties (solubilized C, Fe (II,III), etc.) within the soil matrix level is so low, it doesn't interfere with detection in either method (Huo et al., 1998).

ii. 100-500 g C/kg Addition

A clear threshold is reached at 100 g C/kg, where our proposed method of no heat provides for the highest recovery, consistently, for both COPRs (Fig. A-1, Tables 2-6 and 7). At the 100 g C/kg level, the highest mean %Cr(VI) recovery for MES was with the IC at 73%; for 6500, with DPC at 67% (Tables 2-6 and 7). Interestingly, the Cr(VI) recovery further increased at the 500 g C/kg addition to 91% and 100%, respectively. The rise in Cr(VI) recovery from 100 g C/kg to 500 g C/kg amendment could be due to the

heterogeneity of the COPRs or experimental error of dilutions. Regardless, we obtained a $\geq 91\%$ Cr(VI) recovery at the 500 g C/kg level using the unheated extraction in combination with the dominant analytical technique, IC for MES and DPC for 6500 (Tables 2-6 and 7). The acceptance range for spike recoveries in Method 3060a is 75-125%, indicating that our proposed method is satisfactory according to regulatory guidelines (USEPA, 2014). The statistical difference between analytical techniques for the two COPRs is interesting, especially for MES, and warrants further research, but we cite earlier hypotheses regarding the issues and interferences with the DPC method (Tables 2-6 and 7).

It is noteworthy that even without heat, the compost C humic and fulvic acid solubilization by base was enough to cause some reduction of Cr(VI). This research may be useful to those interested in remediation of COPR by compost C in which Cr(VI) may or may not be reduced in situ, but may not be quantifiable by the alkaline extraction, with or without heat.

Conclusion

The importance of a reliable extraction method for accurate quantification of total Cr(VI) in soils and waste materials cannot be overstated, particularly in environmental contamination situations, because chemical species are not static and are controlled by redox processes for Cr(III,VI). We conclude for both non-contaminated and high Cr(VI) waste materials, to first characterize your sample to the best of your ability: estimate organic carbon, the C/Cr ratio and E_4/E_6. Additionally, we hypothesize from the work of previous researchers that the forms C and Cr(VI) exist in (e.g. soluble fraction of total

Cr(VI), carbon bound by Cr, Cr mineral phases) are important considerations. The following then can be addressed based on these results:

a. Heat or No Heat: The unheated method consistently recovered $\geq$ 100% of the 100 mg Cr(VI)/kg spike for all C amendments. Therefore, the best method is to shake with digestion solution for 1 hour at 22-24°C and quantify Cr(VI). A more specific boundary is we saw 100% MIR around approximately 800 C/Cr (in moles) with the heated method.

b. DPC or IC: Use IC for soils with $\geq$ 10 g C/kg: this is when flocculation in the DPC test tube was first observed. If high CBD Fe, there may be Fe(III)-DPC interactions causing Cr(VI) to be falsely represented, and therefore our recommendation is to use the IC.

For contaminated soils such as COPR, acquire an estimate of the amount of total Cr(VI) by using EPA's Method 3060a with heat (95°C) for 1 hour.

a. Heat or No Heat: Combining the results from both COPRs, we recommend making the switch to the no-heat method at $10 \leq x \leq 100$ g C/kg. The higher contaminated samples (x > 4,000 mg Cr(VI)/kg) may be better with the heated extraction up to the 100 g C/kg input, to enhance dissolution of the more sparingly soluble forms of Cr(VI).

b. DPC or IC: Overall, the IC was preferable with MES, but there was not a better method for analyzing the 6500 COPR extracts, indicating that experimentation may be necessary. Again, though, if there is a high extractable Fe content, our results indicate that IC is the superior choice.

CHAPTER 3

REMEDIATION OF HEXAVALENT CHROMIUM-CONTAMINATED SOILS: EFFECTS OF IRON AND ORGANIC CARBON ON SUBSEQUENT FRACTIONATION OF CHROMIUM

Introduction

Chromium (Cr) is a transition metal that is oxidized in an industrial process from Cr(III) to Cr(VI) in a hot, alkaline roasting of chromite ore ($FeO \bullet Cr_2O_3$), and the solubilized Cr(VI) is used in many industrial processes, such as electroplating, textile production and leather tanning (Darrie, 2001). Major geographic localities affected by chromite ore processing facilities and their solid wastes include Hudson County, NJ, Baltimore County, MD and Glasgow, Scotland (Burke et al., 1991; Graham et al., 2009; Broadway et al., 2010). According to Burke et al. (1991), the chemical reaction of the chromite ore processing can be generalized as (corrected from cited source to balance C and O):

$$4FeCr_2O_4 \ + \ 8Na_2CO_3 \ + \ 7O_2 \ \xrightarrow{\text{1100–1150°C}} \ 8Na_2CrO_4 \ + \ 2Fe_2O_3 \ + \ 8CO_2 \qquad (8)$$
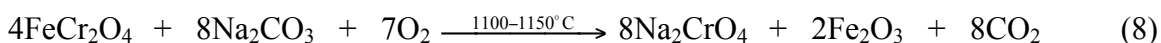
The unleached Cr-rich waste generated has frequently been disposed of on land and in wetlands or landfills, increasing the concentration of Cr(VI) and Cr(III) in the soils, and potentially subjacent groundwater and nearby surface waters. Chromite ore processing has largely been abandoned in the western world, but continues in emerging industrial countries such as China, Russia, India and Pakistan (Geelhoed et al., 2003). An additional source of Cr pollution that does not have a history associated with chromite ore processing is leachate from leaking and unlined coal ash dumps. Between 2000 and 2009, over $5.3 \ x10^7$ kg of Cr compounds were released from coal-fired plants, and subsequently end up in inadequately lined coal ash landfills, ponds and mines (Evans et al., 2011).

Despite the fact that leachate from coal ash taken from a variety of plants in Michigan, Alabama, North Carolina, Florida and Wisconsin measured over 11 to 35 times the current federal drinking water standard (0.1 mg/L), coal ash dumps are not federally regulated, though the Department of Justice (DOJ) recently required the EPA to finalize a regulation addressing the disposal of coal ash by December 2014 (Evans et al., 2011; Evans, 2014).

The continued pollution of soils and natural waters by Cr(VI) from industrial sources is cause for concern. All Cr(VI) species (H_2CrO_4, $HCrO_4^-$, CrO_4^2, $Cr_2O_7^{2-}$) are soluble as the molecular chromic acid or as anions, therefore, Cr(VI) is mobile and bioavailable in soils, natural waters, and living cells. Hexavalent chromium has been documented as a potent carcinogen by inhalation and ingestion, in addition to being mutagenic, corrosive and allergenic (Langard, 1990; Burke et al., 1991; NTP, 2008). In contrast, Cr(III) in the environment (Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_4^-$) is tightly-sorbed to most soil colloidal surfaces or precipitated as oxides or hydroxides, especially at pH > 4 (Cifuentes et al., 1996). Cr(III) is widely accepted as an essential nutrient involved in the metabolism of glucose, insulin and lipids, and is considered particularly beneficial for diabetes patients (Anderson, 2000). Furthermore, Cr(III) as chromium picolinate ($Cr(C_6H_4NO_2)_3$), has exhibited antidepressant effects in atypical depression via increasing the brain's level of serotonin, norepinephrine and melatonin, which help regulate emotion and mood (Davidson et al., 2003; Franklin and Odontiadis, 2003). The mechanism for both the increased metabolism and antidepressant effects is hypothesized to be due to chromium increasing insulin sensitivity, perhaps by increasing

the number of insulin receptors (Anderson, 2000; Davidson et al., 2003; Franklin and Odontiadis, 2003).

The federal drinking water standard in the United States is 0.1 mg/L, and is based on total Cr in solution, due to the possible reduction-oxidation inter-conversions of Cr(III) and Cr(VI) (USEPA, 2012). Total Cr in solution is quantified as all Cr species present, mainly that of Cr(VI) and Cr(III) measured by inductively coupled plasma (ICP) or atomic absorption (AA) spectrophotometry (Parks et al., 2004; Rakhunde et al., 2012). The hazardous implications of Cr contamination are currently leading the States of New Jersey and California (USA) to lower the Cr maximum contaminant level (MCL) in drinking water. The current MCL (maximum contaminant levels) for California is set at 0.05 mg Cr/L, but a MCL specific to Cr(VI) of 0.01 mg Cr(VI)/L is anticipated to be enforced in 2014 (CDPH, 2014). New Jersey expressed their interest in lowering the MCL from 100 μg/L to 0.07 μg/L, but acknowledged that they were not in possession of the ion chromatographic instrumentation with detection limits that low; this instrumentation was employed in this paper (NJDWQI, 2010).

The remediation strategies to cleanup Cr(VI) in soils have involved a wide variety of approaches and designs. Among both *in situ* and *ex situ,* are chemical and/or biological processes. This paper will focus on chemical remediation-by-reduction of Cr(VI) to Cr(III), a common strategy for Cr(VI)-contaminated soil, but since unsterilized, field-moist soil is involved, biologic reactions are possible and will be addressed (James, 2001). We explore reducing agents such as simple organic acids (oxalic acid) and complex mixtures (compost) combined with Fe(II) or Fe(III) in soils amended with Cr(VI) and in COPR. The soils amended with Cr(VI) are intended to represent a

contamination of soil in the landscape, that could be due to, for example, an industrial leak or spill. The chemical reduction-oxidation findings from employing a solution of reducing agents in this paper could be applied to packed-bed column reactors, slurry reactors and permeable reactive redox walls, which are all feasible engineered applications (Blowes et al., 1997; Franco et al., 2009b; Franco et al., 2009a).

There are many possible interactions between organic C, Fe, and Cr that can cause a cycling of electrons, resulting in the reduction of Cr(VI) to Cr(III) to be favorable in solution. Soluble and insoluble organic matter has the ability to reduce hexavalent chromium; furthermore ferrous and ferric iron have been shown to catalyze such reactions (Fendorf et al., 2000; Wittbrodt and Palmer, 1996). Many researchers have investigated what the possible mechanism is of oxalic acid oxidation by Cr(VI). Hasan and Rocek (1972) hypothesized that in the (unlikely) absence of other substrates, oxalic acid undergoes a quantitative oxidation to carbon dioxide following the stoichiometry of eqn. (9)

$$3H_2C_2O_4 \quad + \quad 2Cr(VI) \quad = \quad 6CO_2 \quad + \quad 2Cr(III) \tag{9}$$
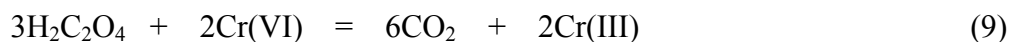
However, a more plausible mechanism of oxalic acid oxidation by chromic acid is one in which a neutral cyclic intermediate (oxalyl chromate) is formed in the first step with a 1:1 Cr(VI):oxalic acid complex. This neutral, cyclic compound then reacts with another oxalic acid present in solution in the second step to form a stable 1:2 dioxalato complex, which is mostly likely in open chain form, with Cr(VI) retaining its usual coordination number of four. However, although this dianion is dominant, the monoanion form $(HO_2CCO_2CrO_3COCO_2^-)$ is a kinetically active reaction intermediate that decomposes directly into $[Cr(H_2O)_6]^{3+}$, three molecules of carbon dioxide (CO_2) and a free radical

carboxylic acid ($\bullet CO_2H$) in a one step, three-electron oxidation reaction. Conversely,

Khan et al. (1998) hypothesized that the formation of an open chain ester containing

$Cr_2O_7^{2-}$ and two oxalic acid groups ($C_2O_4H_2$) was favorable over a cyclic ester.

Iron(II) can directly reduce Cr(VI). The reaction mechanism of the reduction of

Cr(VI) by Fe(II) is well understood as three separate one electron transfers; the

stoichiometry of this reaction is 3 Fe: 1 Cr and corresponds with the aqueous balanced

eqn. 3 for the pH range of 4 to 6 (see eqn. 3; Buerge and Hug, 1997). Fe(III) cannot

directly reduce Cr(VI), but it has been shown that Cr(VI) reduction by Fe(II) was

extremely fast in the presence of goethite (α-FeOOH) and lepidocrocite (γ- FeOOH), two

Fe(III) hydroxides (Buerge and Hug, 1999). Similarly, according to Wittbrodt and Palmer

(1996), the reduction of Cr(VI) by soil humic substances in aqueous solutions is

enhanced by Fe(III). It is hypothesized that this occurs because the Fe(III) is reduced by

the humic substances in solution, and oxidized by the Cr(VI), which can start the redox

cycling over (Fig. 3-1); it was also determined that this reduction reaction occurs faster

with fulvic acids than with humic acids (Wittbrodt and Palmer, 1996).

Another example of Cr(VI) reduction is reductive dissolution. Reductive

dissolution occurs when a sorbed species is capable of donating electrons to a chemical

component of the oxide surface. Sorption is a metal-to-surface interaction. For example,

if it is an Fe(III)(hydr)oxide surface, once the electron transfer occurs from the reducing

agent (e.g., oxalate), it induces the detachment of that newly reduced species (Fe^{2+})

(Schwertmann, 1991). Authors Zhong and Yang (2012) found that malic acid ($C_4O_5H_6$)

(organic acid similar to oxalic acid) did not reduce Cr(VI) alone at pH 3.2 in 0.01 M

$CaCl_2$, but in the presence of an Fe-rich Ultisol (44 g/kg free Fe(III)(hydr)oxides),
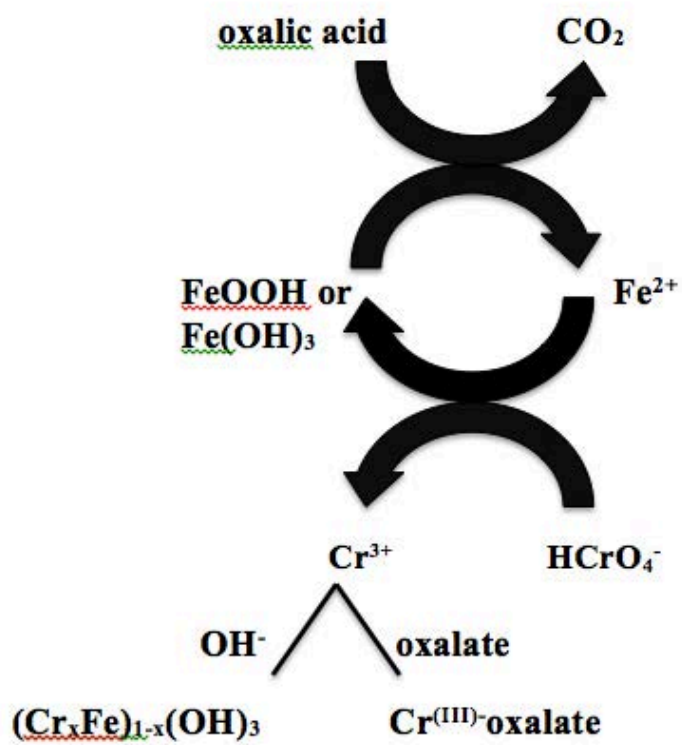
Figure 3-1. Redox cycling scheme.

61% of the initial 100μM Cr(VI) spike was reduced. Their hypothesized reduction mechanism was as follows: (1) the adsorption of malic acid onto the soil surface, (2) Fe(II) is released into solution after the malic acid promoted reductive dissolution of Fe(III)(hydr)oxides, (3) Cr(VI) was reduced in solution by Fe(II). The Fe(II) release, and subsequently the Cr(VI) reduction rate, were both greater in an Ultisol than in an Oxisol, despite the Oxisol having more Fe(III)(hydr)oxides (132 g/kg Fe). A primary hypothesis is that the oxides in the Oxisols were more highly crystallized than those of the Ultisol, and ultimately prevented chemical dissolution, and thus, the catalytic effect (Zhong and Yang, 2012).

It is important to track the final fate of Cr in order to assess the potential risk for re-oxidation after remediation-by-reduction is employed. Soluble Cr(III) salts and freshly-precipitated hydroxides can oxidize rapidly back to Cr(VI) in the presence of oxidants (e.g. Mn(III,IV)(hydr)oxides) in moist soils (Bartlett and James, 1979). This is a prominent issue with remedial efforts in the field, especially with events such as dredging, bioturbation, and fluctuations in the water table; such perturbation may induce a transition from anoxic and reduced redox conditions to oxic and oxidized redox conditions, altering the stability of Cr(III) (Wadhawan et al., 2013). Therefore, in this study, I evaluate the success of the remediation by fractionating Cr(VI) species into soluble, exchangeable and nonexchangeable species. I operationally define the fraction "soluble" from the 10 mM $NaNO_3$ extraction, the fraction "exchangeable" from the 10 mM KH_2PO_4-K_2HPO_4 phosphate buffer extraction, and "nonexchangeable" from these author's modified version of Method 3060a (chapter 2). More specifically, we believe the nonexchangeable fraction to include precipitated and sparingly soluble chromate salts,

and chromate that has been incorporated into mineral phases, also known as para-crystalline. We hypothesized that this would provide information on the oxidation-reduction processes involved in remediation-by-reduction of Cr(VI). The fate of Cr(VI) involves sorption, desorption, complexation, or reduction by such Fe(II,III)-organic acid couples. We hypothesized that there is a synergism in the combination of reducing agents that will prove successful in the earlier discussed engineering applications for *in-situ* remediation-by-reduction of soil-borne Cr(VI).

Materials and Methods

We used two COPR-enriched soil materials in this study, both from Hudson County New Jersey, USA, located in the Piedmont province. We also studied two soil horizon materials taken from two soils that were not known to be contaminated by Cr or other contaminants; both soil materials were sampled from the Coastal Plain physiographic province in the State of Maryland, USA.

Sample Characterization

i. COPR-amended soils

We studied two COPR-enriched soils, sampled in Kearny, NJ, along the Hackensack River at a legacy disposal site for this Cr waste (40.751469, -74.098697). One is named "MES" for "Method Evaluation Study," and is named after its original use (James et al., 1995). The MES COPR contains approximately 1200 mg total Cr(VI)/kg, and 800 mg soluble Cr(VI)/kg based on Method 3060A analysis and batch experiments (USEPA, 2014). It has a dry and dusty appearance (Munsell color 10YR 5/3), explained well with its gravimetric water content of 100 g/kg (Table 3-1). The 6500 COPR (7.5YR

Table 3-1. Soil Characterization Data.

Soil Horizon[a]	Sample Depth (cm)	Color[b]	Texture[c] (% sand, silt, clay)	CBD Fe[de] ---------------	CBD Mn ----- (g/kg)----	Organic C[f] ----------------	Taxonomic Great Group[g]
Atsion Bhs	27-45	5 YR 2.5/2	sand (89, 8, 3)	0.15 ± 0.002	0.0010 ± 0.0	29 ± 1.1	Alaquod
Russett Bt1	>26	10 YR 5/8	loam (40, 42, 18)	19 ± 0.3	0.014 ± 0.001	1.4 ± 0.01	Hapludult
MES COPR	0-30	10YR 5/3	sandy loam (67, 30, 3)	8.3 ± 0.8	0.15 ± 0.008	18 ± 0.80	Anthrosol
6500 COPR	0-30	7.5YR 2/2	sandy loam (61, 38, 1)	16 ± 1	0.16 ± 0.006	17 ± 0.07	Anthrosol
Leafgro® Compost	N/A[e]	Gley 1 2.5/N	N/A	4.5 ± 0	0.73 ± 0.006	$4.0 \times 10^2 \pm 30$	N/A

[a]Soil horizons are designated by their series name (USDA-NRCS), except for MES, 6500 and compost, which are named for their original use (James et al., 1995), contamination level, and product name, respectively.
[b]Color is field-moist and designated by the Munsell color system.
[c]Texture was determined using particle size analysis by pipette method (Gee and Bauder, 1986).
[d]CBD refers to a citrate-bicarbonate-dithionite extraction (Loeppert and Inskeep, 1996).
[e]Values are means and one SEM (n=3).
[f]Determined with LECO after destroying carbonates (Piper, 1942; Nelson and Sommers, 1996).
[g]Natural Resources Conservation Service (NRCS) official series description (Soil Survey Staff, 2014).
[e]Not Applicable.

