ABSTRACT

Title of dissertation: USE OF TARTARIC ACID AND ISOPROPYL ALCOHOL IN THE REDUCTION OF HEXAVALENT CHROMIUM AND APPLICATION TO CHROMIUM CONTAMINATED SOILS AND CHROMITE ORE PROCESSING RESIDUE

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Although chromium (Cr) is a naturally occurring metal, in the oxidation state +(VI), it is a health concern when present in soils and natural waters due to its solubility and toxicity. Tartaric acid and isopropyl alcohol were evaluated for reduction of Cr(VI) at environmentally relevant pH values, in the presence of soils, and from chromite ore processing residue (COPR). Soil samples were taken from profiles located in delineations of five soil mapping units in Maryland, USA: Christiana-Russett Complex, Askecksy, Annapolis, Jackland, and Ingleside. In solution, the rate of reduction of Cr(VI) by the tartaric acid-Cr-isopropyl alcohol complex was lowered from 0.128 to 0.011 h^{-1} as pH was raised from 3.0 to 5.0; however, in the presence of the Russett and Jackland soils, the rates of reduction were 0.037 and 0.020 h^{-1}, respectively despite pH values of 5.3 and 5.0. In addition to Cr(VI) reduction, 97.6 and 89.9 µM Mn(II), and 427 and 67.6 µM Fe(II) were solubilized from the Russett and Jackland soils, respectively. Adding soluble Mn^{2+} and Fe^{3+} to the five soils with tartaric acid and isopropyl alcohol enhanced reduction of Cr(VI) in all soils, with the addition of Mn^{2+} enhancing reduction by an additional 0.27 mM Cr(VI) in the Jackland soil and to 1.46 mM in the Downer soil. Furthermore, the addition of tartaric acid and isopropyl alcohol to Mn-oxide coated sand ($1.8x10^{-1}$ µmol Mn/mg) showed reductive dissolution of Mn(III,/IV)(hydr)oxides, and the resulting Mn(II) enhanced reduction to 1.24 mM (62%) of Cr(VI). When applied to COPR, tartaric acid-Cr-isopropyl alcohol or tartaric acid-Cr-Mn complexes reduced 0.3 mM (30%) Cr(VI), although when COPR was mixed with the Atsion, Collington, or Russett soils, pH values remained below 5.0 and 0.84 mM (84%) of the Cr(VI) was reduced. This work showed that a tartaric acid and isopropyl alcohol solution reductively dissolves Mn(III,/IV)(hydr)oxides from soils, and the resulting Mn(II) enhances reduction of Cr(VI), which can be potentially applied to the reduction of COPR-derived Cr(VI) in a soil remediation strategy.

USE OF TARTARIC ACID AND ISOPROPYL ALCOHOL IN THE REDUCTION OF HEXAVALENT CHROMIUM AND APPLICATION TO CHROMIUM CONTAMINATED SOILS AND CHROMITE ORE PROCESSING RESIDUE

By

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CHAPTER 1

USE OF TARTARIC ACID AND ISOPROPYL ALCOHOL IN THE REDUCTION OF HEXAVALENT CHROMIUM AND APPLICATION TO CHROMIUM CONTAMINATED SOILS AND CHROMITE ORE PROCESSING RESIDUE: LITERATURE REVIEW