2/2) is named for its total Cr(VI) contamination level, and contains 1900 mg soluble

Cr(VI)/kg. It has a 350 g/kg gravimetric water content, which may be responsible for

some of its darker color (Table 3-1). Both COPRs have heterogeneous "beebees," which

are hard, brittle beads and chunks of residue with bright yellow interiors and containing a

very concentrated amount of Cr(VI). With a solution:soil ratio of 20 and a background

electrolyte of 10 mM $NaNO_3$, the pHs of MES and 6500 are 8.1 and 11.2, respectively,

making both Cr(VI)-amended soils very alkaline. Total C and N were determined by

combustion at 950°C with LECO CHN Analyzer. For organic C determination, $CaCO_3$

was destroyed by reacting samples (1 g) with 2-5 mL of 5% sulfurous acid (H_2SO_3),

depending on the continuation of bubbling with additional H_2SO_3. Once the reaction

ceased, the soils were dried in a vacuum desiccator (20 h), followed by an oven (20 h at

105^oC), reground, and then analyzed by LECO (Piper, 1942; Nelson and Sommers,

1996). Calcium carbonate-carbon was calculated, by difference of total and organic C, to

be 4 and 1 mg C/kg for MES and 6500, respectively. Although there isn't any available

data for the exact sample location, nearby soils are from the delineation of the

Transquaking mapping unit, and are similar to the Transquaking series (euic, mesic Typic

Sulfihemists), which could explain their ≥ 17 g organic C/kg contents (Table 3-1) (Soil

Survey Staff, 2014).

ii. Uncontaminated Maryland Soils

The Maryland soil samples were taken from locations with delineations of the

mapping units Askecksy and Russett-Christiana Complex. The two soil materials were

sampled from Bhs and Bt1 horizons of the two profiles, respectively. We chose to study

subsurface B horizons because they were not that deep, beginning at approximately 27 cm (Table 3-1) and, therefore, represent the type of soil that would be damaged by a spill in the field, especially if the affected land underwent tillage or has biopores created by roots, earthworms, and other organisms (Brady and Weil, 2010). Also, subsurface horizons have the potential to be affected by hazards like leaking underground storage tanks (LUST). The horizons sampled on June 8, 2011 from the profile in the Askecksy unit (coordinates: 38.214475, -75.522236) were similar to the Atsion series (sandy, siliceous, mesic, Aeric Alaquod) and the profile from the Russett-Christiana Complex unit sampled on June 7, 2011 was similar to the Russett series (fine-loamy, mixed, semiactive, mesic Typic Hapludult). Both soil materials are from the Coastal Plain, but the Russett soil is more inland and closer to the border of the Piedmont physiographic province (coordinates: 39.012697, -76.854069). At each location, a hole was dug to expose the upper B horizon or to an even lower depth; the samples were taken from the vertical face of the profile. The two soils studied provide large differences in texture, mineralogy and organic C content. For example, Atsion Bhs has a considerable amount of organic C (29 ± 1.1 g organic C/kg) as compared to Russett Bt1 (1.4 ± 0.01 g organic C/kg), but Russett Bt1 (19 ± 0.3 g Fe/kg) far surpasses Atsion Bhs (0.15 ± 0.002 g Fe/kg) in dithionite extractable Fe or the free Fe(III)(hydr)oxides (Table 3-1) (Loeppert and Inskeep, 1996).

The soils were spiked using a 52.0 mg Cr(VI)/L solution in a 0.01 M $NaNO_3$ background electrolyte solution, which was chosen because of its similarity to field conditions. Also, a calcium salt (e.g. $CaCl_2$) might precipitate the Cr(VI). The solution was then added to 1.25 g oven-dried equivalent of field-soil weighed into 50 mL, Oak

Ridge type, polycarbonate centrifuge tubes. This resulted in a soil contamination of 1040 mg Cr(VI)/kg, comparable to that of the COPRs.

After field sampling, all of the soil samples were passed through a 4-mm, polyethylene sieve and kept at field-moist water content (approximately -10 kPa water potential, or "field capacity"). Drying and storing soils increases reduced manganese (Mn^{2+}) as well as the solubility and oxidizability of organic matter (Bartlett and James, 1980). The samples were stored in covered plastic buckets at room temperature (22-24°C).

Remediation Treatments

Iron(II) and Fe(III) chloride were used for the Fe(II) and Fe(III) species to reduce Cr(VI) directly or in an electron shuttling reaction. Based on preliminary trials, we chose a 10X stoichiometric excess of Fe(II), and Fe(III), relative to Cr(VI), that could reduce all of the Cr(VI) in the treatments, as well being a practical treatment for the total mass of Fe(II,III) salts delivered to the system in centrifuge tubes (results not shown). Increasing the excess any higher might lower the pH too much due to Fe(III) hydrolysis. Since the stoichiometry of the aqueous balanced reaction of Fe(II) with Cr(VI) corresponds with a ratio of 3 Fe: 1 Cr, we used a 30:1 excess (Table 3-2). Fe(III) is reduced to Fe(II) by another species in solution (e.g. oxalic acid) before it can reduce Cr(VI), therefore the same stoichiometric excess was used. As for oxalic acid and compost, we used a 20x stoichiometric excess of oxalic acid and delivered Leafgro® compost with the same percentage of C as oxalic acid, since the molecular formula and weight of the Leafgro® are unknown. The stoichiometric excess of oxalic acid is identical to Fe(II,III) since the stoichiometric ratio is 1.5 oxalic acid: 1 Cr, and with 20x this becomes 30:1 (Table 3-2).

Table 3-2. Possible redox reactions and corresponding log K values during remediation scheme.

Reducing agent	Reaction	Log K[a] (pe at pH 0)	pe[b] pH 5	pH 7
Fe(II)	$HCrO_4^- + 3Fe^{2+} + 8H_2O \rightarrow Cr(OH)_3 + 3Fe(OH)_3 + 5H^+$	1.8	10.2	13.5
Fe(III) hydroxide	$6Fe(OH)_3 + 3H_2C_2O_4 + 12H^+ \rightarrow 6CO_2 + 6Fe^{2+} + 18H_2O$	26.8	16.8	12.8
Fe(III) (hydr)oxides)	$2FeOOH + H_2C_2O_4 + 4H^+ \rightarrow 2CO_2 + 2Fe^{2+} + 4H_2O$	24.1	14.1	10.1
Oxalic Acid	$HCrO_4^- + 1.5H_2C_2O_4 + H^+ \rightarrow Cr(OH)_3 + 3CO_2 + H_2O$	28.6	27	26.3

[a]Calculations same as in Table 1-1.
[b]Calculations same as in Table 1-1.

Leafgro® is a commercially available, Prince George's County leaf compost, rich in C, N, and Mn (4.0×10^2, 18 and 0.73 g/kg, respectively) (Table 3-1). With a solution:soil ratio of 20 and a background electrolyte of 10 mM $NaNO_3$, the pH of compost was a little above neutral, at pH 7.4. The compost is an extremely dark, humic substance (Gley 1 2.5/N) with a gravimetric water content of 1480 g/kg (Table 3-1).

Fractionation Method

The various chemical reactions in the remediation treatments were tracked by fractionating the soluble, exchangeable, and nonexchangeable portions of Cr(VI). Soluble Cr(III) was also quantified. The operationally defined procedures and chemical analyses are described below and in the chronological order that they were performed and also represented in Fig. 3-2.

i. Soluble Cr(VI) and Soluble Cr(III)

Triplicates of 1.25 g oven-dried equivalent of field-soil were weighed into 50 mL, Oak Ridge type, polycarbonate centrifuge tubes. The control treatments were the soil alone with the background electrolyte 10 mM $NaNO_3$; 25 mL were used, creating a solution:soil ratio of 20. There was also a "no soil," treatment, which was just the chemicals in 10 mM $NaNO_3$ solution. This was used to see if the Cr(VI) reduction was more chemical- or soil-based. The tubes were placed in a plastic rack and shaken at 100 cycles/min on a rotary shaker for a week (168 ± 5 hours), and set at a timer to shake one hour on and one hour off (60 ± 1 min).

The soil solutions were centrifuged at 20°C for 15 min at 15,000 x g. An aliquot of the supernatant liquid was used to measure pH and Eh using pH and Pt combination electrodes (Ag/AgCl reference) connected to digital pH meters. The Pt electrode values
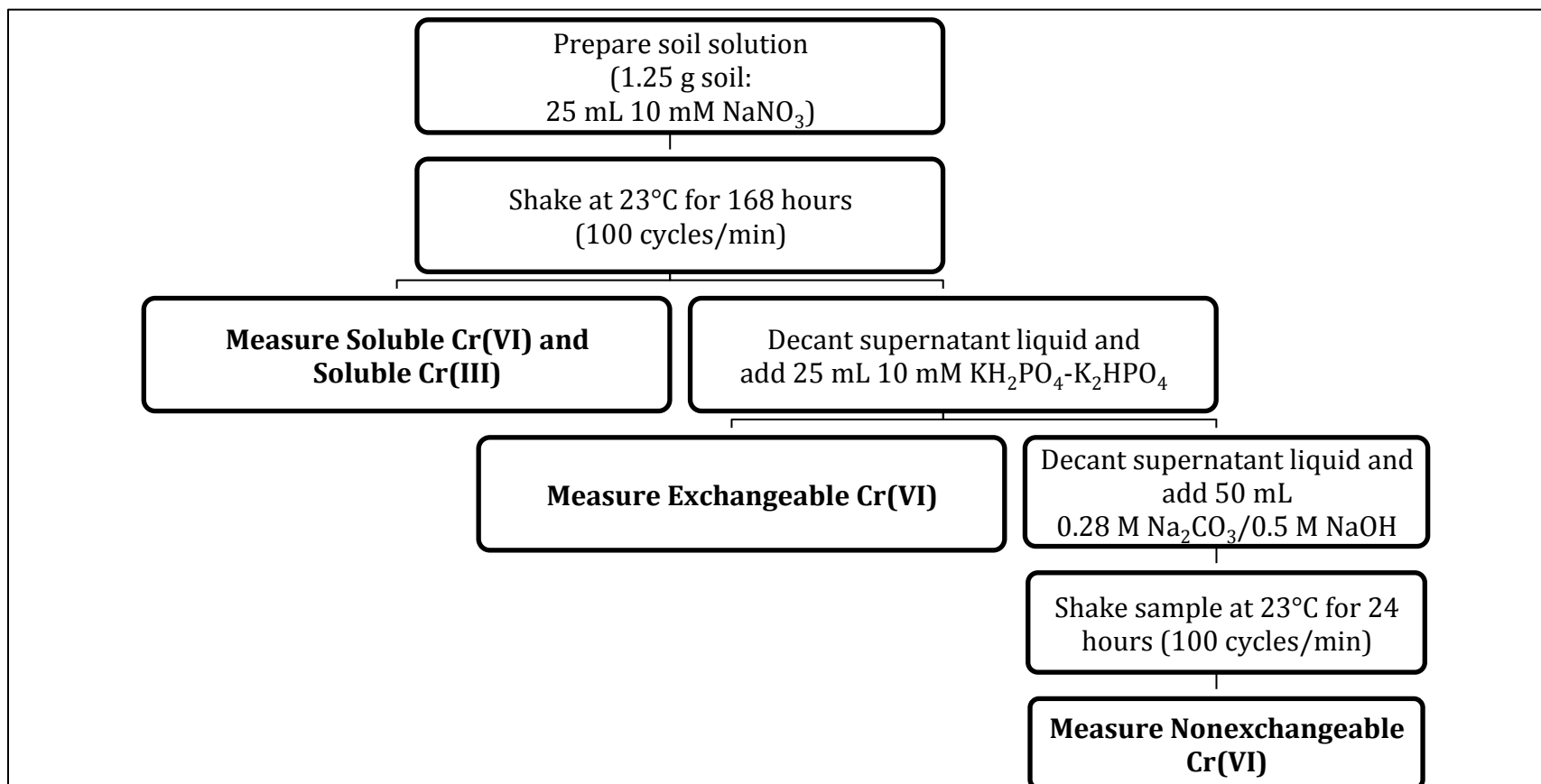
Figure 3-2. Fractionation Method Flow Chart. The soluble Cr(VI) was measured using ion chromatography for analysis and is operationally defined as the fraction of total Cr(VI) dissociated in a dilute salt solution (10mM $NaNO_3$). Soluble Cr(III) was calculated by measuring the total Cr in solution with flame atomic absorption spectroscopy (FAAS) and subtracting the previously calculated soluble Cr(VI) to acquire soluble Cr(III). Exchangeable and nonexchangeable Cr(VI) were measured using ion chromatography for analysis. The method for extracting nonexchangeable Cr(VI) was a modified EPA method (USEPA, 1996c; chapter 2).

were corrected for Ag/AgCl reference electrode by adding 199 mV to calculate the Eh value relative to the standard hydrogen electrode. The pH and Eh were measured after 24 ± 2 hours of being stored in the refrigerator ($4\pm1°C$) for the MD soils experiment, while the COPR soils experiment were measured 7 ± 2 hours of being stored in the refrigerator. Additional aliquots were used to determine the soluble Cr(VI) by ion chromatographic (IC) analysis on a Metrohm 850 Professional ion chromatograph (chapter 2).

Seven Cr(VI) standards ranging from 0.05 to 10.0 mg Cr(VI)/L were made via a series of dilutions of a 1000 mg Cr(VI)/L stock. The stock was made from oven-dried K_2CrO_4. The ion chromatographic method with conductimetric detection (chap. 2) was used analysis in place of the common colorimetric 1,5-diphenylcarbazide method (DPC) because any reducing agents in solution can compete with DPC to reduce Cr(VI) (Pettine and Capri, 2005a; Pettine and Capri, 2005b; chap. 2). Additionally, humic compounds absorb light at the same wavelength as does the Cr(III)-DPC complex (540 nm) (Pettine and Capri, 2005a; Pettine and Capri, 2005b). The IC method does not use colorimetric analysis. Instead the sample dilutions (ranging 1:10-1:100) were drawn up through peristalsis, injected into a carbonate-bicarbonate eluent (3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$) and pumped onto the anion exchange column (150x4.0mm). The column has a positively charged solid support where negatively charged anions in are slowed in accordance with anion size and charge (Claudia et al., 2002). The higher the anion charge and the larger the ion, the longer the retention time will be on the column. Once leached, a Digital Signal Processing (DSP) conductivity detector analyzed the electrical conduction of the anion after the eluent background conductivity is suppressed by injection of 0.1 M H_2SO_4. The limit of detection (LOD) is 0.01 mg Cr(VI)/L.

Lastly, an aliquot of the centrifugate was used to measure total Cr on a Perkin-Elmer 400 flame atomic absorption spectrophotometer (FAAS) with a Cr hollow cathode lamp. In order to calculate soluble Cr(III), the soluble Cr(VI) results from the IC method were subtracted from the total Cr concentrations from the AA method. The limit of detection (LOD) is 0.05 mg Cr(VI)/L.

ii. Exchangeable Cr(VI)

The 50 mL polycarbonate centrifuge tubes containing soil and the remaining unused supernatant liquid were carefully decanted into a waste container. The remaining soil and residual solution after decanting was then weighed in order to calculate and account for any residual Cr(VI) prior to the next fractionation step. Next, 0.25 mL of 1.0 M KH_2PO_4/K_2HPO_4 phosphate buffer (pH 7.2) and 25.0 mL of nanopure water (18 MΩ specific conductance) were added to the centrifuge tubes containing the soil plug. The tubes were recapped and shaken for another 2 h (120 ± 5 min) at 100 cycles/min. This solution desorbs Cr(VI) on exchange sites (Bartlett and James, 1979). It is also possible that some of this Cr(VI) would be released despite the phosphate buffer addition. The Cr(VI) exchangeable concentrations were quantified with use of the IC method again. However, soluble Cr(III) was not calculated again because Cr(III) is likely precipitated by the P buffer.

iii. Nonexchangeable Cr(VI)

The remaining tubes containing supernatant liquid and soil plugs from the P-buffer extraction were decanted and weighed as previously described. The tubes were washed and vortexed with approximately 30 mL of 18 MΩ nanopure water in order to resuspend and transfer the soil quantitatively to a 250-mL, Pyrex® heavy-duty graduated

beakers for the unheated, alkaline extraction of insoluble Cr(VI) (chapter 2). A volume of 50 mL, alkaline (pH 11.5) digestion solution (0.28 M Na_2CO_3/0.5 M NaOH) was added.

The alkaline extraction method was used with some changes to determine the nonexchangeable fraction of Cr(VI) (USEPA, 2014; chap. 2). The 60 ± 5 minutes of heating at 90-95°C was replaced with 24 ± 1 hours of shaking (100 cycles/min) at room temperature, 22-24°C. After the digestion period, the beakers were brought to a total solution volume of 100 mL based on weight (knowing the beaker and soil masses) with 18 MΩ nanopure water. The suspensions were swirled, an aliquot was poured into a 15-mL polyethylene centrifuge tubes, and they were centrifuged (4,000 x g, 15 min, 22°C). Sample dilutions (1:10-1:100) were made and analyzed with the IC.

Preliminary results indicated that this unheated extraction, coupled with IC analysis was optimal for recovery of Cr(VI) spikes of uncontaminated soils, such as the Atsion and Russett soils (Fig. 2-5 to 7 and A-1) (chapter 2). The heated method may recover more sparingly soluble forms of Cr(VI) in COPRs, especially in soils with low organic C contents, but we removed the heat for all treatments for comparison purposes.

Results and Discussion

Uncontaminated Maryland Soils

The control treatments of Atsion Bhs and Russett Bt1 with Cr(VI) spikes and no added reducing agents had pHs of 5.0 and 5.4, respectively, and had Eh values in the range of 470-500 mV (Table 3-3). The position of these values on the Eh-pH diagram Fig. 3-3, allows one to predict the species of Cr in solution based on thermodynamics; reduction of Cr(VI) would occur for the conditions that lie below the Cr(VI)-Cr(III) line.

Table 3-3. pH and Eh for Maryland soils after 1-week Cr(VI) extraction in 0.01M $NaNO_3$ alone.

Treatment	Atsion Bhs		Russett Bt1		Chemicals Alone	
	pH[a]	Eh[b]	pH	Eh	pH	Eh
Control[cd]	5.0[c]	471[c]	5.4[c]	498[c]	7.2[d]	580[d]
Oxalic Acid	2.2	442	2.0	345	1.9	689
Oxalic Acid, Fe(II)	1.9	487	1.7	445	1.6	475
Oxalic Acid, Fe(III)	1.6	652	1.5	652	1.5	667
Compost	5.7	455	6.3	416	7.4	575
Compost, Fe(II)	3.3	461	2.8	495	3.0	550
Compost, Fe(III)	2.0	749	1.8	773	2.1	828
Fe(II)	3.3	455	2.6	495	2.7	580
Fe(III)	2.0	822	1.8	881	1.9	919
Fe(II), Fe(III)	2.0	670	1.7	683	1.7	721

[a]pH meter and combination hydrogen -Ag/AgCl reference electrode.
[b]199 mV were added to the measured value (by Pt electrode) to account for SHE.
[c]Soil in 0.01M $NaNO_3$ alone for Atsion Bhs and Russett Bt1.
[d]Spiked 52 mg Cr(VI)/L with background electrolyte 0.01M $NaNO_3$ for no-soil controls.
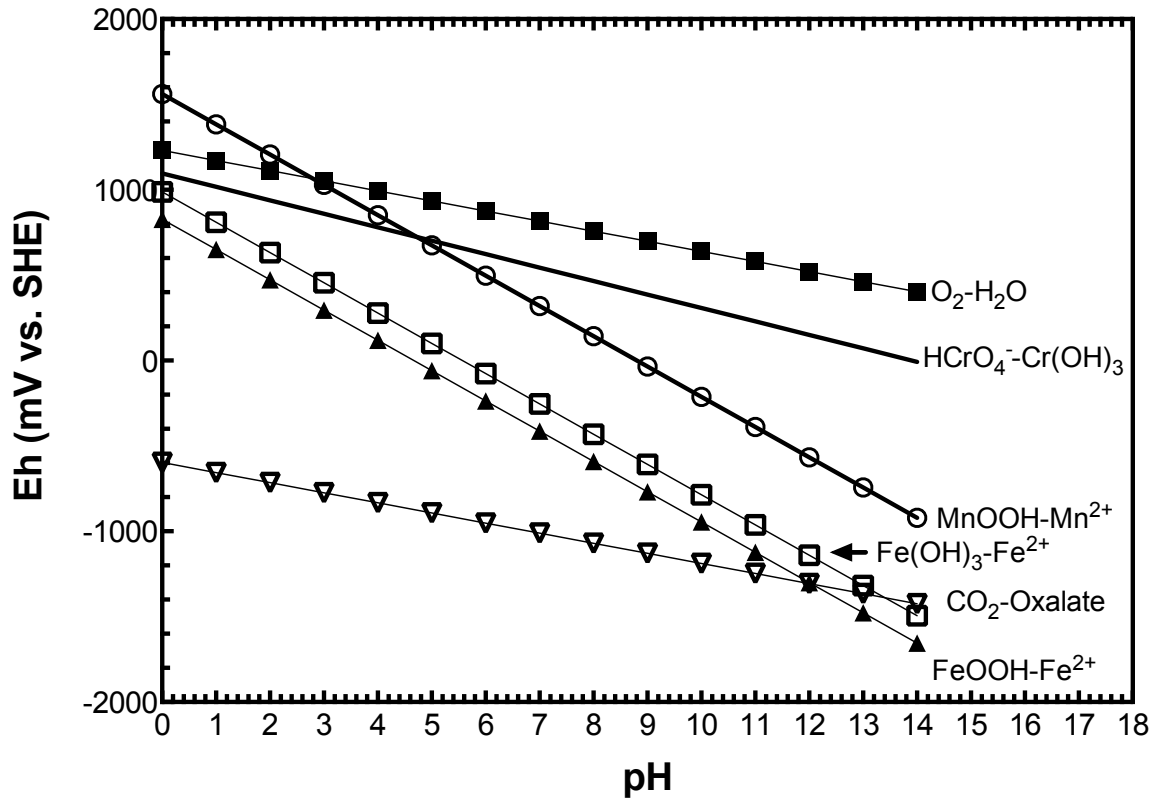
Figure 3-3. Eh-pH Diagram for thermodynamically-possible reductants of Cr(VI) and oxidants of Cr(III). See Table 1-1, C-1 and C-8 for complete description of activity calculations.

Theoretically, the amount of Cr(VI) reduced decreases as pH increases, indicated by the slanting line in Fig. 3-3, and as reduction occurs with time and Cr(VI) concentrations decrease, the line will shift lower on the diagram (Brose, 2012). According to the theoretical calculations, Cr should exist as Cr(III) within the soil controls, which is only partially true for Atsion, with 4.6% (of the total measured 980 mg Cr/kg) reduction from soluble Cr(VI) to soluble Cr(III) (Table 3-4). Russett showed 1.3% of the added Cr(VI) was reduced, which is not significantly different from 0% Cr(VI) reduced ($p \leq 0.05$), suggesting that this measurement could be from standard error of the analytical technique (Table 3-4). It is worth nothing that Russett Bt1 sorbed 13% of added Cr(VI), presumably onto colloidal surfaces dominated by Fe(III)(hydr)oxides (Fig. 3-4, Table 3-4). After summing the fractions of Cr, 1105 mg Cr/kg was recovered in the Russett control treatment. The target Cr(VI) spike was 1040 mg Cr/kg for the MD soils and is indicated by the dotted line in Fig. 3-4 to 3-6. If a bar is below this dotted line, we know from our operational definitions that Cr(III) has been removed from solution via either precipitation or sorption.

Many of the treatments were in the pH range 2-3, which is a somewhat lower than a practical target pH for environmentally sound, remediation-by-reduction work in the field (e.g. pH 4-6) (Brose and James, 2013). Treatments containing Fe(III) had the lowest range of pH (1.5-2.1), and we hypothesize this was due to proton-producing hydrolysis (Table 3-3). The Fe(III) treatments had the highest Eh values (822-919) (most oxidizing environment) when in soil solution alone, indicating the influence of the strong oxidizing agent and low pH. These Eh measurements were close to the predicted ~750 mV at low pH in the constructed Eh-pH diagram for $Fe(OH)_3$ and $FeOOH$ (Fig. 3-3). Conversely,

Table 3-4. Cr and Fe data for MD soils after fractionation.

Treatment	% Cr(VI) reduced[a]		Soluble Cr(III)[b]		Soluble Fe[c]	
	Atsion	Russett	Atsion	Russett	Atsion	Russett
Control	4.6 ± 0.4	1.3 ± 1.0	45 ± 7.0	nd[d]	0.02± 0.005	0.03± 0.006
Oxalic Acid	94 ± 0.2	100 ± 0.0	919 ± 10	1011 ± 10	2.6 ± 0.03	91± 0.8
Oxalic Acid, Fe(II)	100 ± 0.0	100 ± 0.0	991 ± 0.0	1032 ± 41	603± 5.5	594 ± 17
Oxalic Acid, Fe(III)	100 ± 0.0	100 ± 0.0	1001 ± 21	939 ± 10	558± 14	663 ± 15
Compost	12 ± 1.0	15 ± 3.0	40 ± 10	nd	0.08 ± 0.003	0.15 ± 0.02
Compost, Fe(II)	86 ± 0.2	92 ± 0.1	5.1 ± 0.1	107 ± 1.0	517± 8.3	534 ± 15
Compost, Fe(III)	92 ± 0.3	94 ± 0.2	919 ± 27	774 ± 18	374± 11	440 ± 25
Fe(II)	87 ± 0.3	100 ± 0.0	7.1 ± 0.3	291 ± 3.1	592± 10	603 ± 7.3
Fe(III)	80 ± 0.2	42 ± 1.0	712 ± 0.0	265 ± 16	393± 22	495 ± 5.5
Fe(II), Fe(III)	100 ± 0.0	100 ± 0.0	908 ± 10	433 ± 0.0	1000± 7.3	1157± 31

[a]Includes exchangeable, soluble and not exchangeable Cr(VI) reduced. Divided by 980 mg Cr(VI)/kg for Atsion and 1098 mg Cr(VI)/kg for Russett, as determined by the control treatments.

[b]mg Cr(III)/kg

[c]μmol Fe (added as 750 μmol)

[d]nd is <LOD. LODs are 0.01 mg Cr(VI)/L for % Cr(VI) reduced as measured by the IC, and 0.05 mg Cr(VI)/L for soluble Cr(III) and soluble Fe, as measured by the FAAS.
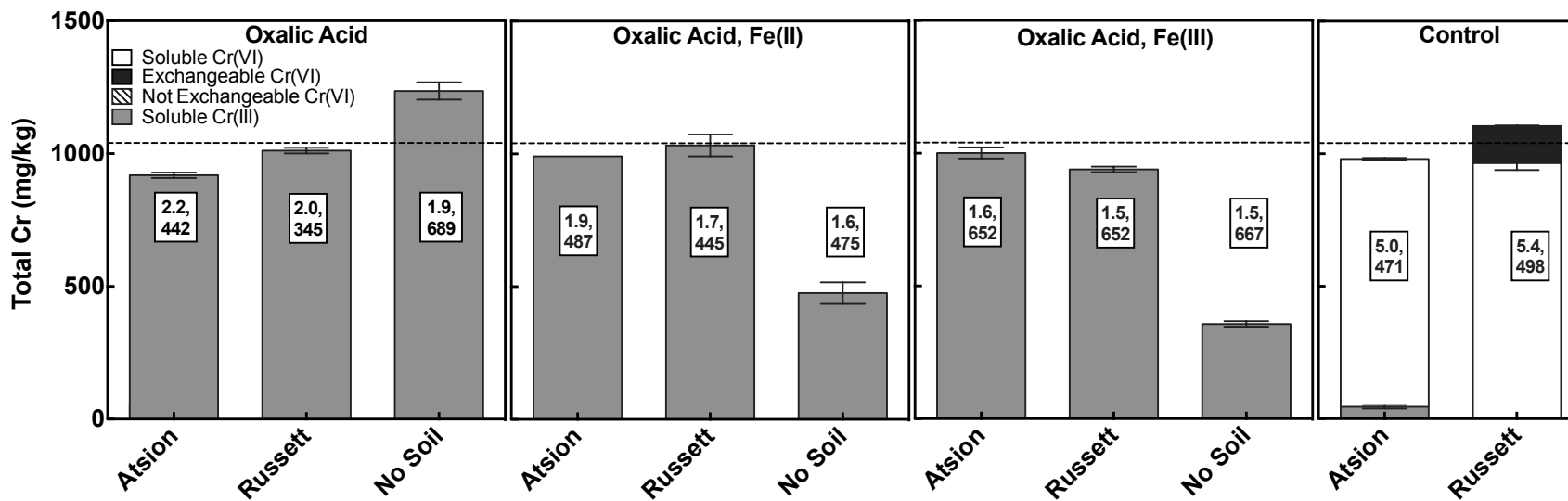
Figure 3-4. Total Cr for the oxalic acid treatments of Atsion Bhs, Russett Bt1 and chemicals alone or "no soil." Aliquots of the B horizons (1.25 g oven-dried equivalent) of Atsion and Russett were artificially contaminated with 1040 mg Cr(VI)/kg. See Fig. 3-2 for method details. The pH and Eh of the 1-week Cr(VI) extraction ("soluble fraction") are provided in the box (see Table 3-3 for method details). The dotted line indicates the target Cr(VI) contamination of 1040 mg Cr(VI)/kg.
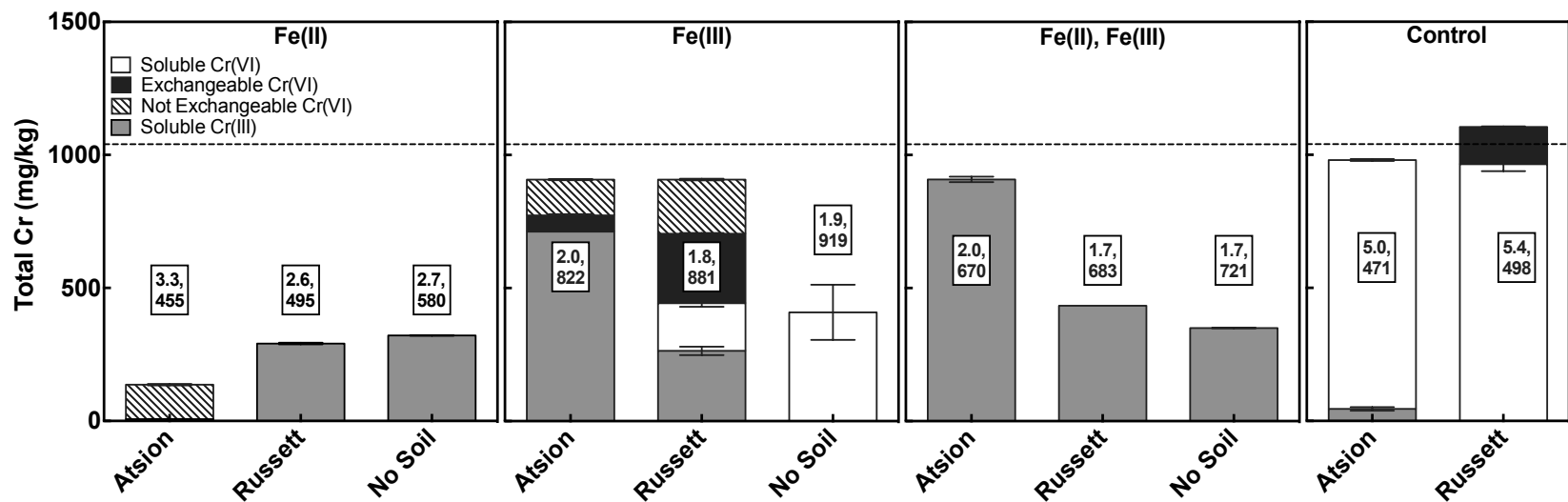
Figure 3-5. Total Cr for the iron treatments of Atsion Bhs, Russett Bt1 and chemicals alone or "no soil." Aliquots of the B horizons (1.25 g oven-dried equivalent) of Atsion and Russett were artificially contaminated with 1040 mg Cr(VI)/kg. See Fig. 3-2 for method details. The pH and Eh of the 1-week Cr(VI) extraction ("soluble fraction") are provided in the box (see Table 3-3 for method details). The dotted line indicates the target Cr(VI) contamination of 1040 mg Cr(VI)/kg.
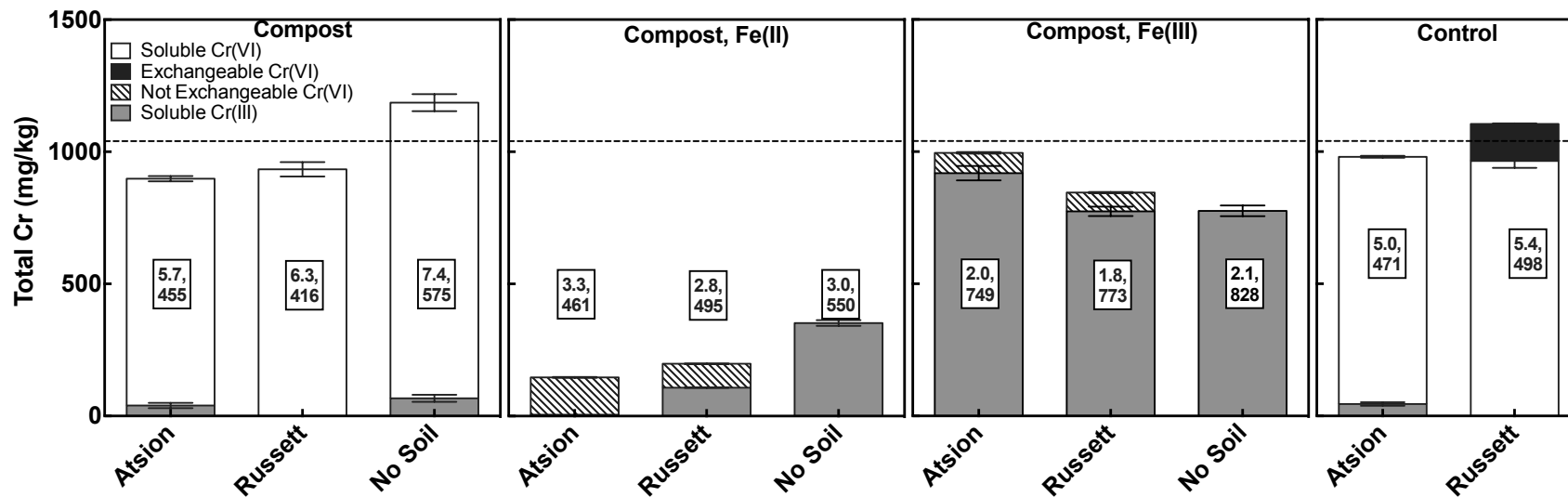
Figure 3-6. Total Cr for the compost treatments of Atsion Bhs, Russett Bt1 and chemicals alone or "no soil." Aliquots of the B horizons (1.25 g oven-dried equivalent) of Atsion and Russett were artificially contaminated with 1040 mg Cr(VI)/kg. See Fig. 3-2 for method details. The pH and Eh of the 1-week Cr(VI) extraction ("soluble fraction") are provided in the box (see Table 3-3 for method details). The dotted line indicates the target Cr(VI) contamination of 1040 mg Cr(VI)/kg.

the pH in the compost treatments increased approximately 1 pH unit relative to the controls for both soils, indicating either the release of hydroxyl-bearing groups from organic matter or H^+ in solution exchanging with cations in the organic matter, and subsequently being taken out of solution (Table 3-3). Another theory is that the protons in solution are involved with CrO_4^{2-} adsorption (Vargas et al., 2012). The authors hypothesized that the H^+ in solution are taken up via compost protonation (specifically the oxo groups) (C_xO and C_xO_2), which then allowed the adsorption of CrO_4^{2} to the newly protonated oxo group (C_xOH^+) on the compost (Vargas et al., 2012).

The oxalic acid treatments (Atsion, Russett and No Soil) reduced 94-100% of the 52 mg Cr(VI)/L spike (Fig. 3-4). Oxalic acid ($pKa_1=1.3$, $pKa_2=4.1$) (Bjerrum, 1957) is at its highest reducing power at $pH \leq 4$, since the electrons in the C-H bond remain intact. This pH range corresponds well to the experimental conditions, not considering the soil controls, which is one possible explanation for the high percentage of Cr(VI) reduced (Fig. 3-4, Table 3-4). Additionally, when the experimental data for oxalic acid from Table 3-3 are plotted on a theoretical Eh-pH diagram, all points fall below the Cr(VI)-Cr(III) line, indicating favorable conditions for Cr(VI) reduction (Fig. A-3). Atsion Bhs-oxalic acid was the only treatment significantly different ($p < 0.05$), where 100% reduction was not seen due to 6% of the added Cr(VI) becoming a part of the nonexchangeable fraction; we presume that this Cr(VI) may have precipitated (e.g., as $Fe_2(CrO_4)_3$) with the Fe(III) (0.15 ± 0.002) added to or present in the spodic horizon (Table 3-1). Another possibility is chemisorption. Nonexchangeable Cr(VI) includes precipitated and/or "chemisorbed," forms of Cr(VI) not replaceable by 10 mM phosphate solution. Chemisorption occurs when the anionic chromate (CrO_4^{2-}) becomes tightly adsorbed to the soil as an inner sphere complex with the structural Fe(III) or Al of the soil mineral. Low pH and high

ionic strength promote such retention, especially on colloidal surfaces dominated by pH-dependent charge, similar to those of the Atsion spodic horizon. The chemisorption of Cr(VI) is also possible with freshly precipitated $Cr(OH)_3$ (James and Brose, 2013). Our results agree with an earlier publication that showed an Fe-rich soil (15 g Fe/kg from a CBD extraction), similar to our Russett Bt1 (19 g Fe/kg from a CBD extraction), which did not adsorb Cr(VI) in the presence of oxalic acid (Table 3-1). The authors hypothesized that this was the case due to either competition for binding sites or an increased negative soil surface charge resulting in electrostatic repulsion once oxalic acid did bind to Fe oxide surfaces (Yang et al., 2008).

We predicted oxalic acid to be a favorable reductant thermodynamically, due to the high log K of 28.6 (Table 3-2). Since oxalic acid alone (without soil) reduced the entirety of the Cr(VI) spike, it is hard to say if (when present) the soil contributed to the reduction. This result is the same for oxalic acid in combination with Fe(II,III), though Suter et al. (1988) did show that the combination of Fe(II) and oxalate is a special case in which oxalate is capable of complexing the sorbed Fe(II). The resulting complex is a stronger reductant than aqueous Fe(II) alone. The oxalate bidentate ligand also develops a bridge where electron shuttling between Fe(II) and the Fe(III) surface is possible. Overall, oxalic acid is an excellent reducing agent in a stoichiometric excess of 20x. We recognize that the solubilization of Cr(III) post-reduction (Cr^{3+}) (Cr^{3+}-oxalate) and the low pH range (1.5-2.2) are issues that engineers looking to apply this work will have to consider (Fig. 3-4, Tables 3-3 to 4).

There were distinct differences in Cr(VI) speciation due to adding Fe(II), Fe(III), and Fe(II)/(III) together on Cr(VI) reduction (Fig. 3-5). Aqueous Fe(II) has long been

documented as a successful reducing agent for Cr(VI) (James and Bartlett, 1983c; Buerge and Hug, 1998; Fendorf et al., 2000). In the absence of other reductants, the reaction mechanism for the reduction of Cr(VI) by Fe(II) is well understood as three separate one electron transfers, with the conversion of Cr(VI) to Cr(V) the rate-determining step in which the first electron is transferred (Buerge and Hug, 1997). Our results contradict that of earlier reports on the fractionation of Cr in relation to pH. Buerge and Hug (1997) hypothesized that in acidic pH ranges (pH <4), the reduction of $HCrO_4^-$ with Fe^{2+} consumes H^+ to form soluble Cr^{3+} and Fe^{3+} species, while under more alkaline conditions (pH > 4), the reaction yields H^+ and forms either Fe(III) hydroxo species (e.g., $Fe(OH)_2^+$) or precipitated Fe(III)-Cr(III) hydroxide ($Fe_3Cr(OH)_{12}$). Based on the operational definitions of our study, the majority of the reduced Cr(VI) was removed from solution as sparingly soluble Cr(III) compounds (Fig. 3-5). We believe the two primary reasons for the difference in speciation our results compared to those of others are (1) the differences in experimental time, and (2) initial Cr(VI) and Fe(II) concentrations. For example, our experimental results come from over 1 week of contact between the reactants, while Buerge and Hug (1997) investigated the reaction over 4 h. Their initial values were $[Cr(VI)]_0$=20 μM and $[Fe(II)]_0$=60 μM, and ours were $[Cr(VI)]_0$=1.0x10^3 μM (25μmol) and $[Fe(II)]_0$= 3.0x10^4 μM (750 μmol). The stoichiometric excess of 10x of Fe may have favored the precipitation with Cr(III), and thus the formation of Fe(III)-Cr(III) hydroxides. From our measured soluble Fe(II,III) values after the 1-week extraction, we calculated that for the Fe(II) treatment with Atsion Bhs, 21% of the added Fe precipitated (158μmol); in the Russett Bt1 20% (147μmol) (Table 3-4). The percentages could be even higher if reductive dissolution of Fe(III) (hydr)oxides occurred, placing more Fe in

solution. The control (no soil) showed less precipitation at 17% (126 μmol). We cite the discussion from the Atsion Bhs+oxalic acid treatment, and attribute the portion (13%) of the added Cr(VI) that became nonexchangeable in the Atsion Bhs+Fe(II) treatment likely to be chemisorbed (Fig. 3-5). Despite its sandy texture, the Al (3.0 g/kg) (Condron, 1990) and OM (29 g/kg) content within the spodic horizon are the dominant providers for chemisorption sites, with the low Fe and Mn content remaining as possibilities (Table 3-1). We hypothesize that Russett+Fe(II) showed 100% Cr(VI) reduction because of the high content of Fe(III) (hydr)oxides, e.g. goethite, present in the soil, which in combination with added Fe(II) is capable of enhancing Cr(VI) reduction via the cycling of electrons (Fig. 3-1, Table 3-4). This theory will be further addressed shortly when the Fe(II)+Fe(III) box of Fig. 3-5 is discussed.

The Atsion Bhs-Fe(III) reduced Cr(VI) and solubilized Cr(III), while Fe(III) in contaminated Russett Bt1 caused an even division of the Cr fractions; or nearly a 1:1:1:1 ratio of soluble, exchangeable, nonexchangeable Cr(VI) and soluble Cr(III) (Fig. 3-5). Iron (III) alone would not reduce Cr(VI), as it is the highest, stable oxidation state of Fe in soils and natural waters, but there are redox cycling mechanisms that may be occurring (Fig. 3-1). The dissolution of Fe(III)(hydr)oxides has been shown to be faster in the presence of a ligand-reductant pair, such as oxalate and ascorbate, than in their absence (Suter et al., 1988; Banwart et al., 1989). Such simple organic acids might be present, but only in low quantities within the fulvic and humic acid SOM fractions, since the chosen Atsion and Russett are subsurface horizons. As the reducing agent (e.g., ascorbate) reduces Fe(III) to Fe(II), a complexing agent (e.g. oxalate, citrate) forms an inner-sphere complex (also at the sesquioxide surface), and rapidly dissolves Fe(II), becoming more

reactive to oxalate reduction of Cr(VI) (Banwart et al., 1989). A catalytic electron shuttling cycle is also possible; if FeOOH is reduced by an organic acid (or DOC), and newly-formed, sorbed Fe(II) is oxidized by sorbed Cr(VI), the cycling of Fe(II,III) oxidation states will enhance surface-catalyzed Cr(VI) reduction (Fig. 3-1) (Deng and Stone, 1996a; Tian et al., 2010). Tian et al. (2010) found that Fe(III) in soil particles reacts with citric and tartaric acid to form a photochemically active complex that follows a pathway of a metal-ligand-electron transfer; this results in a stronger overall reductant than the original organic acid. Therefore, if Fe(II) is present in the soil, sorption of Cr(VI) to Fe(III)(hydr) oxides can be coupled to reduction, followed by precipitation of paracrystalline Fe(III)/Cr(III) oxides and hydroxides (Buerge and Hug, 1999).

Lastly, Fe(III) hydrolysis dramatically lowers the pH, solubilizing any natural reducing agents (e.g. Fe^{2+}, S^{2-}, C) within the soil (Fig. 3-5). It might also enhance sorption of $HCrO_4^-$ onto oxide surfaces on which reduction could take place. With this hypothesis, we can explain that Atsion (80% Cr(VI) reduced) performed better than Russett (42% Cr(VI) reduced) due to its natural reducing agents within the soil, chiefly the dissolved organic C (Table 3-1 and 3-4).

The results for the no soil Fe(III) treatment are noteworthy; Fe(III) in spiked Cr(VI) solution alone caused 63% reduction of Cr(VI) (Fig. 3-5). In fact, the percentage of Cr(VI) reduced was not significantly different from that of the two soil horizons ($p \leq 0.05$), which suggests that the soils aren't responsible for the reduction seen. We added Fe(III) as $FeCl_3$ salt, but it could have formed an iron(III) (hydr)oxide precipitate if its IAP>Ksp. Borer et al. (2009) showed that photolysis of surface Fe(III)-hydroxo groups (e.g. lepidocrocite (γ-FeOOH)) takes place in the absence of organic ligands at pH

3, which coincides well with our study (Fig. 3-5). However, the authors used a 1,000 W xenon light source as a solar-simulator, while our batch experiments were in the basement of a building, with most of the light source being fluorescent light bulbs. Sunlight does reach our lab, but glass windows filter it first. Theoretically though, the process would be photoreductive dissolution and involve the (1) photoreduction of Fe(III) at the (hydr)oxide surface, followed by (2) release of surface-bound Fe(II) (and •OH radical) into solution, which is then capable of reducing Cr(VI) (Borer et al., 2009).

A second theory regarding photoreduction is slightly more relatable to our study because it involves NO_3^- and a Fe-Cl complex; the ions present in the Fe(III) no soil treatment (Fig. 3-5) were Na^+, NO_3^-, $HCrO_4^-$, Fe^{3+} and Cl^-. Tzou et al. (2008) showed approximately 50% reduction of an initial 35.8 μM Cr(VI) solution with just 0.1 M NO_3^- added; this result was attributed to the photolysis of NO_3^-, leading to the production of NO_2^- and H_2O_2, which both can serve as reductants for Cr(VI). The addition of Fe(III) to NO_3^- did not significantly increase the photoreduction of Cr(VI), but 35.8 μM Fe(III), 0.1 M NO_3^- and 0.1 M Cl^- together resulted in a 100% Cr(VI) reduction in 90 minutes. It is hypothesized a Fe-Cl complex ($[Fe(OH_2)_5Cl]^{2+}$) is formed, and the photolysis of both this complex and NO_3^- produced Fe(II) and NO_2^- as reductants for Cr(VI). Again, these experiments were conducted under a 100 W mercury UV lamp, a much more concentrated and powerful light source than ours (Tzou et al., 2008).

Our last, and perhaps most plausible, theory is that over the 1-week extraction, microbial reduction of Fe(III) in the depletion of O_2 as an electron acceptor occurred, and the Fe(II) could then reduce Cr(VI) to Cr(III). For example, Fe(III)-reducing bacteria such as *Schewanella alga* BrY in the presence of Fe(III) can potentially lead to extensive

Cr(VI) reduction. The reduction of Fe(III) by the bacterial strain BrY to Fe(II) with successive re-oxidation to Fe(III) by reaction with Cr(VI) reveals a catalytic role of Fe in this system (Fendorf et al., 2000). However, the pH and Eh values for our Fe(III) treatments (pH$\leq$2, Eh$\geq$822) do not necessarily back this theory (Table 3-3 and Fig. 3-3); though, if introduced to oxygen during or after the 24$\pm$2 h refrigeration, error could have been induced.

Of all of the Fe treatments, Fe(II) and Fe(III) combined was the most favorable remediation scheme, resulting in 100% Cr(VI) reduction in all three treatments (Fig. 3-5). There is a notable difference between the Cr fractionation from Atsion-Fe(II) (first box in Fig 3-5) and that of Atsion-Fe(II)+Fe(III) (third box in Fig 3-5). The portion of Cr(VI) that was measured as not exchangeable with just $FeCl_2$ (13%), was fully reduced to soluble Cr(III) through the addition of $FeCl_3$ salt. Conversely, there is no significant difference between Russett-Fe(II) and Russett-Fe(II)+Fe(III). We hypothesize that this is because Russett is an Fe-rich soil, and the reducing power of Fe(III) was already accounted for, without an Fe(III) salt addition. The implication of these particular treatments is that a soil horizon deficient in Fe(III) (hydr)oxides may require an Fe(III) input to the remediation, as opposed to a soil already high in Fe(III) (hydr)oxides. It is also interesting to note the similarity between crystalline forms of Fe(III) and the highly, soluble acidic $FeCl_3$ salt, in their effective reduction of Cr(VI). We are unsure of the specific mechanism of reduction, but have a few hypotheses. According to Buerge and Hug (1999), Cr(VI) reduction by Fe(II) was extremely fast in the presence of goethite (α-FeOOH) and lepidocrocite (γ- FeOOH), two Fe(III) hydroxides. The authors suggest that Cr(VI) sorption is coupled to its reduction, followed by precipitation of paracrystalline

Fe(III)/Cr(III). Perhaps the Fe(III) salt behaves similarly to the hydroxides used in this study. It is also possible that the org. C in Atsion Bhs is reducing the added Fe(III), creating more Fe(II) in the system (Fig. 3-1). Lastly, Fe(III) hydrolysis could be occurring as mentioned earlier, except in this treatment, the hydrolysis has lowered the pH *and* Fe(II) is present to reduce the Cr(VI), in addition to the native soil reducing agents. Although soluble Cr(III) is formed and has the potential to re-oxidize, one could adjust the pH to 4 post-remediation to ensure precipitation of Cr(III) (Hong et al., 2012).

Compost in the form of Leafgro® had no reducing effect (Table 3-4 and Fig. 3-6). The soluble Cr(VI) measured for the Atsion and Russett soil controls were not significantly different from their respective compost treatments ($p \leq 0.05$). We hypothesize that the small amount of reduction seen in Atsion Bhs (12%) and Russett Bt1 (15%) was due to the reducing agents of the soil, not the compost (Table 3-4). In a preliminary study, we qualitatively determined the compost to have a significant portion of humic acids, as shown when an alkaline extract was adjusted to pH 2, an abundance of precipitation occurred in the test tube (chap. 2). The organic C within the dark humic substance is a less reactive, more recalcitrant form of C with higher molecular aggregate weights than fulvic acids (Wittbrodt and Palmer, 1995; Rivero et al., 2004). A ratio of the absorbances measured at wavelengths 465 and 665 nm ($\lambda_{465}/\lambda_{665}$) has been correlated with particle size and therefore molecular weight of the dissolved organic compounds (Chen et al., 1977; Thurman, 1985). A lower ratio corresponds to humification (Thurman, 1985). When we adjusted the pH to 12, the E_4/E_6 was 6.9; humic acids (HA) from soils fall in the range of 6.5-10 and soil fulvic acids (FA) from 2-5, so our value is on the borderline between the two, indicating an appreciable fraction of both HA and FA (Chen

et al., 1977; Schnitzer and Khan, 1978; Thurman, 1985; chap. 2: Table 2-5). When

portions of the same Leafgro® compost were mixed with soil at high pH (11.5) and high

temperature (90°C), there was 100% reduction of a 100 mg Cr(VI)/kg spike (chap. 2).

Therefore, we know the more reactive, reducing humic substances are present in the

compost, but they were not being solubilized without heat. We hypothesize that at the pH

of the treatments in this study (5.7-7.4), both the humic and fulvic fraction are soluble, so

perhaps slow kinetics were governing Cr(VI) reduction since high pH retards this

electron transfer (Fig. 3-6) (Wittbrodt and Palmer, 1995; Xiao et al., 2012). The gap

between the Cr(VI)-Cr(III) line and the line of an organic acid, e.g. CO_2-Oxalate, shrinks

on Fig. 3-3, but the separation remains large at ~1500 mV. In the case of the MD soils,

the theoretical predictions do not match experimental results, as shown on Fig. A-3.

However, the no soil treatment of compost alone in solution is accurately predicted, since

the data points cross above the Cr(VI)-Cr(III) line into the zone where Cr(VI) reduction is

not favorable (Fig. A-3).

Our results are similar to those of Leita et al. (2009) who found soil humic acids

in solution with humic acids did not cause Cr(VI) reduction to Cr(III). The authors

confirmed this using XANES spectroscopy that Cr(VI) remained tetrahedral coordinated

in solution, and the resonance peak with humic acids added was identical to the peak

without humic acids. Rather, they found that the addition of soil humic acids led to the

formation of Cr(VI)–HAs micelles via supramolecular chemical processes. That is, humic

acids behave as supramolecules, extremely large bound molecules, which polymerize,

aggregate and exhibit zwitterionic characteristics that make the attraction to the anionic

Cr(VI) possible (Pacheco et al., 2003; Leita et al., 2009). We are unsure of the nature of

the binding site, but assuming this is what is in fact occurring, the complexation of the

HA-Cr(VI) molecules would remain soluble, according to our fractionation results. As

for stability, Pacheco et al. (2003) found HA forming quite stable supramolecular entities

with tested anions such as Cl⁻, with a log K of 3.1.

The addition of Fe(II) to compost decreased the pH (≤ 2.5 pH units) and reduction

of Cr(VI) was observed ($\geq 86\%$) (Table 3-4 and Fig. 3-6). The percent Cr(VI) reduced for

the control treatment of compost + Fe(II) was not significantly different from that of the

control treatment Fe(II) alone, indicating that Fe(II) was responsible for the reduction (p

< 0.05). However, the soils were significantly different in those same treatments, largely

due to the increased fraction of nonexchangeable Cr(VI) in the compost treatments. As

for compost in combination with Fe(III), the chemical control (no soil) reduced 100% of

the soluble Cr(VI) spike, and the soils both exhibited 92-94% reduction, with 6-8%

remaining in the nonexchangeable fraction, an increase over Fe(II) and compost, which

was 86 and 92% reduction for Atsion and Russett, respectively (Table 3-4). We cite our

earlier discussion of electron cycling between Fe(II), Fe(III) and organic C for our

hypothesis on why compost+Fe(III) is the superior method among compost treatments

(Fig. 3-1 and 6).

COPR-Amended Soils

The results for the COPR soils were harder to evaluate than for the spiked soils,

due to uncertainty related to Cr-containing minerals and compounds in COPR. For

instance, we knew for the Maryland soils that a single, soluble Cr(VI) spike was added,

and we fractionated it following equilibration. The COPRs have a long history of Cr

addition and stabilization in the field prior to sampling and these remediation

amendments. Therefore, we first characterized the control treatments in order to understand fully the remediation effects on native Cr(VI) in these soil-waste materials. The pH of the MES COPR was lower than the 6500 COPR due to the way the chromite ore was processed (Table 3-5). Both COPRs were derived from high heat process, which also included the addition of soda ash (Na_2CO_3) and CaO to react with the chromite in order to form water-soluble sodium chromate (Burke et al., 1991). The residual material, therefore, is highly alkaline (at or above pH 8), containing an array of soluble chromate salts. The 6500 COPR was derived from a high-lime process, which resulted in a higher purity product, but lower recovery of Cr(VI) product, whereas the MES was a low-lime process with a low purity product, but higher recovery. As a result, the high lime process results in more alkaline, higher Cr(VI) COPR.

MES COPR was fractionated into 1282 mg soluble Cr(VI)/kg, 224 mg sorbed Cr(VI)/kg and 69 mg nonexchangeable Cr(VI)/kg for a total of 1575 Cr(VI)/kg. The 6500 COPR had 2422 mg soluble Cr(VI)/kg, 2326 mg sorbed Cr(VI)/kg and 1588 mg not exchangeable Cr(VI)/kg for a total solubility of 6336 Cr(VI)/kg. Although the total Cr(VI) content in 6500 COPR is approximately four times that of the MES COPR, the soluble Cr(VI) fraction does not hold that ratio; that is, it is only about twice the solubility of MES (control boxes in Fig. 3-7 to 9). Therefore, it is important to note that when calculating the stoichiometric Cr(VI) that was needed to be reduced by the added reducing agents, we used the overall total Cr(VI) as determined by Method 3060a: 1200 mg Cr(VI)/kg for the MES COPR and 6500 mg Cr(VI)/kg for 6500 COPR (USEPA, 2014). The reasoning for this was to attempt to reduce all Cr(VI) fractions possible.

Table 3-5. pH and Eh for COPR soils after 1-week Cr(VI) extraction in 0.01M NaNO$_3$ alone.

Treatment	MES pH[a]	MES Eh[b]	Chemicals Alone (MES) pH	Chemicals Alone (MES) Eh	6500 pH	6500 Eh	Chemicals Alone (6500) pH	Chemicals Alone (6500) Eh
Control	8.2[c]	354[c]	7.2[d]	580[d]	11.3[c]	241[c]	7.2[d]	580[d]
Oxalic Acid	7.1	450	1.9	683	5.7	515	1.4	683
Oxalic Acid, Fe(II)	5.8	165	1.7	477	3.5	418	0.9	475
Oxalic Acid, Fe(III)	4.2	517	1.5	675	1.9	761	0.8	706
Compost	8.1	434	7.4	535	9.5	351	7.1	573
Compost, Fe(II)	6.1	145	2.9	540	3.8	395	2.6	547
Compost, Fe(III)	6.4	404	1.9	819	3.3	599	1.4	782
Fe(II)	6.2	144	4.2	571	3.6	364	2.1	590
Fe(III)	6.4	412	2.1	923	2.6	761	1.4	926
Fe(II), Fe(III)	4.8	295	1.6	717	2.6	484	1.4	718

[a]pH meter and combination hydrogen -Ag/AgCl reference electrode.
[b]199 mV were added to the measured value (by Pt electrode) to account for SHE.
[c]Soil in 0.01M NaNO$_3$ alone (MES and 6500).
[d]Spiked 52 mg Cr(VI)/L with background electrolyte 0.01M NaNO$_3$ (no-COPR control).
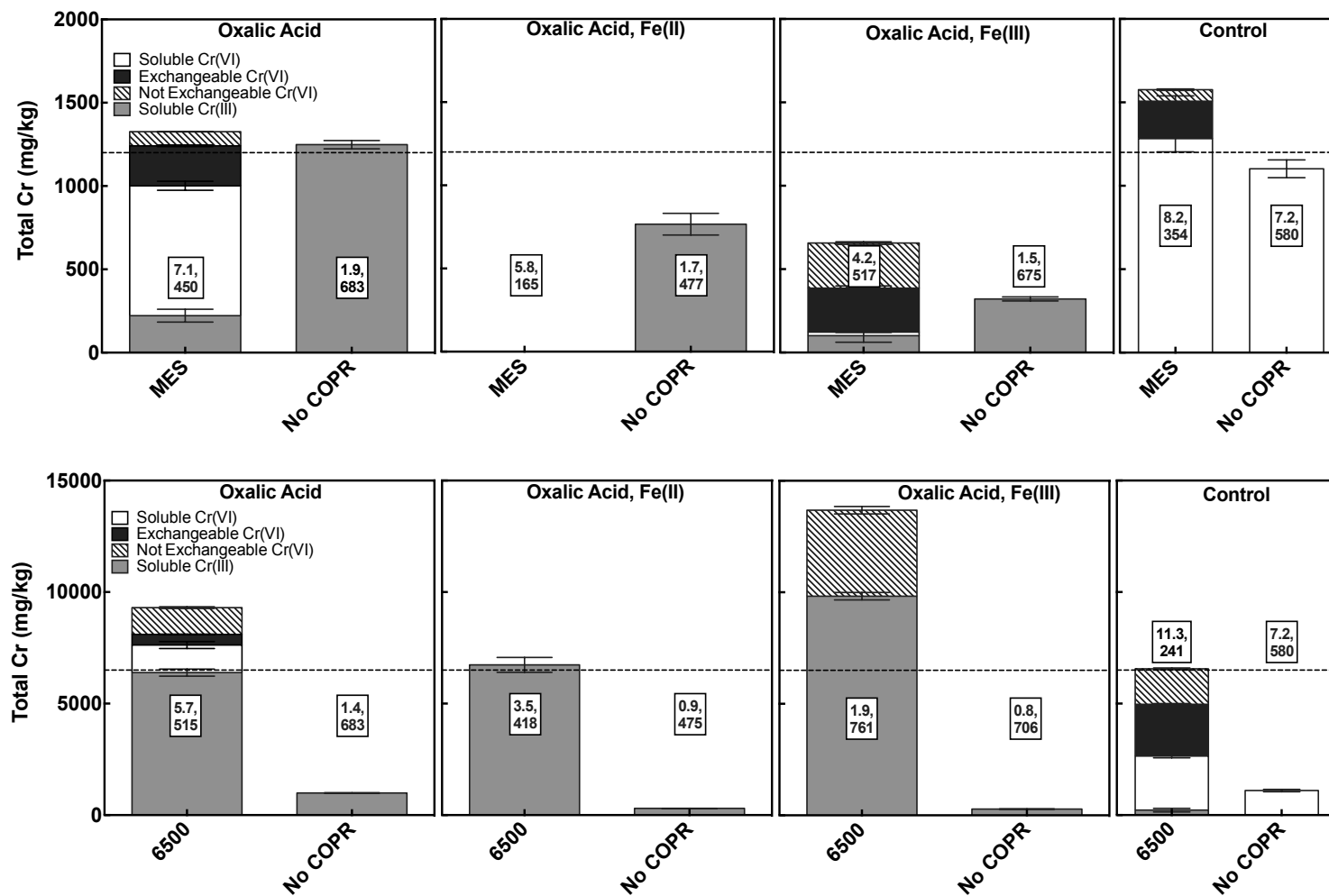
Figure 3-7. Total Cr for the oxalic treatments of MES, 6500 and chemicals alone or "no COPR." See Fig. 3-2 for method details. The pH and Eh of the 1-week Cr(VI) extraction ("soluble fraction") are provided in the box (see table 3-5 for method details). The dotted line indicates the total Cr(VI) level in the COPRs: 1200 mg Cr(VI)/kg for MES and 6500 mg Cr(VI)/kg for 6500.
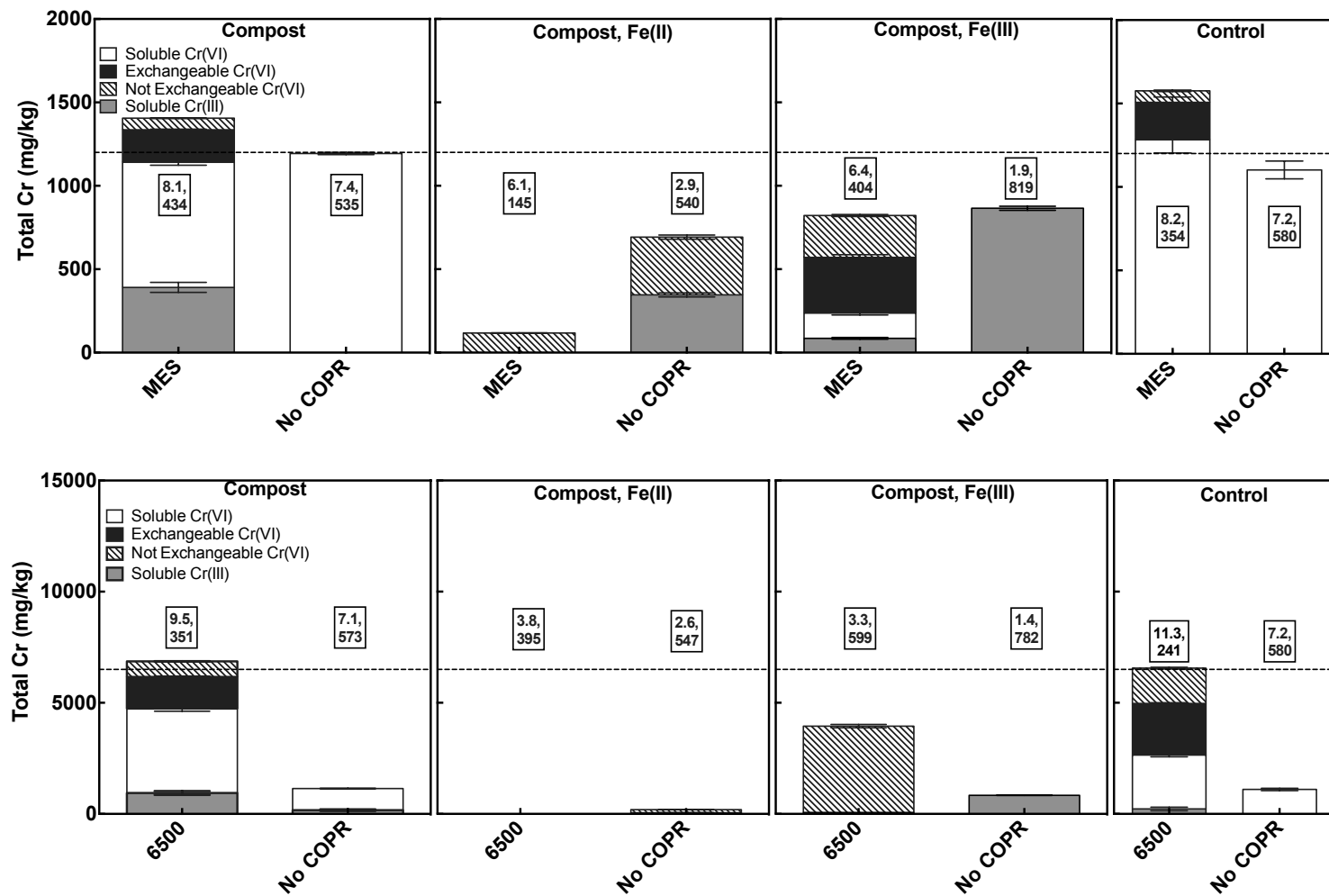
Figure 3-8. Total Cr for the compost treatments of MES, 6500 and chemicals alone or "no COPR." See Fig. 3-2 for method details. The pH and Eh of the 1-week Cr(VI) extraction ("soluble fraction") are provided in the box (see table 3-5 for method details). The dotted line indicates the total Cr(VI) level in the COPRs: 1200 mg Cr(VI)/kg for MES and 6500 mg Cr(VI)/kg for 6500.
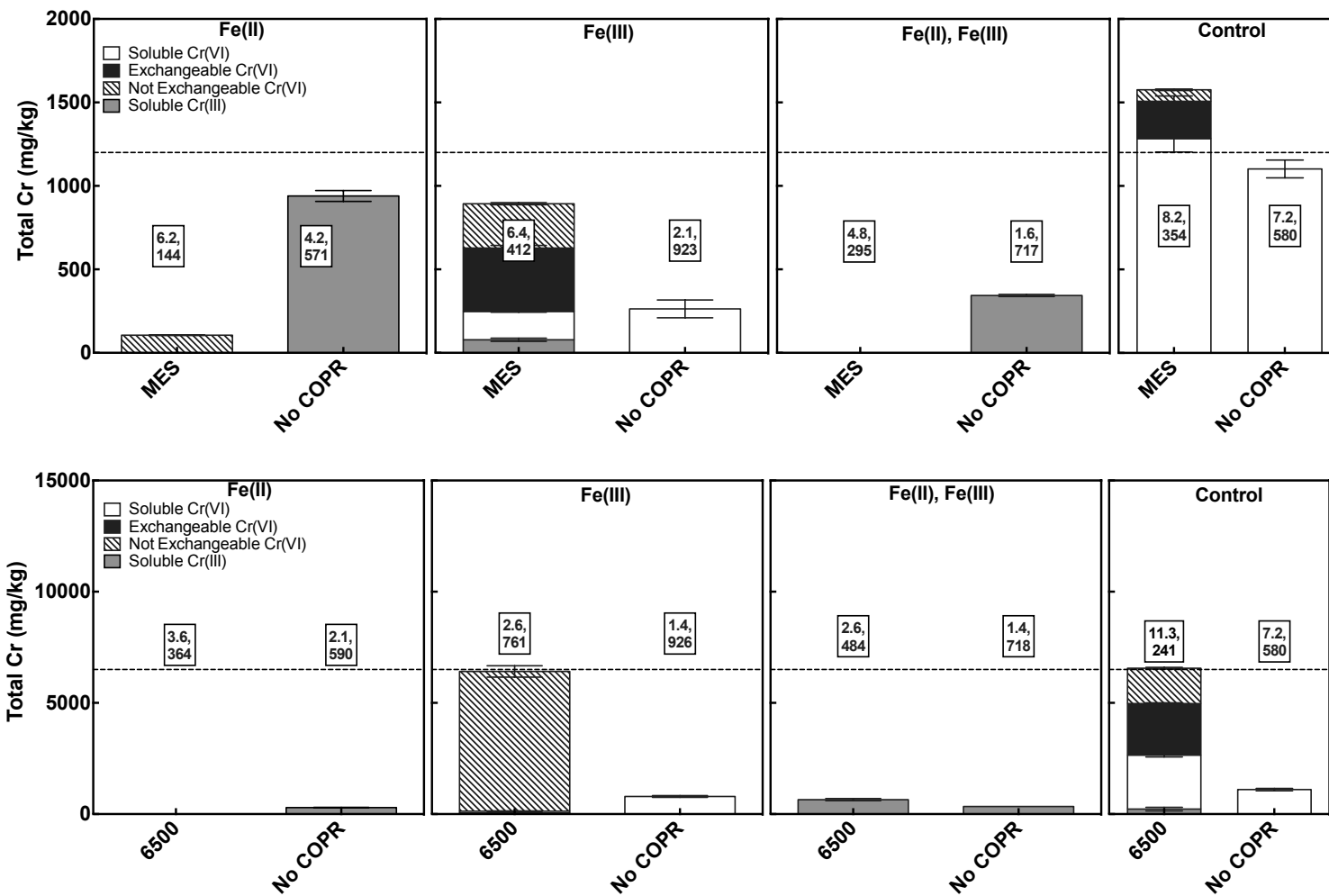
Figure 3-9. Total Cr for the iron treatments of MES, 6500 and chemicals alone or "no COPR." See Fig. 3-2 for method details. The pH and Eh of the 1-week Cr(VI) extraction ("soluble fraction") are provided in the box (see table 3-5 for method details). The dotted line indicates the total Cr(VI) level in the COPRs: 1200 mg Cr(VI)/kg for MES and 6500 mg Cr(VI)/kg for 6500.

However, theoretically if the reducing agents added were only capable of targeting the soluble Cr(VI) fraction, we added a higher amount than what is required for 6500, which may look as if the remediation scheme was favorable to 6500 COPR over MES COPR, or that 6500 was more naturally reducing. That is, there was an excess of reducing agents added for 6500, if you were to base it solely on the soluble fraction, while there was not for MES. This is simply a caution to the reader while interpreting results.

The "no COPR," control treatment was just 52 mg Cr(VI)/L spiked solution and was measured as 1102 soluble mg Cr(VI)/kg, which was not significantly different from the target 1040 mg Cr(VI)/kg at $p \leq 0.05$ (p=0.3096 in unpaired t test). This "no COPR," contamination was used as the solution to test the reducing power of the chemicals alone, in the same quantity as delivered the COPRs. We chose to keep the same contamination value for both MES and 6500 for (1) comparison purposes between the two COPRs and the MD soils and (2) due to preliminary studies (Fig. A-5 to 6), which indicated multiple and varied Cr(VI) release over multiple shake times. This signified the difficulty in predicting how much Cr(VI) will be released.

The three most efficacious treatments for both COPRs were (1) Fe(II) and Fe(III) (2) Fe(II), and (3) oxalic acid and Fe(II) (Fig. 3-7 and 9, Table 3-6). Treatment ranks 1 and 3 were the only two that reduced 100% of the Cr(VI) in both COPRs, but we chose to rank Fe(II) in the middle because although the Fe(II) treatment for the MES COPR reduced slightly less Cr(VI) (93%), there was little to no solubilization of Cr(III), decreasing the potential of re-oxidation (Fig. 3-7 and 9, Table 3-6). Conversely, oxalic acid and Fe(II) induced 6737 mg Cr(III)/kg to solubilize for 6500. The fourth best remediation was compost and Fe(II), reducing 93% of the Cr(VI) in the MES

Table 3-6. Cr and Fe data for COPR soils after fractionation.

Treatment	% Cr(VI) reduced[a]		Soluble Cr(III)[b]		Soluble Fe[c]	
	MES	6500	MES	6500	MES	6500
Control	nd[d]	3.4 ± 1.6	nd	223 ± 80	0.02 ± 0.003	0.008 ± 0.003
Oxalic Acid	30 ± 1.8	56 ± 1.9	222 ± 38	6390 ± 158	nd	145 ± 5
Oxalic Acid, Fe(II)	100 ± 0.0	100 ± 0.0	nd	6737 ± 333	62 ± 8	1194 ± 12
Oxalic Acid, Fe(III)	65 ± 1.4	41 ± 2.6	101 ± 39	9827 ± 167	0.09 ± 0.01	1559 ± 19
Compost	36 ± 1.1	9.7 ± 1.8	391 ± 30	940 ± 88	nd	0.008 ± 0.003
Compost, Fe(II)	93 ± 0.10	100 ± 0.0	nd	1.2 ± 0.1	10 ± 3	936 ± 15
Compost, Fe(III)	54 ± 2.1	41 ± 1.1	87 ± 5.0	64 ± 0.9	0.04 ± 0.003	8.3 ± 3
Fe(II)	93 ± 0.10	100 ± 0.0	nd	1.5 ± 0.0	7.5 ± 0.7	1059 ± 18
Fe(III)	48 ± 0.94	4.2 ± 2.8	79 ± 9.6	54 ± 6	0.03 ± 0.0	15 ± 0.3
Fe(II), Fe(III)	100 ± 0.0	100 ± 0.0	nd	649 ± 47	128 ± 5.3	3006 ± 33

[a]Includes exchangeable, soluble and not exchangeable Cr(VI) reduced. Divided by 1569 mg Cr(VI)/kg for MES and 6500 mg Cr(VI)/kg for 6560, as determined by the control treatments.

[b]mg Cr(III)/kg

[c]μmol Fe (added as 870 μmol for MES and 4.8×10^3 μmol for 6500)

[d]nd is <LOD. LODs are 0.01 mg Cr(VI)/L for % Cr(VI) reduced as measured by the IC, and 0.05 mg Cr(VI)/L for soluble Cr(III) and soluble Fe, as measured by the FAAS.

COPR and 100% in the 6500 (Table 3-6).

Of those four remediation treatments, we believe Fe(II) in combination with Fe(III) is the most favorable because there is complete Cr(VI) reduction to Cr(III), as well as a high removal of Cr(III) from solution. In fact, there was no soluble Cr(III) detected in the MES COPR (<LOD) (not considering the Cr(III) in residual chromite ore) and 6500 has just 649 mg Cr(III)/kg, 10% of the total original Cr(VI) (Table 3-6). The pH is ≤4.8 for all Fe(II)+Fe(III) treatments, placing it in the pH range where Fe(II) oxidation by Cr(VI) remains favorable over O_2 (Mitrakas et al., 2011) and the high pH doesn't cause problems as seen by Geelhoed et al. (2003) (Fig. 3-9, Table 3-5).

Compost and oxalic acid were the two least effective treatments at removing Cr(VI) from solution, despite the fact that oxalic acid as a reducing agent is very thermodynamically favorable (Fig. 3-7 and 8; Table 3-2 and 6). The fractionated Cr(VI) after compost addition was nearly identical to the respective COPR controls (Fig. 3-8). The oxalic acid treatment was not as successful for the COPRs as it was for the spiked Maryland soils, reducing only 30% of the total Cr(VI) in MES and 56% for 6500, both entirely from the soluble fraction (Fig. 3-7, Table 3-6). We do not think the difference in success is because of less accessible or soluble Cr(VI) in the COPRs since the soluble fractions of the control treatments (1282 and 2422 mg Cr(VI)/kg) were much different from the soluble spike of 1040 mg Cr(VI)/kg to the Maryland soils; *and* the chemicals delivered to the COPR treatments were higher, having a greater remediation potential. Instead, we hypothesize that this is a result of inhibited Cr(VI) reduction at the neutral pH of the treatments (Table 3-5). For example, the oxalic acid treatments had pH values of 7.1 and 5.7 for MES and 6500, respectively, and the chemical control treatment reduced

100% of the 1100 mg Cr(VI)/kg at pH < 2 (Table 3-5 and Fig. 3-7). The compost

treatments had pH values of 8.1 and 9.5 for MES and 6500, respectively, and reduced 36

and 10% of total Cr(VI). Compost alone (no COPRs) in a contaminated Cr(VI) solution

remained at neutral pH as well (7.1-7.4), reducing only 0-12% Cr(VI) (Table 3-5). The

experimental values plotted on the theoretical Eh-pH diagram for MES, 6500, and the

chemical controls all fall at or above the Cr(VI)-Cr(III) line, accurately predicting that

Cr(VI) reduction is not thermodynamically favorable (Fig. A-4).

One more important effect of the oxalic acid treatments on the COPRs was

inducing Cr(III) to come into solution in large quantities (Fig. 3-7, Table 3-6).

Ammonium oxalate is commonly used as an extracting chemical in soils due to oxalate

complexing and dissolving Fe and Al in poorly crystallized oxides, as well as giving a

preliminary assessment for the organically bound metals (Balint et al., 2013). Therefore,

we hypothesize that the added oxalate dissolved paracrystalline Fe and Mn oxides bound

by Cr(III) within the COPRs, and thereby placing the soluble Cr(III) in solution to be

measured by FAAS. This corresponds well with a study done by Elzinga and Cirmo

(2010), in which the authors estimated the organically complexed Cr(III)-DOM within a

COPR sample was as high as 56% of the total Cr.

The Fe(III) treatments are again quite inexplicable. When $FeCl_3$ was shaken in a

1102 mg Cr(VI)/kg spiked solution with background electrolyte, Cr(VI) reduction

occurred (Fig. 3-9). In fact, even more reduction was seen without COPR (just Fe(III) salt

in an electrolyte solution) than with COPR (COPR and Fe(III) salt in electrolyte solution

together). In the case of the 6500 COPR, only 4.2% was reduced in the presence of

COPR and 28% without; and for the MES COPR, 48% of Cr(VI) was reduced with

COPR and 76% without (Fig. 3-9, Table 3-6). Our hypothesis remains that the occurrence is either photoreduction or microbial-related, although it is unclear on how the microbes caused less reduction. Perhaps some of the newly-reduced Cr(III) re-oxidized, decreasing the total % Cr(VI) reduced. An alternative hypothesis is that the low pH may have enhanced Cr(VI) reduction by chloride (Cl^-) or nitrate (NO_3^-). This is quite an enigma and further research is required here.

Conclusion

The key to remediation is to reduce Cr(VI) and prevent re-oxidation. Therefore, we need to understand whether the Cr(VI) removal from solution is by sorption, precipitation of the anion, or reduction to Cr(III), possibly followed by precipitation as Cr(III) (hydr)oxides. Examples of target Cr(III) precipitates are Fe(III)-Cr(III) hydroxides, Cr_2O_3 and/or $Cr(OH)_3$ in an non-oxidizing environment. Also, some organic complexes such as Cr(III)-humates or –humins are sparingly soluble, resulting in the immobilization of Cr(III), which further prevents the species from changing back to the toxic Cr(VI) in any environmental conditions. Our fractionation method proved to be successful for the needs of this investigation. If a remediation of just COPR-amended soils was required, though, these authors recommend returning to the original USEPA Method 3060a with heat (Chap. 2).

The overall best remediation scheme in this study, factoring in % Cr(VI) reduced and immobilization of Cr(III), was Fe(II) in combination with Fe(III). Compost was the only treatment that did not lower the pH from that of the natural soil pH. The use of compost in the form of Leafgro® was an unsuccessful treatment at pH 5-7, but should be

tested at an adjusted lower pH to see if it is effective then. Oxalic acid should only be used for non-COPR soils. Lastly, it seems that soil generally inhibits reduction instead of enhancing it, as compared to the chemicals in a spiked Cr(VI) solution alone, with the exception of Fe(III) and compost treatments. Further research should be directed to learning more about characterizing the reduction of Cr(VI) by Fe(III) in a solution, conceivably with varying light sources, pH and background electrolytes.

CHAPTER 4

SIGNIFIGANCE OF THIS RESEARCH

Through a variety of weathering processes, mineral nutrients within the Earth's bedrock have been released into the soil, water and air. Soil provides minerals to plants and thus, animals and humans. These essential elements (in trace amounts) include Zn, Fe, Mn, and Cr and they participate in critical functions in the body, whether it is a metabolic or biochemical process (Gupta and Gupta, 2014). However, it is often misleading to represent such essential nutrients in their elemental form, as they exist in distinctive species and not all forms are valuable to human and/or environmental health. Speciation refers to the chemical (e.g. oxidation state) and physical form (e.g. solid, liquid, gas) of the metal and environmental conditions such as pH, Eh, co-constituents in solution, etc. play a critical role in determining the species the element will take on (Reeder et al., 2006). This thesis focused on the study of chromium in a variety of settings designed to observe the inter-conversions between Cr in the toxic oxidation state $+(VI)$ to the nontoxic Cr$+(III)$ in both soils and waters. Cr is an excellent model to study due to its' speciation changes, as well as its ability to participate in the many processes of sorption, precipitation, complexation with organic ligands, dissolution and biological uptake. The complex chemistry is relatable to other anions such as phosphate (PO_4^{3-}) and cations such as aluminum (Al^{3+}).

The mining of chromite ore ($FeO \cdot Cr_2O_3$) and subsequent redistribution for industrial use has caused a global Cr contamination concern. In 1958, the World Health Organization (WHO) International Standards for drinking water recommended a maximum allowable concentration of 0.05 mg Cr(VI)/L based on health concerns, and

maintains that standard today, though, both Cr(III) and Cr(VI) have been under review since 2004 to lower the standard even further (WHO, 2004). The federal drinking water standard in the United States (0.1 mg/L) is based on total Cr in solution and quantified as all Cr species present, mainly that of Cr(VI) (H_2CrO_4, $HCrO_4^-$, CrO_4^2, $Cr_2O_7^{2-}$) and Cr(III) (Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_4^-$). Atmospheric pollution, from sources such as urban dust, is also a Cr-related health issue. The particulate matter (PM) standard set by the EPA (National Ambient Air Quality Standard) is 12.0 μg m^{-3}, which is comparable to the guidelines set in Canada, Australia, Japan, Mexico and the WHO (Jiang et al., 2014).

Chapter 2 of this master's thesis presents an alternative method to the current, standard extraction for Cr(VI) in soils, or EPA's Method 3060A alkaline, digestion extraction. We discovered the flaws of the method while analyzing soils spiked with Cr(VI). There was as low as a 40% Cr(VI) spike recovery, indicating soil-induced reduction. However, taking into account the extent of the reduction after simply storing the contaminated soil in a dry, cool bucket, this result was unusual and led to further investigation. After removing the aggressive step of 1 hour of heat at 95°C and replacing it with shaking at 100 cycles/min at room temperature (23°C), we recovered 100% of the original Cr(VI) spike. These preliminary studies indicated that Method 3060A was providing false results of decreased Cr(VI). This method induced reduction of Cr(VI) to Cr(III) means that if an engineer, chemist, or analyst is attempting to quantify the extent of a Cr(VI) contamination site prior to remediation, they would believe that the Cr(VI) contamination is a lot less than in actuality. This is a major problem that could end up costing those involved both time and money. After discovering a simple, feasible and

economical solution of shaking in place of heat, we wanted to investigate further the cause of this problem, as well as at what point is a heated method favorable over a non-heated method. We used a wide range of soils to answer these questions in order to provide for a diverse environment of reducing agents, organic carbon form, mineralogy and both soluble and insoluble Cr(VI); this included soils (sampled from MD), soil amendments (a local compost product), and waste materials (COPRs).

The work in Chapter 2 shows that heat is solubilizing reducing agents in the soils, and the main cause of MIR is the amount of carbon present and not the presence of extractable free iron oxides. Furthermore, we believe the more easily degradable and accessible C within soil fulvic acids are responsible for the majority of the Cr(VI) reduction. Though, at ≥ 10 g C/kg there were enough humic acids present from the compost amendments to flocculate in the test tube at pH <2 when reacted with DPC above. We conclude that for a more typical, pedogenically-driven soil, one should use the method without heat and analysis by IC, as this methodology consistent recovered 100% of Cr(VI) across all C measures (0-500 g C/kg). As originally hypothesized, the COPRs behaved differently. It is hypothesized that the mineralogy of Cr plays a much larger role in the extraction. The Cr(VI) in COPR soils have been identified in mineral phases, and thus, require a more aggressive extraction method. Not until about 100 g C/kg amendments was the no-heat method favorable for COPRs.

Lastly, two analytical methods were compared: the colorimetric reaction DPC as analyzed by a UV-VIS spectrophotometer and an ion chromatograph employing an anion column for separation and a conductivity detector. There were, surprisingly, little

differences between the two, especially in the grand scheme of commercial analysis. Either method would suffice, with IC being slightly more preferable overall.

Further research should simulate these experiments, but also include analysis with XRD to better understand the forms of Cr and carbon. It would also be interesting to use a different carbon amendment (e.g. organic acid) in place of the dark humus compost material and see how those results compare to ours. Similarly, delving more into the various pools of carbon (e.g. a complete fractionation of C in soils) and how they affect this method would be beneficial to future researchers, remedial contractors and policymakers. The importance of this work is to be able to protect human and environmental health through the enforcement of regulatory analytical methodology and technology. Whether the source is natural Cr(VI) or Cr(VI) from improper industrial disposal, it is critical that we have the tools to accurately, reliably and effectively extract hexavalent Cr alone without inducing reduction-oxidation processes.

In Chapter 3, a remediation scheme was employed to reduce a 1040 mg Cr(VI)/kg spike in the B horizons of the MD soil series Atsion and Russett, and the 1200 mg Cr(VI)/kg contamination in MES COPR and 6500 mg Cr(VI)/kg in 6500 COPR. The reducing agents were Fe and organic carbon. Iron(II) and Fe(III) were delivered as ferrous and ferric chloride, respectively. Iron(II) is common in remediating Cr(VI), but not as $FeCl_2$. Iron(III) isn't a reducing agent, but provides for an electron shuttle; the presence of soil organic acids are capable of reducing Fe(III) in solution, producing Fe(II) that can then be oxidized by the Cr(VI), starting the redox cycle over. Organic C was delivered as oxalic acid, common in fruits (blackberries, blueberries) and vegetables (spinach, celery). Carbon was also added in the form of local Prince George's County,

MD leaf compost to explore the capability of its' constituents reducing Cr(VI), as well as possible sorption reactions.

For MD soils, the two remediation arrangements of (1) oxalic acid and (2) Fe(II) and Fe(III), reduced 100% of the 1040 mg Cr(VI)/kg spike, which is towards the higher end of Cr(VI) contamination in soils. This research may be applied to implementing reducing solutions for large-scale cleanups, whether the engineer is employing packed column beds, PBRs, or slurry reactors. This thesis showed that pH played a major role in the redox processes in soils. The only treatment that didn't lower the pH was the leaf compost, and no Cr(VI) was reduced at pH 5-7. The neutral pH also impacted the compost's ability to adsorb Cr(VI), inhibiting further surface reduction and/or precipitation. We recommend future research with Leafgro at an adjusted pH because it exhibited high reducing ability in Chapter 2 and it is an extremely economical solution ($5/40 lb leaf bag).

Iron(II) and Fe(III) reduced 100% of the respective contaminations for MES and 6500 COPR, slightly higher than Fe(II) alone, exhibiting the importance of electron cycling. Another important conclusion of this thesis was the organic carbon sources were poor reductants for the COPR-amended soils, ranging from a 10-56% success. Since Cr(VI) was delivered as a soluble spike to the MD soils, perhaps carbon sources are better at reducing soluble amounts of hexavalent chromium, as opposed to the more insoluble forms, where Fe(II) and Fe(III) prevail.

A novel and noteworthy result from this thesis work was that Fe(III) is capable of not only reducing Cr(VI) in the presence both MD and COPR-amended soils, but also alone in solution, with 28% Cr(VI) reduction or higher. Iron(III) inducing Cr(VI)

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reduction in the presence of soils was also surprising, but not entirely impossible since we did not destroy the microbes within the soil. There are many pathways with microbial metabolism that could allow Cr(VI) reduction, with one of them being the microbes could oxidize Fe(III), placing Fe(II) in solution. However, for the purely chemical reaction of Fe(III) reducing Cr(VI) in solution with background concentrations of Cl^-, H^+, Na^+, NO_3^- is extremely novel and requires further investigation. To date, these chemical constituents are not known to be capable of reducing Fe(III) to Fe(II) for the Cr(VI) reduction to occur, in the absence of light. Perhaps a microbiologist should be the next to investigate this behavior, due to their expertise on microorganisms in the air and water. We did not apply photochemical light; the reaction occurred in a room with light from fluorescent light bulbs and windows.

Soil decontamination is of growing importance in the world today for a multitude of reasons. A major overpopulation issue includes the increasing demand for healthy, fertile, and non-contaminated soil to grow crops on. Additionally, toxins in the soil have shown to increase cancer rates in homes in cities affected by industrial spills, leaks or accidents. The chemical processes of Cr in soils and natural waters do not remain stable for long and are controlled by the master variables pH and Eh, as well as reduction-oxidation reactions. We discovered the use of Fe and C to reduce Cr(VI) through thermodynamically favorable chemical reactions, in addition to their interactions with mineral surfaces of soils, as they would behave in a natural landscape, for both an *in situ* and *ex situ* remediation. Furthermore, this thesis has presented a more accurate way to quantify the extent of Cr(VI) contamination in soils to progress the cleanup of Cr in our soils.

Table A-1. Cr(VI) extraction and analysis comparison with heat (95°C) or without (23°C) and analyzed by IC or DPC: Glenelg A1 and compost-amended Glenelg A1 results.

Carbon Addition (g C/kg)	Heat Treatment[a]			
	Unheated[b]		Heated[b]	
	IC	DPC	IC	DPC
0	106 ± 1 a	104 ± 0 a	nd[c] b	1 ± 1 b
10	106 ± 1 a	102 ± 1 b[d]	nd c	1 ± 1 c
100	105 ± 0 a	93 ± 3 b	nd c	N/A[e]
500	104 ± 0 a	84 ± 4 b	nd c	N/A

[a]Statistically significant differences were identified within the same carbon addition treatment (in each row) with two-way ANOVAs ($p \leq 0.05$), except for the last two rows, where one-way ANOVA had to be used due to the absence of results for Heat-DPC.

[b]Means are given in mg Cr(VI)/kg compost-amended soil and errors are SEM (n=3).

[c]nd is <LOD. The LOD is 0.01 mg Cr(VI)/L for the IC.

[d]P value for the difference between IC and DPC for the unheated treatment is 0.0135.

[e]N/A indicates no analyses were conducted due to flocculation of organics in the DPC test tube.

Table A-2. Cr(VI) extraction and analysis comparison with heat (95°C) or without (23°C) and analyzed by IC or DPC: Atsion Bhs and compost-amended Atsion Bhs results.

| Carbon Addition (g C/kg) | Heat Treatment[a] | | | |
| | Unheated[b] | | Heated[b] | |
	IC	DPC	IC	DPC
0	106 ± 0 a	101 ± 1 b	nd[c] c	3 ± 0 c
10	107 ± 0 a	95 ± 3 b	nd c	3 ± 1 c
100	106 ± 0 a	77 ± 1 b	nd c	N/A[d]
500	104 ± 0 a	78 ± 4 b	nd c	N/A

[a]Abbreviations as in Table A-1.

[b]Abbreviations as in Table A-1.

[c]Abbreviations as in Table A-1.

[d]Abbreviations as in Table A-1.

Table A-3. Cr(VI) extraction and analysis comparison with heat (95°C) or without (23°C) and analyzed by IC or DPC: Flickinger A1 and compost-amended Flickinger A1 results.

Carbon Addition (g C/kg)	Heat Treatment[a]			
	Unheated[b]		Heated[b]	
	IC	DPC	IC	DPC
0	107 ± 1 a	110 ± 0 b	103 ± 1 a	105 ± 0 a
10	106 ± 0 a	109 ± 1 a	87 ± 4 b	77 ± 5 b
100	104 ± 0 a	94 ± 0 b	nd[c] c	N/A[d]
500	104 ± 0 a	86 ± 1 b	nd c	N/A

[a]Abbreviations as in Table A-1.

[b]Abbreviations as in Table A-1.

[c]Abbreviations as in Table A-1.

[d]Abbreviations as in Table A-1.

Table A-4. Cr(VI) extraction and analysis comparison with heat (95°C) or without (23°C) and analyzed by IC or DPC: Flickinger Bt1 and compost-amended Flickinger Bt1 results.

Carbon Addition (g C/kg)	Heat Treatment[a]			
	Unheated[b]		Heated[b]	
	IC	DPC	IC	DPC
0	108 ± 0 a	108 ± 1 a	104 ± 1 b	106 ± 0 ab
10	106 ± 1 a	107 ± 0 a	86 ± 1 b	83 ± 1 b
100	105 ± 0 a	89 ± 1 b	nd[c] c	N/A[d]
500	105 ± 0 a	87 ± 1 b	nd c	N/A

[a]Abbreviations as in Table A-1.

[b]Abbreviations as in Table A-1.

[c]Abbreviations as in Table A-1.

[d]Abbreviations as in Table A-1.

Table A-5. Cr(VI) extraction and analysis comparison with heat (95°C) or without (23°C) and analyzed by IC or DPC: Glenelg Bt1 and compost-amended Glenelg Bt1 results.

Carbon Addition (g C/kg)	Heat Treatment[a]			
	Unheated[b]		Heated[b]	
	IC	DPC	IC	DPC
0	109 ± 0 ab	114 ± 3 b	100 ± 1 c	102 ± 1 ac
10	109 ± 1 a	116 ± 3 a	74 ± 4 b	67 ± 0 b
100	105 ± 1 a	94 ± 1 b	nd[c] c	N/A[d]
500	104 ± 0 a	91 ± 1 b	nd c	N/A

[a]Abbreviations as in Table A-1.

[b]Abbreviations as in Table A-1.

[c]Abbreviations as in Table A-1.

[d]Abbreviations as in Table A-1.
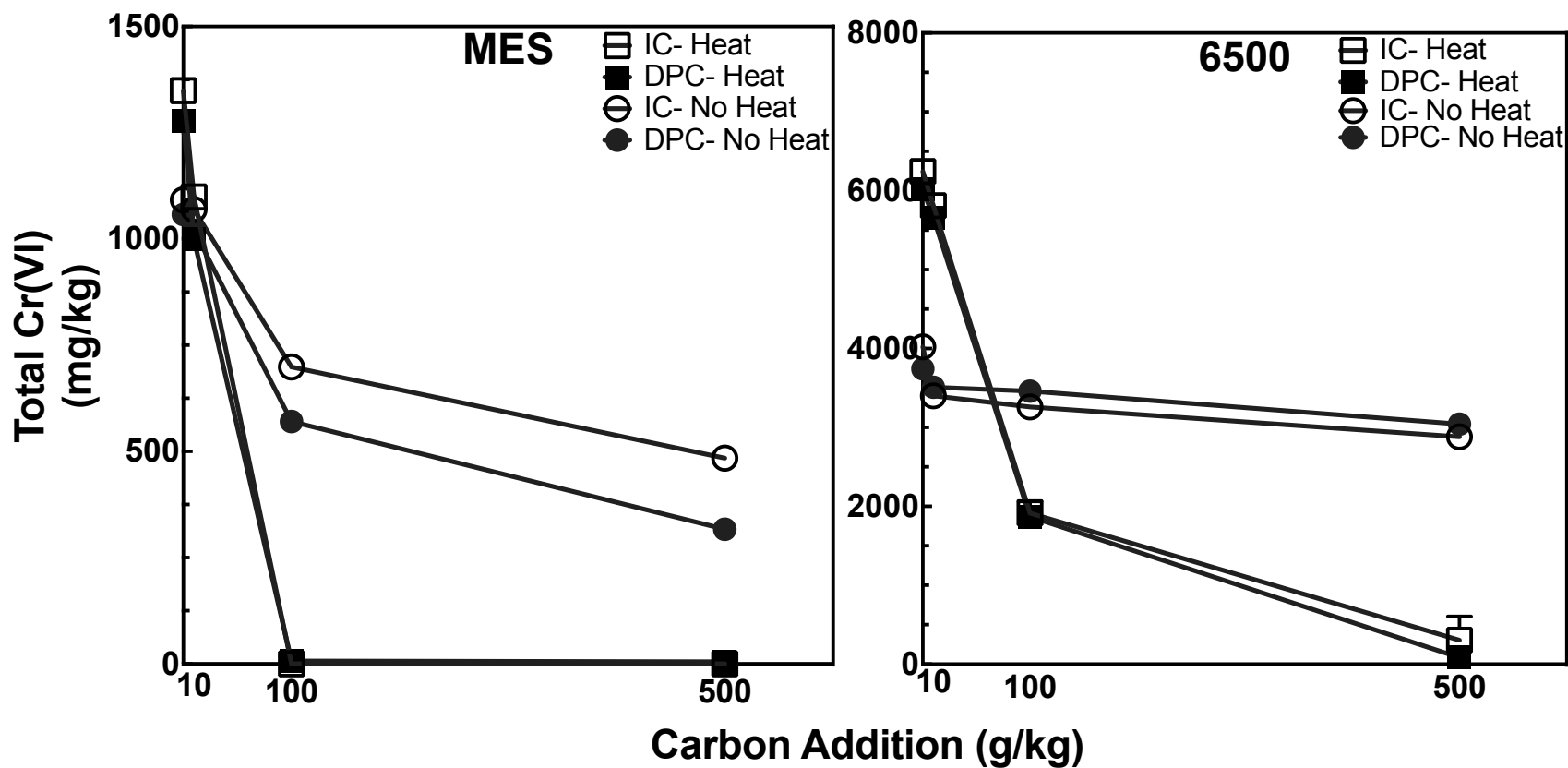
Figure A-1. MES and 6500 COPR with 0-500 g C/kg additions. 6500 and MES horizons were incubated for 1 week (168 ± 5 hours) with 0 g, 1 g, 10 g and 50 g C equivalent additions of compost to 100 g of soil. Method 3060a was run with and without heat, and analyzed by IC and DPC ($p \leq 0.05$). The error bars represent one SEM (n=3).
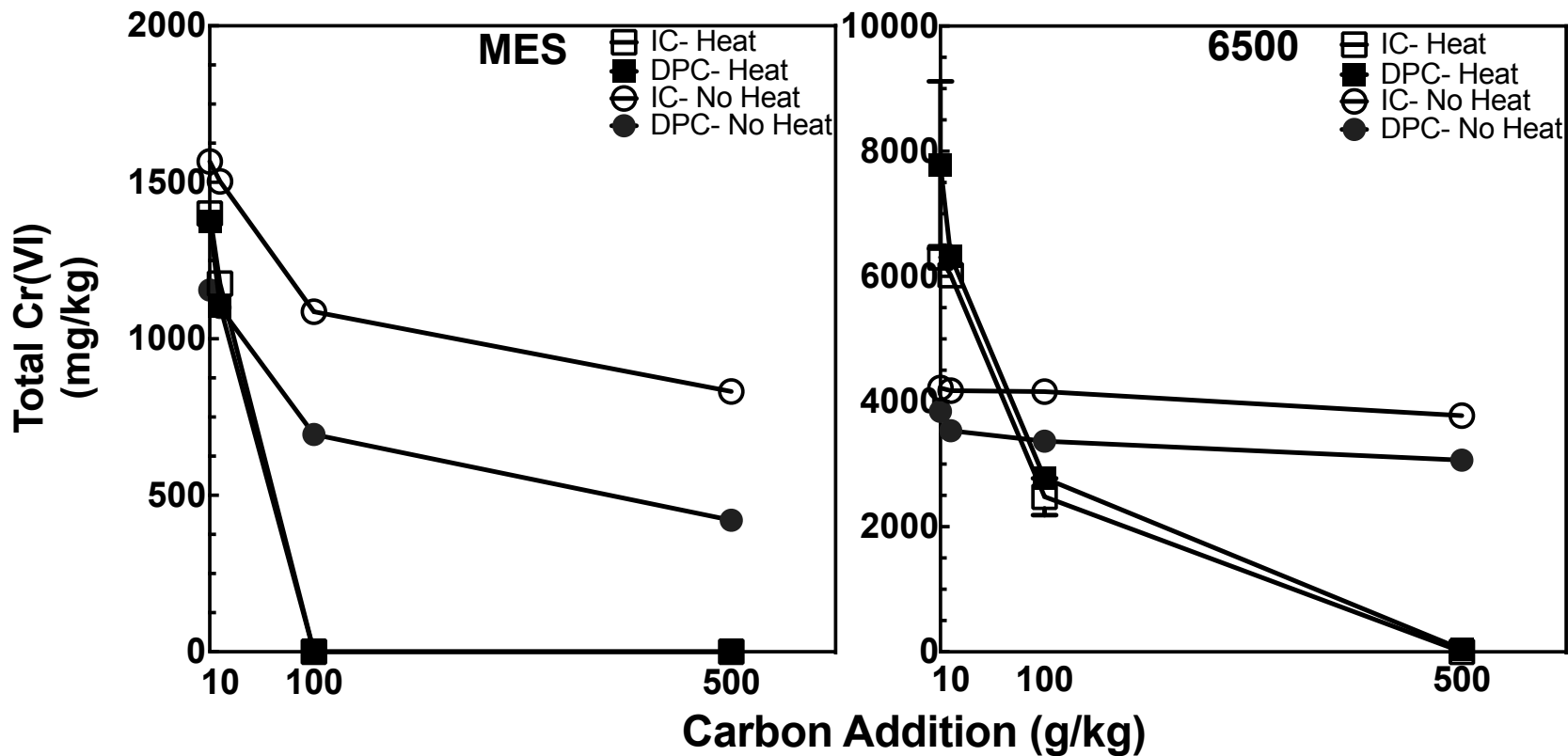
Figure A-2. Pre-digestion Cr(VI) spikes of MES and 6500 with 0-500 g C/kg additions. The 6500 and MES soils were incubated for over 1 week (168 ± 5 hours) with 0 g, 1 g, 10 g and 50 g C equivalent additions of compost to 100 g of soil. A pre-digestion spike of 100 mg Cr(VI)/kg was added just prior to running Method 3060a. Method 3060a was run with and without heat, and analyzed by IC and DPC (p≤0.05). The error bars represent one SEM (n=3).
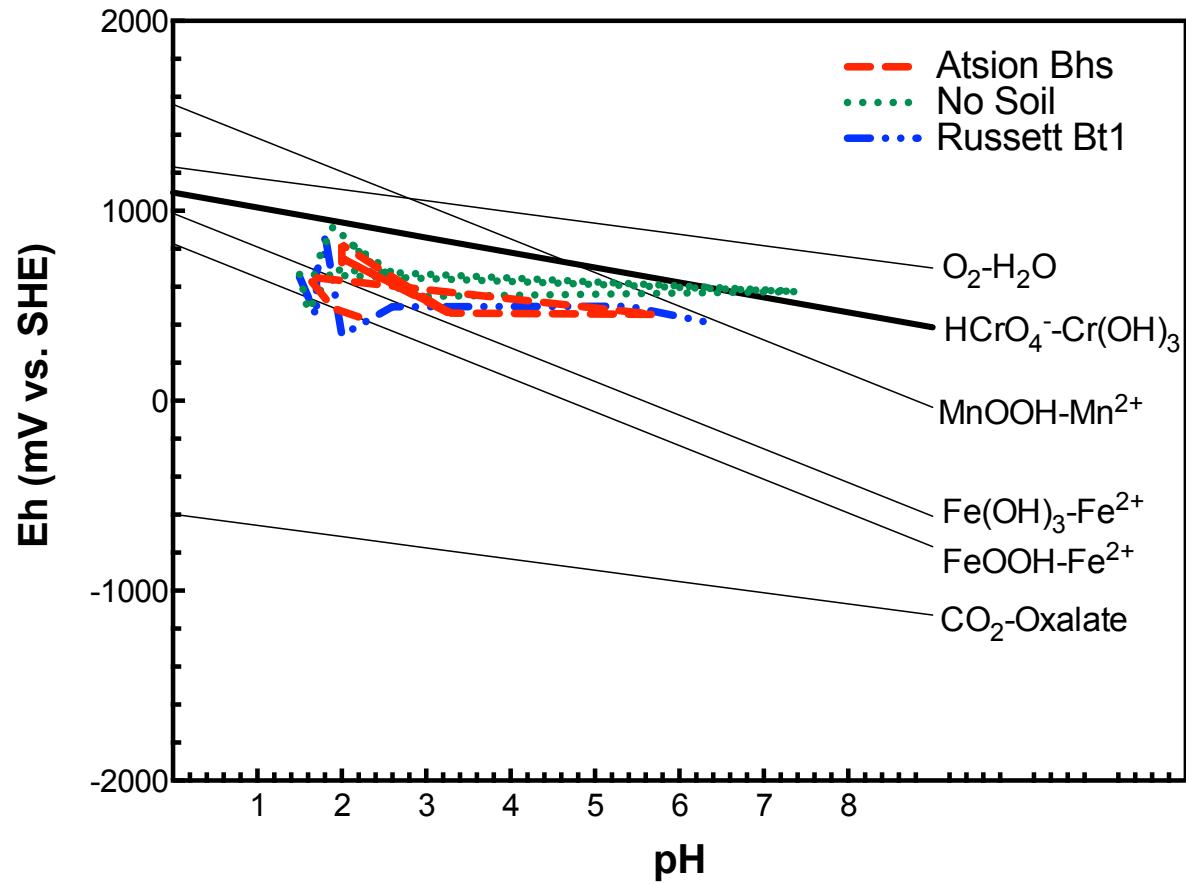
Figure A-3. Eh-pH Diagram for thermodynamically-possible reductants of Cr(VI) and oxidants of Cr(III). See Table 1-1, C-1 and C-8 for complete description of activity calculations. The experimental results of Atsion Bhs, Russett Bt1, and No Soil from Table 3-3 are also shown on the plot.
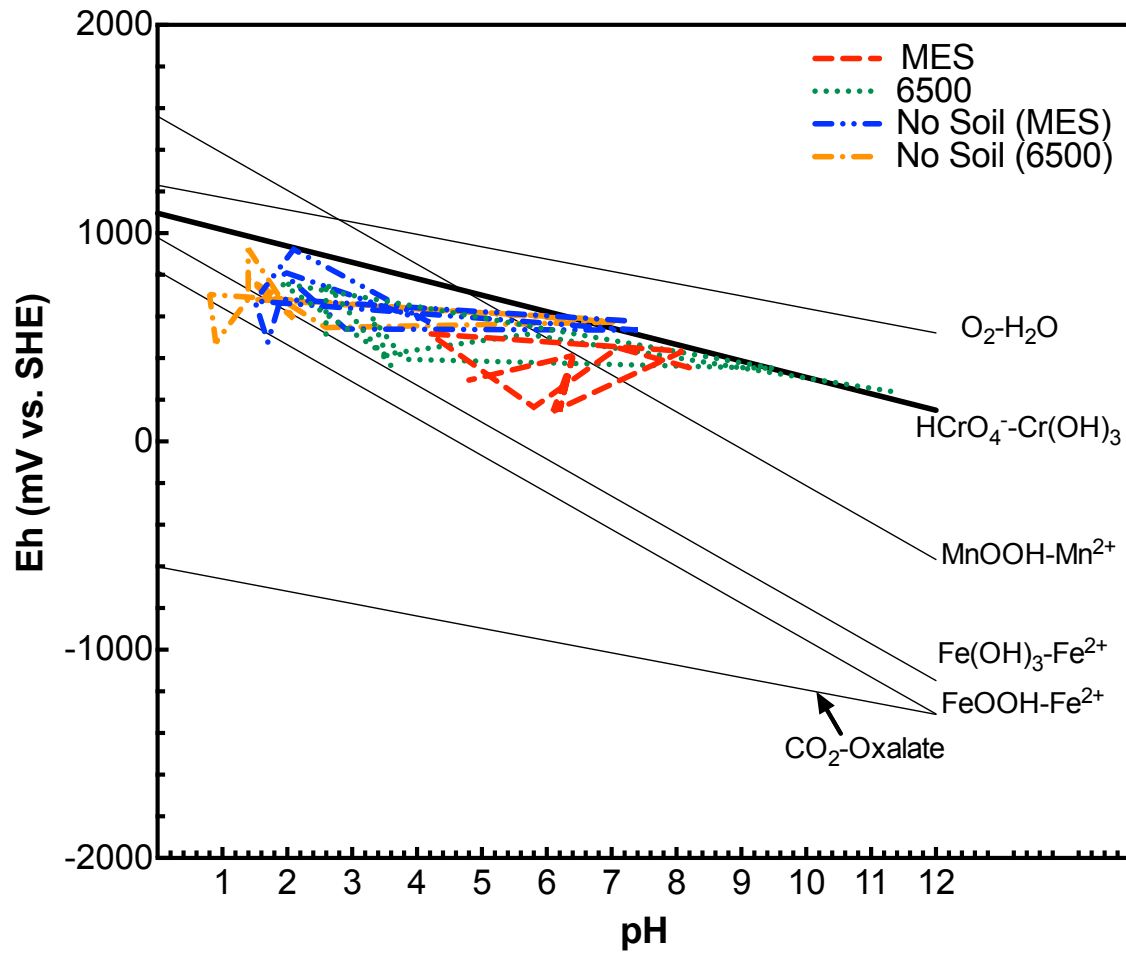
Figure A-4. Eh-pH Diagram for thermodynamically-possible reductants of Cr(VI) and oxidants of Cr(III). See Table 1-1, C-1 and C-8 for complete description of activity calculations. The experimental results of MES, 6500, No Soil (MES), and No Soil (6500) from Table 3-5 are also shown on the plot.
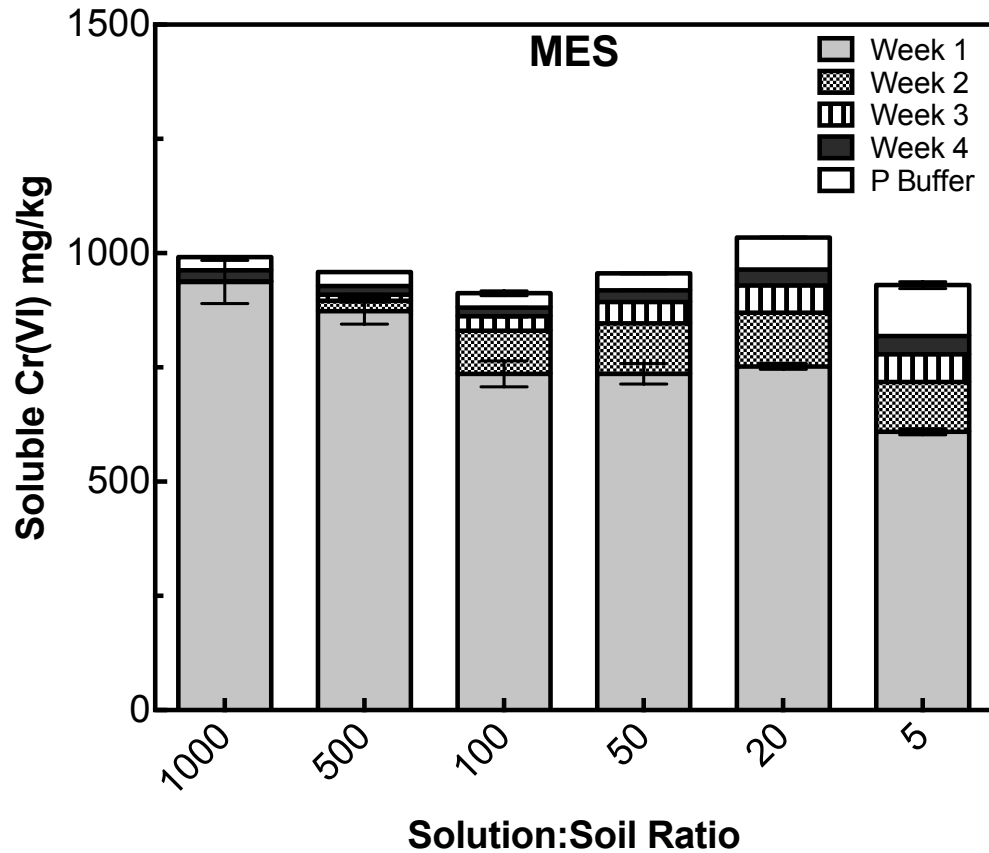
Figure A-5. Characterization of Soluble Cr(VI) in MES. MES COPR was shaken (100 cycles/min) with a range of solution: soil ratios for 1 month. The soluble Cr(VI) was analyzed weekly by the DPC method. After 4 weeks of shaking and subsequent measurements, 0.01 M phosphate buffer was used to measure exchangeable Cr(VI). All treatments were made in 25 mL of 0.01 M $NaNO_3$. The average pH and Eh were 8 and 366 mV, respectively.
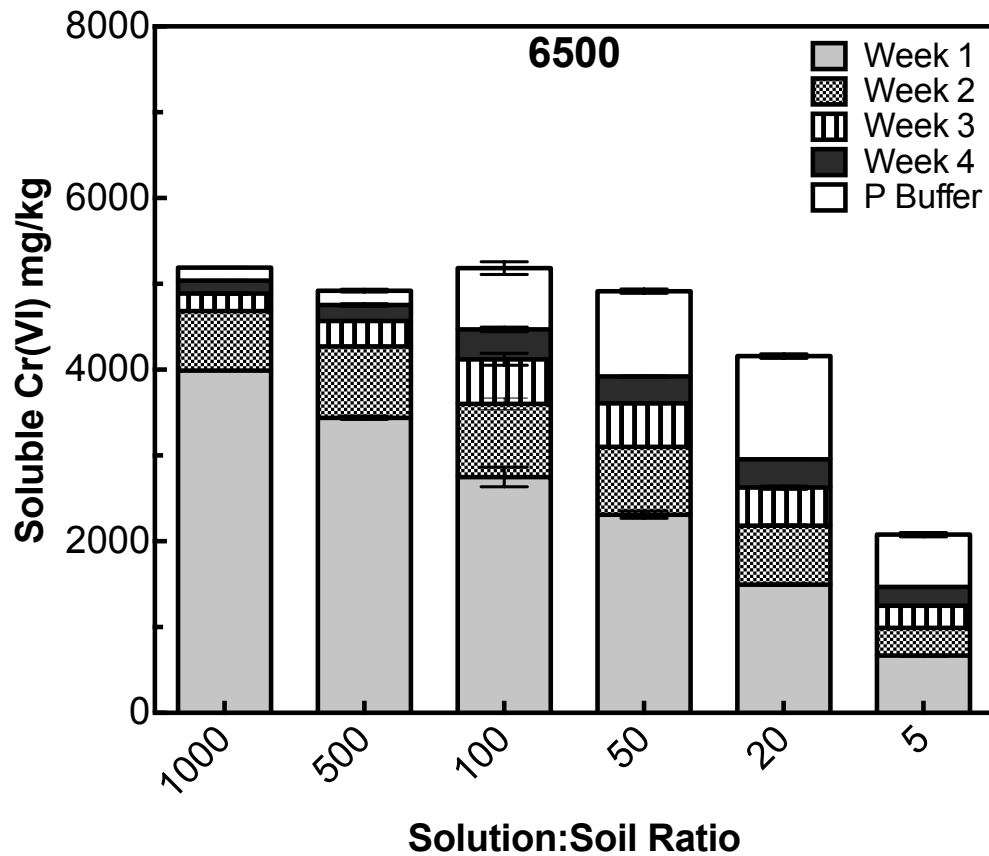
Figure A-6. Characterization of Soluble Cr(VI) in 6500. 6500 COPR was shaken (100 cycles/min) with a range of solution: soil ratios for 1 month. The soluble Cr(VI) was analyzed weekly by the DPC method. After 4 weeks of shaking and subsequent measurements, 0.01 M phosphate buffer was used to measure exchangeable Cr(VI). All treatments were made in 25 mL of 0.01 M NaNO$_3$. The average pH and Eh were 11 and 238 mV, respectively.

APPENDIX B

SOIL SAMPLING AND CHARACTERIZATION OVERVIEW

The four soil profiles sampled from Maryland, USA were from delineations of four different mapping units: Askecksy, Glenelg, Russett-Christiana Complex, and Conestoga. The corresponding soil series most similar to the profiles were Atsion, Glenelg, Russett, and Flickinger, respectively (Soil Survey Staff, 2014). Samples from the Conestoga mapping unit were not similar to any known soil series, so they were designated 'Flickinger' after the name of the farmer using the land for crop production (Bourgault, 2008).

At each site a hole was dug so that at least the upper B horizon was exposed; the soils were then sampled from the major horizons in the profile. Approximately 15±5 L of soil was taken by carefully excavating soil material out of the horizon with a knife and onto the head of a shovel, which was then transferred to a 20 L plastic bucket. The sampling was conducted when soil matric water potentials were nearly -5 to -10 kPa (field capacity moisture). The soil was brought into the laboratory, passed through a 4-mm polyethylene sieve, mixed by hand, and stored in a dark, plastic bucket ($22 \pm 2°C$) lined with 1-mm thick plastic garbage bags. Moist paper towels were placed between the plastic garbage bags; this overall design was used to minimize soil drying, while sustaining the aerobic status of the soil (Brose, 2012).

The COPRs (6500 and MES) used in this study were collected from a site in Hudson County, NJ along the Hackensack River watershed. MES was named for its original use (method evaluation study) and 6500 for its contamination level (6500 mg Cr(VI)/kg). The COPRs were sampled by other researchers and sent to the head of our

soil chemistry laboratory, Dr. Bruce James, for research and teaching purposes. Both COPRs were sampled from Kearny, NJ at a site called Diamond Shamrock. It is thought that the COPRs were mixed with other fill material and deposited as surface materials prior to 1974, in order to reclaim marshlands for commercial and industrial uses (James et al., 1995). The region of the deposition may be described as abandoned industrial land; the location where the COPR was sited is now capped with asphalt. Although there isn't any available information on soil mapping unit designations for the exact location, nearby soils are from the delineation of the Transquaking mapping unit and are similar to the Transquaking series (euic, mesic Typic Sulfihemists) (Soil Survey Staff, 2014). This corresponds well with the groundwater depth, which is typically 2-3 m below the soil surface. Warehousing, transportation routes, and commercial activity are the primary land uses (James et al., 1995).

Soil properties were analyzed for each horizon sampled and for the COPRs received by our laboratory. The soils were analyzed for gravimetric water content by drying at 105º C for 24 h (Gardner, 1986), for salt pH (5 solution:soil in 0.01 M $CaCl_2$), and for Eh (lab) potentiometrically with platinum electrode (relative to standard hydrogen electrode (SHE)). Also performed was particle size analysis by pipette method to determine textural data for each horizon (Gee and Bauder, 1986), and LECO analysis for % C, N, and H (Nelson and Sommers, 1996). Dithionite extractable Fe and Mn were determined using a modified Na-citrate and $Na_2S_2O_4$ extraction method (Loeppert and Inskeep, 1996). Soil color was determined field-moist and designated by the Munsell color system. The following descriptions summarize the soil characterization for the four soils sampled and the two COPR-amended soils that were used in the current work.

Atsion Soil

A soil profile from a delineation of the Askecksy mapping unit was dug to 84 cm, allowing for sampling from the O/A, E, Bh, Bhs, and C horizons on June 8, 2011 (Fig. B-1). The profile was similar to the Atsion series (sandy, siliceous, mesic, Aeric Alaquod) (Brose, 2012). The soil horizon characterizations are given in Table B-1.

Figure B-1. Profile sampled from Atsion soil shown by Google Earth GPS image with Soil Survey overlay (38.214475, -75.522236) (above) and soil profile photograph (right).

Table B-1. Soil characterization data for the Atsion soil profile. CBD refers to the citrate-bicarbonate-dithionite extraction.

Characteristics	Soil Horizons				
	O/A (0-12 cm)	E (12-27 cm)	Bh (27-45 cm)	Bhs (27-45 cm)	C (45-84) cm
Texture (% sand, silt, clay)	N/A	Sand (94, 6, 0)	Sand (88, 10, 2)	Sand (89, 8, 3)	Sand (94, 4, 2)
Color	5YR 2.5/1	7.5YR 2/0	5YR 2.5/1	5YR 2.5/2	2.5Y 5/4
Water Content (g/kg)	170	44.0	304	220	59.0
Salt pH	2.39	2.55	3.55	3.81	4.15
Lab Eh (mV)	530	524	477	484	488
Organic Carbon (g/kg)	120 ± 8.0	20 ± 0.4	44 ± 2.1	29 ± 1.1	1.9 ± 0.02
CBD Fe (g/kg)	0.42 ± 0.02	0.14 ± 0.02	0.16 ± 0.004	0.15 ± 0.002	0.19 ± 0.004
CBD Mn (g/kg)	0.003 ± 0.0	0.001 ± 0.0	0.001 ± 0.0	0.001 ± 0.0	0.000 ± 0.0

Glenelg Soil

A soil profile from a delineation of the Glenelg mapping unit was dug to 99 cm, allowing for sampling from the Ap, A1, Bt1, Bt2, Bt3 and BC horizons on November 14, 2011 (Fig. B-2). The profile was similar to the Glenelg series (fine-loamy, mixed, semiactive, mesic Typic Hapludults). The soil horizon characterizations are given in Table B-2.

Figure B-2. Profile sampled from Glenelg soil shown by Google Earth GPS image with Soil Survey overlay (39.2618294, -76.9260483) (above) and soil profile photograph (right).

Table B-2. Soil characterization data for the Glenelg soil profile. CBD refers to the citrate-bicarbonate-dithionite extraction.

Characteristics	Soil Horizons					
	Ap (0-11 cm)	A1 (11-23 cm)	Bt1 (23-39 cm)	Bt2 (39-58 cm)	Bt3 (58-80 cm)	BC (80-99 cm)
Texture (% sand, silt, clay)	Loam (37, 50, 13)	Silt Loam (39, 54, 7)	Clay Loam (40, 28, 32)	Clay Loam (41, 25, 34)	Sandy Clay Loam (52, 22, 26)	Sandy Loam (61, 21, 18)
Color	10YR 5/4	10YR 3/3	7.5 YR 4/6	7.5 YR 4/6	10YR 5/6	10YR 5/8
Water Content (g/kg)	128	236	189	225	221	247
Salt pH	5.09	4.84	5.52	5.69	5.53	4.87
Lab Eh (mV)	435	444	426	422	423	444
Organic Carbon (g/kg)	7.0 ± 1.2	24.0 ± 0.2	4.6 ± 1.1	1.2 ± 0.6	0.9 ± 0.6	2.2 ± 1.4
CBD Fe (g/kg)	9.0 ± 0.7	9.0 ± 0.7	18 ± 0.3	27 ± 0.4	23 ± 0.6	26 ± 0.1
CBD Mn (g/kg)	0.12 ± 0.01	0.12 ± 0.005	0.036 ± 0.001	0.062 ± 0.003	0.10 ± 0.008	0.13 ± 0.03

Russett Soil

A soil profile from a delineation of the Russett-Christiana Complex mapping unit was dug to 66 cm, allowing for sampling from the Ap, AB, and Bt1 horizons on June 7, 2011 (Fig. B-3). The profile was similar to the Russett soil series (fine-loamy, mixed, semiactive, mesic Typic Hapludult). The soil horizon characterizations are given in Table B-3.

Figure B-3. Profile sampled from Russett soil shown by Google Earth GPS image with Soil Survey overlay (39.012697, -76.854069) (above) and soil profile photograph (right).

Table B-3. Soil characterization data for the Russett soil profile. CBD refers to the citrate-bicarbonate-dithionite extraction.

Characteristics	Soil Horizons		
	Ap **(0-14 cm)**	**AB** **(14-26 cm)**	**Bt1** **(>26 cm)**
Texture **(% sand, silt, clay)**	Sandy loam (58, 37, 5)	Sandy loam (53, 38, 9)	Loam (40, 42, 18)
Color	10YR 4/3	10YR 3/4	10YR 5/8
Water Content **(g/kg)**	82	86	132
Salt pH	5.09	4.84	5.52
Lab Eh **(mV)**	577	507	540
Organic Carbon **(g/kg)**	25 ± 0.1	6.3 ± 0.03	1.4 ± 0.07
CBD Fe **(g/kg)**	6.5 ± 0.1	7.3 ± 0.3	19 ± 0.3
CBD Mn **(g/kg)**	0.23 ± 0.01	0.24 ± 0.01	0.014 ± 0.001

Flickinger Soil

A soil profile from a delineation of the Conestoga mapping unit was dug to 115 cm, allowing for sampling from the Ap, A1, Bt1, and Bt2 horizons on November 14, 2011 (Fig. B-4). The profile wasn't similar to any known soil series, so it was designated as 'Flickinger'. Therefore the NRCS taxonomy for this particular soil series remains uncharacterized. The soil horizon characterizations are given in Table B-4.


Figure B-4. Profile sampled from Flickinger soil shown by Google Earth GPS image with Soil Survey overlay (39.54805, -77.17803) (above) and soil profile photograph (right).

Table B-4. Soil characterization data for the Flickinger soil profile. CBD refers to the citrate-bicarbonate-dithionite extraction.

Characteristics	Soil Horizons			
	Ap (0-27 cm)	A1 (27-43 cm)	Bt1 (43-87 cm)	Bt1 (87-115 cm)
Texture (% sand, silt, clay)	Loam (43, 47, 10)	Clay loam (31, 35, 34)	Clay (29, 29, 42)	Clay (29, 27, 44)
Color	10YR 3/3	7.5YR 3/4	5YR 2.5/2	10YR 2/1
Water Content (g/kg)	212	254	356	414
Salt pH	6.46	6.67	6.62	6.51
Lab Eh (mV)	397	391	397	406
Organic Carbon (g/kg)	30 ± 0.4	3.7 ± 0.1	2.9 ± 0.1	2.0 ± 0.1
CBD Fe (g/kg)	13 ± 0.7	22 ± 2	31 ± 1	29 ± 4
CBD Mn (g/kg)	1.6 ± 0.04	2.7 ± 0.1	8.8 ± 0.2	12 ± 0.6

COPR-Amended Soils

The anthropogenic COPR-amended soils were sampled separately, with MES on November 22, 1993 and 6500 on October 1, 1997. However, the location of the sampling took place at the same disposal site (Figure B-4). The soil horizon characterizations are given in Table B-5.
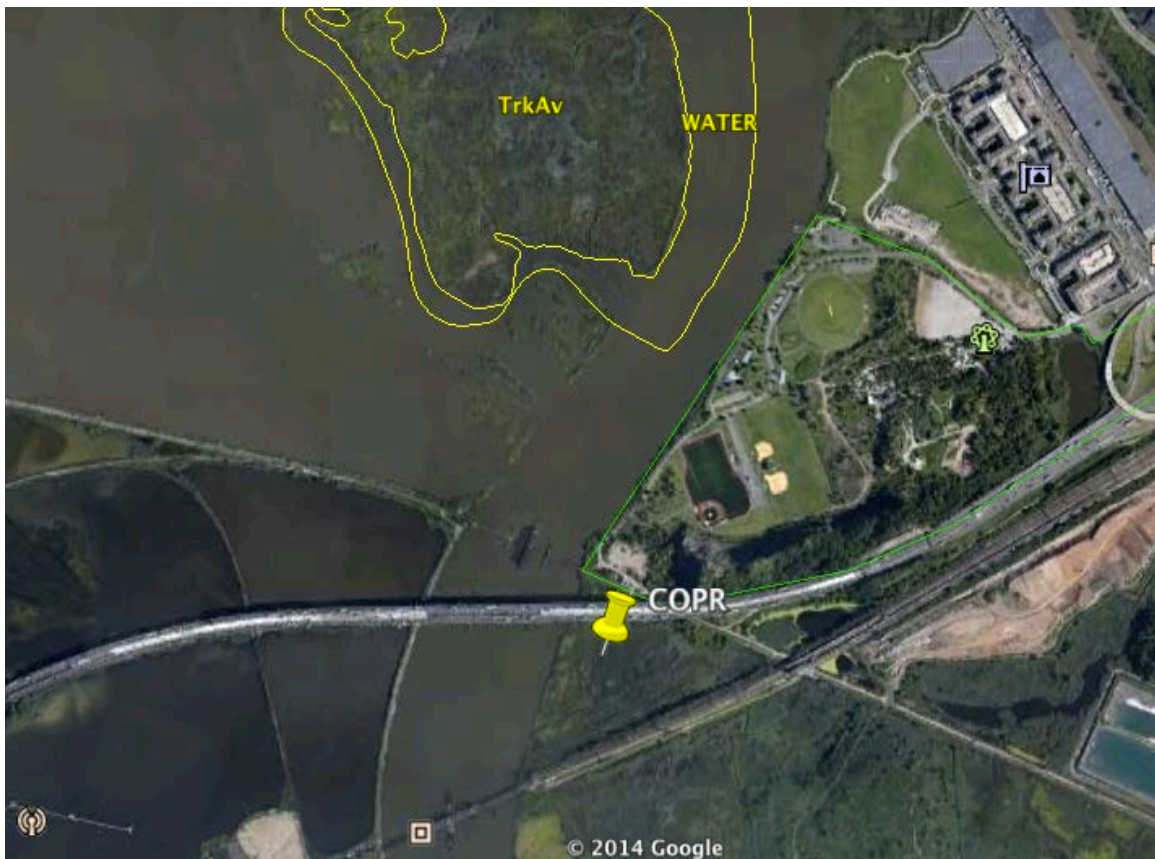
Figure B-5. Google Earth GPS image with Soil Survey overlay (40.751469, -74.098697) of COPR sample site (photograph of profile not available).

Table B-5. Soil characterization data for MES and 6500 COPR. CBD refers to the citrate-bicarbonate-dithionite extraction and N/A is not analyzed.

Characteristics	COPR Surface Material	
	MES	**6500**
Texture (% sand, silt, clay)	Sandy loam (67, 30, 3)	Sandy loam (61, 38, 1)
Color	10YR 5/3	7.5YR 2/2
Water Content (g/kg)	104	346
Salt pH	N/A	N/A
Lab Eh (mV)	N/A	N/A
Organic Carbon (g/kg)	18 ± 0.8	17 ± 0.07
CBD Fe (g/kg)	8.3 ± 0.8	16 ± 1
CBD Mn (g/kg)	0.15 ± 0.008	0.16 ± 0.006

Table C-1. Activity calculations for Table 1-1.

Soil Materials[a]	Soluble Species	Initial Concentration[b] (mol/L)	Activity[c]
Atsion Bhs and Russett Bt1	$HCrO_4^-$	0.001	0.001
	$H_2C_2O_4$	0.03	0.027
	Fe^{2+}	0.03	0.027
	Fe^{3+}	0.03	0.027
MES	$HCrO_4^-$	0.0012	0.001
	$H_2C_2O_4$	0.035	0.031
	Fe^{2+}	0.035	0.031
	Fe^{3+}	0.035	0.031
6500	$HCrO_4^-$	0.0062	0.006
	$H_2C_2O_4$	0.19	0.17
	Fe^{2+}	0.19	0.17
	Fe^{3+}	0.19	0.17

[a]The Maryland (Atsion and Russett), MES and 6500 soil materials had variable initial Cr(VI) concentrations, resulting in 3 different remedial schemes and their subsequent activities for each species (see chap. 3).
[b]Initial concentration of soluble species, added at the beginning of the remediation scheme in Chapter 3.
[c]Calculated by multiplying the activity coefficient by initial concentration. The activity coefficient was derived by the Debye-Hückel equation (Sparks, 2003) for 0.01 M $NaNO_3$, which was computed to be 0.89.

Table C-2 Data Set for Figure 2-2. Concentration in mg Cr(VI)/L and data in absorbance units for DPC (at 540 nm) and area under the IC curve [(μS/cm)xmin] for IC. (IC=Ion Chromatograph, DPC = Diphenylcarbazide).

Concentration	DPC			IC		
	Absorbance			Area		
0.01	0.008	0.008	0.008	-----	-----	-----
0.05	0.038	0.035	0.04	0.007	0.007	0.007
0.1	0.079	0.079	0.078	0.015	0.016	0.016
0.5	0.361	0.377	0.378	0.082	0.082	0.083
1	0.73	0.75	0.706	0.168	0.168	0.165
2	1.42	1.44	1.42	0.354	0.354	0.356

Table C-3 Data Set for Figure 2-5. Data in mg Cr(VI)/kg for method temperatures (No Heat=23°C, Heat=95°C) and analytical techniques (IC=Ion Chromatograph, DPC = Diphenylcarbazide). nd is <LOD. LODs are both 0.01 mg Cr(VI)/L for IC and DPC.

Soil	IC-Heat			IC-No Heat			DPC-Heat			DPC-No Heat		
Flickinger A1	103	104	104	110	105	107	107	109	105	110	111	110
Glenelg A1	nd	nd	nd	106	105	107	2.00	1.00	nd	104	105	104
Flickinger Bt1	94.0	106	106	108	107	108	108	111	107	107	107	110
Glenelg Bt1	53.0	59.0	68.0	109	109	109	101	103	103	108	118	115
Atsion Bhs	nd	nd	nd	106	106	107	6.00	3.00	1.00	99.0	104	101

Table C-4 Data Set for Figure 2-6. Data in mg Cr(VI)/kg for method temperatures (No Heat=23°C, Heat=95°C) and analytical techniques (IC=Ion Chromatograph, DPC = Diphenylcarbazide). nd is <LOD. LODs are both 0.01 mg Cr(VI)/L for IC and DPC.

Soil	IC-Heat			IC-No Heat			DPC-Heat			DPC-No Heat		
Flickinger A1	98.0	90.0	94.0	106	106	107	68.0	66.0	66.0	108	109	110
Glenelg A1	nd	nd	nd	106	107	105	1.00	3.00	1.00	101	104	102
Flickinger Bt1	94.0	87.0	91.0	106	108	104	82.0	84.0	82.0	108	107	107
Glenelg Bt1	43.0	40.0	38.0	108	110	108	63.0	59.0	57.0	122	115	110
Atsion Bhs	nd	nd	nd	107	107	108	2.00	6.00	8.00	101	94.0	89.0

Table C-5 Data Set for Figure 2-7. Data in mg Cr(VI)/kg in increasing carbon addition (g C/kg) for method temperatures (No Heat=23°C, Heat=95°C) and analytical techniques (IC=Ion Chromatograph, DPC = Diphenylcarbazide). NA means that the samples could not be analyzed due to flocculation in the DPC test tubes. nd is <LOD. LODs are both 0.01 mg Cr(VI)/L for IC and DPC.

Carbon Addition	Soil	IC-Heat			IC-No Heat			DPC-Heat			DPC-No Heat		
100	Flickinger A1	nd	nd	nd	104	104	104	NA	NA	NA	94.0	94.0	94.0
500	Flickinger A1	nd	nd	nd	104	104	103	NA	NA	NA	88.0	84.0	86.0
100	Glenelg A1	nd	nd	nd	105	105	106	NA	NA	NA	88.0	96.0	95.0
500	Glenelg A1	nd	nd	nd	103	104	104	NA	NA	NA	91.0	78.0	83.0
100	Flickinger Bt1	nd	nd	nd	105	106	105	NA	NA	NA	87.0	88.0	91.0
500	Flickinger Bt1	nd	nd	nd	105	104	105	NA	NA	NA	88.0	84.0	88.0
100	Glenelg Bt1	nd	nd	nd	106	106	104	NA	NA	NA	92.0	95.0	96.0
500	Glenelg Bt1	nd	nd	nd	103	104	104	NA	NA	NA	90.0	92.0	90.0
100	Atsion Bhs	nd	nd	nd	106	106	105	NA	NA	NA	75.0	78.0	77.0
500	Atsion Bhs	nd	nd	nd	103	104	104	NA	NA	NA	71.0	83.0	80.0

Table C-6 Data Set for Figure A-1. Data in mg Cr(VI)/kg in increasing carbon addition (g C/kg) for method temperatures (No Heat=23°C, Heat=95°C) and analytical techniques (IC=Ion Chromatograph, DPC = Diphenylcarbazide). nd is <LOD. LODs are both 0.01 mg Cr(VI)/L for IC and DPC.

Carbon Treatment	Soil	IC-Heat			IC-No Heat			DPC-Heat			DPC-No Heat		
0	MES	1360	1328	1360	1104	1104	1068	1279	1263	1290	1050	1072	1050
10	MES	1108	1072	1116	1048	1072	1088	1006	996.0	996.0	1011	1011	1039
100	MES	nd	nd	nd	700	708	688	5.00	5.00	10.0	555	589	567
500	MES	nd	nd	nd	484	476	492	nd	10.0	5.00	311	300	339
0	6500	6052	6276	6408	4044	4080	3944	5943	6002	6115	3646	3824	3757
10	6500	5828	5704	5904	3404	3388	3408	5611	5574	5799	3546	3463	3524
100	6500	2144	1960	1640	3368	3180	3232	2238	1815	1552	3452	3468	3463
500	6500	nd	nd	10.00	2808	2932	2908	85.0	69.0	91.0	3074	3079	2974

Table C-7 Data Set for Figure A-2. Data in mg Cr(VI)/kg in increasing carbon addition (g C/kg) for method temperatures (No Heat=23°C, Heat=95°C) and analytical techniques (IC=Ion Chromatograph, DPC = Diphenylcarbazide). nd is <LOD. LODs are both 0.01 mg Cr(VI)/L for IC and DPC.

Carbon Treatment	Soil	IC-Heat			IC-No Heat			DPC-Heat			DPC-No Heat		
0	MES	1388	1388	1424	1516	1616	1568	1333	1383	1410	1139	1167	1161
10	MES	1160	1196	1172	1468	1500	1540	1093	1104	1121	1061	1106	1134
100	MES	nd	nd	nd	1116	1084	1060	nd	nd	nd	728	672	683
500	MES	nd	nd	nd	836	832	828	nd	nd	nd	439	411	411
0	6500	6228	6404	6280	4228	4140	4284	6336	6553	10449	3813	3857	3863
10	6500	6028	5976	6060	4260	3956	4304	6336	6280	6358	3641	3440	3518
100	6500	2716	2832	1892	4160	4188	4132	2746	2796	2785	3374	3274	3457
500	6500	nd	nd	nd	3712	3864	3752	25.0	52.0	47.0	3007	3024	3163

Table C-8. Data Set for Figure 3-3. Calculated using free energy of formation data listed in Table 1-1 and from tabulated log K values, and (red) and (ox) activities for all soluble ions and molecules used in the remediation scheme in Chapter 3. The activities of solid phases=1 and for trace gases, 0.21 atm for O_2 and 0.00032 for CO_2. The slight differences in the activities for 6500 COPR did not notably affect the final log K or pe, thus the activities for the MD soils and MES COPR were used (see Table C-1 for activity calculations).

pH	$HCrO_4-$ $Cr(OH)_3$	O_2- H_2O	$Fe(OH)_3-$ Fe^{2+}	$Fe(OOH)-$ Fe^{2+}	CO_2- Oxalate	$MnOOH-$ Mn^{2+}
	Eh (mV)					
0.0	1096.0	1230.6	987.3	827.4	-597.1	1561.0
1.0	1017.2	1171.5	810.0	650.1	-656.2	1383.7
2.0	938.4	1112.4	632.7	472.8	-715.3	1206.4
3.0	859.6	1053.3	455.4	295.5	-774.4	1029.1
4.0	780.8	994.2	278.1	118.2	-833.5	851.8
5.0	702.0	935.1	100.8	-59.1	-892.6	674.5
6.0	623.2	876.0	-76.5	-236.4	-951.7	497.2
7.0	544.4	816.9	-253.8	-413.7	-1010.8	319.9
8.0	465.6	757.8	-431.1	-591.0	-1069.9	142.6
9.0	386.8	698.7	-608.4	-768.3	-1129.0	-34.7
10.0	308.0	639.6	-785.7	-945.6	-1188.1	-212.0
11.0	229.2	580.5	-963.0	-1122.9	-1247.2	-389.3
12.0	150.4	521.4	-1140.3	-1300.2	-1306.3	-566.6
13.0	71.6	462.3	-1317.6	-1477.5	-1365.4	-743.9
14.0	-7.2	403.2	-1494.9	-1654.8	-1424.5	-921.2

Table C-9 for Figure 3-4. Data for total Cr fractionation post-oxalic acid remediation is in mg Cr/kg. nd is <LOD. LODs are 0.01 mg Cr(VI)/L for soluble Cr(VI), exchangeable Cr(VI) and not exchangeable Cr(VI) as measured by the IC, and 0.05 mg Cr(VI)/L for soluble Cr(III), as measured by the FAAS.

Fraction of Cr	Soil	Oxalic Acid			Oxalic Acid, Fe(II)			Oxalic Acid, Fe(III)			Control		
Soluble Cr(III)	Atsion	929	929	898	991	991	991	1021	1022	960	62.4	42.6	62.4
	Russett	1022	991	1022	1115	991	991	929	960	929	nd	nd	nd
	No Soil	1224	1187	1298	556	445	426	371	337	363	nd	nd	nd
Soluble Cr(VI)	Atsion	nd	nd	nd	nd	nd	nd	nd	nd	nd	928	917	928
	Russett	nd	nd	nd	nd	nd	nd	nd	nd	nd	917	1007	951
	No Soil	nd	nd	nd	nd	nd	nd	nd	nd	nd	1126	1126	1126
Exchangeable Cr(VI)	Atsion	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Russett	nd	nd	nd	nd	nd	nd	nd	nd	nd	144	135	140
	No Soil	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Not Exchangeable Cr(VI)	Atsion	57.6	62.1	57.6	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Russett	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	No Soil	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table C-10 for Figure 3-5. Data for total Cr fractionation post-iron remediation is in mg Cr/kg. nd is <LOD. LODs are 0.01 mg Cr(VI)/L for soluble Cr(VI), exchangeable Cr(VI) and not exchangeable Cr(VI) as measured by the IC, and 0.05 mg Cr(VI)/L for soluble Cr(III), as measured by the FAAS.

Fraction of Cr	Soil	Fe(II)			Fe(III)			Fe(II), Fe(III)			Control		
	Atsion	7.8	6.8	6.8	712	712	712	898	929	898	62.4	42.6	62.4
	Russett	285	294	294	281	234	281	433	433	433	nd	nd	nd
Soluble Cr(III)	No Soil	323	319	323	nd	nd	nd	352	349	349	nd	nd	nd
	Atsion	nd	nd	nd	17.8	13.2	12.8	nd	nd	nd	928	917	928
	Russett	nd	nd	nd	155	200	178	nd	nd	nd	917	1007	951
Soluble Cr(VI)	No Soil	nd	nd	nd	244	382	600	nd	nd	nd	1126	1126	1126
	Atsion	nd	nd	nd	66	51.4	64.8	nd	nd	nd	nd	nd	nd
	Russett	nd	nd	nd	265	255	263	nd	nd	nd	144	135	140
Exchangeable Cr(VI)	No Soil	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Atsion	129	134	125	132	140	133	nd	nd	nd	nd	nd	nd
	Russett	nd	nd	nd	198	204	209	nd	nd	nd	nd	nd	nd
Not Exchangeable Cr(VI)	No Soil	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table C-11 for Figure 3-6. Data for total Cr fractionation post-compost remediation is in mg Cr/kg. nd is <LOD. LODs are 0.01 mg Cr(VI)/L for soluble Cr(VI), exchangeable Cr(VI) and not exchangeable Cr(VI) as measured by the IC, and 0.05 mg Cr(VI)/L for soluble Cr(III), as measured by the FAAS.

Fraction of Cr	Soil	Compost			Compost, Fe(II)			Compost, Fe(III)			Control		
	Atsion	36.7	70.3	47.9	5.3	5.0	5.0	929	867	960	62.4	42.6	62.4
	Russett	nd	nd	nd	108	108	105	805	774	743	nd	nd	nd
Soluble Cr(III)	No Soil	80.0	40.4	80.8	334	352	371	764	749	816	nd	nd	nd
	Atsion	861	828	850	nd	nd	nd	nd	nd	nd	928	917	928
	Russett	872	940	962	nd	nd	nd	nd	nd	nd	917	1007	951
Soluble Cr(VI)	No Soil	1179	1109	1069	nd	nd	nd	nd	nd	nd	1126	1126	1126
	Atsion	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Russett	nd	nd	nd	nd	nd	nd	nd	nd	nd	144	135	140
Exchangeable Cr(VI)	No Soil	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Atsion	nd	nd	nd	143	143	138	80.0	80.0	71.1	nd	nd	nd
	Russett	nd	nd	nd	93.5	89.0	89.0	66.6	71.1	75.5	nd	nd	nd
Not Exchangeable Cr(VI)	No Soil	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table C-12 for Figure 3-7. Data for total Cr fractionation post-oxalic acid remediation is in mg Cr/kg. nd is <LOD. LODs are 0.01 mg Cr(VI)/L for soluble Cr(VI), exchangeable Cr(VI) and not exchangeable Cr(VI) as measured by the IC, and 0.05 mg Cr(VI)/L for soluble Cr(III), as measured by the FAAS.

Fraction of Cr	Soil	Oxalic Acid			Oxalic Acid, Fe(II)			Oxalic Acid, Fe(III)			Control		
Soluble Cr(III)	MES	174	300	203.9	nd	nd	nd	178.0	77.5	48.5	nd	nd	nd
	6500	6265	6725	6243	7342	6193	6675	9679	9642	10161	419	211	162
	No Soil (MES)	1224	1298	1223	742	890	668	334	297	334	nd	nd	nd
	No Soil (6500)	968	1001	1005	304	297	300	271	290	278	nd	nd	nd
Soluble Cr(VI)	MES	828	738	760	nd	nd	nd	19.0	18.9	25.6	1119	1354	1354
	6500	1522	1063	1063	nd	nd	nd	nd	nd	nd	2251	2385	2508
	No Soil (MES)	nd	nd	nd	nd	nd	nd	nd	nd	nd	1126	1180	1000
	No Soil (6500)	nd	nd	nd	nd	nd	nd	nd	nd	nd	1126	1180	1000
Exchangeable Cr(VI)	MES	2434	246	230	nd	nd	nd	262	242	288	289	190	194
	6500	489	461	480	nd	nd	nd	nd	nd	nd	2303	2283	2393
	No Soil (MES)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	No Soil (6500)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Not Exchangeable Cr(VI)	MES	83.5	83.1	88.5	nd	nd	nd	275	255	279	62.0	67.7	77.6
	6500	1126	1222	1250	nd	nd	nd	4105	3536	3917	1650	1516	1601
	No Soil (MES)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	No Soil (6500)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table C-13 for Figure 3-8. Data for total Cr fractionation post-iron remediation is in mg Cr/kg. nd is <LOD. LODs are 0.01 mg Cr(VI)/L for soluble Cr(VI), exchangeable Cr(VI) and not exchangeable Cr(VI) as measured by the IC, and 0.05 mg Cr(VI)/L for soluble Cr(III), as measured by the FAAS.

Fraction of Cr	Soil	Fe(II)			Fe(III)			Fe(II), Fe(III)			Control		
Soluble Cr(III)	MES	nd	nd	nd	91.7	84.9	60.2	nd	nd	nd	nd	nd	nd
	6500	1.50	1.50	1.50	46.0	50.0	66.4	556	686	704	419	211	162
	No Soil (MES)	927	1001	890	nd	nd	nd	356	334	341	nd	nd	nd
	No Soil (6500)	297	304	278	nd	nd	nd	345	341	337	nd	nd	nd
Soluble Cr(VI)	MES	nd	nd	nd	168	175	162	nd	nd	nd	1119	1354	1354
	6500	nd	nd	nd	72.7	92.0	67.1	nd	nd	nd	2251	2385	2508
	No Soil (MES)	nd	nd	nd	165	347	278	nd	nd	nd	1126	1180	1000
	No Soil (6500)	nd	nd	nd	742	764	867	nd	nd	nd	1126	1180	1000
Exchangeable Cr(VI)	MES	nd	nd	nd	411	371	359	nd	nd	nd	289	190	194
	6500	nd	nd	nd	nd	nd	nd	nd	nd	nd	2303	2283	2393
	No Soil (MES)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	No Soil (6500)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Not Exchangeable Cr(VI)	MES	102	107	107	255	277	264	nd	nd	nd	62.0	67.7	77.6
	6500	nd	nd	nd	6283	5840	6723	nd	nd	nd	1650	1516	1601
	No Soil (MES)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	No Soil (6500)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table C-14 for Figure 3-9. Data for total Cr fractionation post-compost remediation is in mg Cr/kg. nd is <LOD. LODs are 0.01 mg Cr(VI)/L for soluble Cr(VI), exchangeable Cr(VI) and not exchangeable Cr(VI) as measured by the IC, and 0.05 mg Cr(VI)/L for soluble Cr(III), as measured by the FAAS.

Fraction of Cr	Soil	Compost			Compost, Fe(II)			Compost, Fe(III)			Control		
Soluble Cr(III)	MES	363	371	457	nd	nd	nd	89.3	77.0	93.8	nd	nd	nd
	6500	1587	1826	1514	1.10	1.50	1.10	63.2	62.9	65.8	419	211	162
	No Soil (MES)	nd	nd	nd	371	334	334	853	853	890	nd	nd	nd
	No Soil (6500)	113	154	247	55.6	51.9	48.2	853	831	827	nd	nd	nd
Soluble Cr(VI)	MES	749	704	693	nd	nd	nd	133	134	166	1119	1354	1354
	6500	2901	3181	3158	nd	nd	nd	nd	nd	nd	2251	2385	2508
	No Soil (MES)	1200	1200	1180	nd	nd	nd	nd	nd	nd	1126	1180	1000
	No Soil (6500)	1000	959	940	nd	nd	nd	nd	nd	nd	1126	1180	1000
Exchangeable Cr(VI)	MES	199	188	197	nd	nd	nd	327	310	365	289	190	194
	6500	1417	1455	1462	nd	nd	nd	nd	nd	nd	2303	2283	2393
	No Soil (MES)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	No Soil (6500)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Not Exchangeable Cr(VI)	MES	65.8	70.8	70.6	116	116	120	244	246	263	62.0	67.7	77.6
	6500	708	681	706	nd	nd	nd	4015	3755	3881	1650	1516	1601
	No Soil (MES)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	No Soil (6500)	nd	nd	nd	125	134	143	nd	nd	nd	nd	nd	nd

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