Challenges to the Remediation of Hexavalent Chromium

Chromium is a naturally occurring, transition metal found in the environment mostly in the trivalent state, such as the chromium ore ferrochromite ($FeO \bullet Cr_2O_3$). For commercial use, ferrochromite ore is mined and roasted at high temperatures under alkaline conditions by addition of sodium carbonate (soda ash); thereby oxidizing insoluble Cr(III) to soluble Cr(VI) which is then leached from the roast to be used in a wide array of industrial and consumer products (Darrie, 2001). Chromite ore processing residue (COPR), the remaining solid waste product from this process, contains variable amounts of unreacted ore and soluble and insoluble forms of Cr(VI), and is a persistent source of Cr(VI) contamination in notable locations such as Baltimore, Maryland; Hudson County, New Jersey; and Glasgow, Scotland (Burke et al., 1991; Darrie, 2001; Deakin et al., 2001). COPR has also been used as fill material for construction purposes because of its resemblance to a sandy soil, such as in the Dundalk Marine Terminal in Baltimore, MD (CH2M Hill, 2011); however, residual Cr(VI) can persist as a potential pollutant of soils, air, and groundwater from this soil-like material. For example, in Hudson County, New Jersey, it was used to fill wetlands and poorly-drained landscapes for use in industrial activity and development during the twentieth century (James, 1996).

Current remediation practices for COPR use either an Fe- or S-based reducing agent, with the former resulting in concretions or clogging of pores with oxidized Fe(III) minerals formed as Cr(VI) is reduced to Cr(III); the use of S results in delayed ettringite ($Ca_6Al_2(SO_4)_3 \bullet 32H_2O$) formation, which results in extensive swelling and buckling of paved surfaces when used as fill material for roads (Dermatas et al., 2006; Ludwig et al., 2008). In contrast to these reducing agents, this research will investigate the potential use of tartaric acid in an alcohol-water solution as an effective alternative to Fe- or S-based reducing agents in the reduction of COPR derived Cr(VI). Remediation-by-reduction is a soil clean-up strategy that can be used in an attempt to mitigate the toxic effects of Cr(VI) and to clean up Cr contaminated sites to meet regulatory standards and protect human health (James, 1996).

Health Concerns and Regulatory Context of Hexavalent Chromium

Concerns regarding the presence of Cr in the environment focus on the potential adverse health effects of Cr(VI)-contaminated soils, groundwater, and drinking water supplies. Regulation of Cr is currently based, not on the oxidation state of Cr, but on total chromium concentration [i.e., the sum of Cr(III) and Cr(VI)]. The U.S. Environmental Protection Agency's national standard for total Cr in drinking water is 100 µg/L (100 ppb), except in California, whose current drinking water standard is 50 µg/L (CDPH, 2009; USEPA, 2010). In 1999, California set a Public Health Goal of 2.5 µg/L, which was based on a 1968 study in Germany that found stomach tumors in animals that repeatedly ingested Cr(VI). The EPA rejected that study as flawed and determined there was no evidence it was carcinogenic in water, which resulted in the state rescinding its goal in 2001 and reverting back to the 50 µg/L standard (CDPH, 2009). The point of contention regarding the 1968 study was on whether Cr(VI) is reduced to Cr(III) in the stomach by gastric acids at pH 1-2.

Chromium(VI) is genotoxic in a number of *in vitro* and *in vivo* toxicity assays (IARC, 1990). Because the mechanisms of genotoxicity and carcinogenicity are not fully understood, the National Toxicology Program (NTP) conducted animal tests to assess the potential for cancer due to ingestion of Cr(VI) (Stout et al., 2009). Reduction of Cr(VI) to Cr(III) is hypothesized to occur primarily in the stomach, as a mechanism of detoxification. In this 2-year NTP study, observed increases in abnormal growths in the small intestine of mice, toxicity to red and white blood cells and bone marrow, and uptake of Cr(VI) into tissues suggested that at least a portion of the administered Cr(VI) was not reduced in the stomach (Stout et al., 2009).

This finding, in addition to the absence of increases in abnormal growths in the small intestine in rats or mice exposed to chromium picolinate monohydrate (CPM), an organically bound form of Cr(III) (NTP, 2008), provides evidence that Cr(VI) is not completely reduced in the stomach and is responsible for these carcinogenic effects. Additionally, it should be noted that Cr(III), like that found in CPM, is essential for human health in trace amounts as an activator of insulin (ATSDR, 2000), but exists predominantly in nature in cationic forms that are only sparingly-soluble in near-neutral pH soils, plants, cells, and natural waters (Kimbrough et al., 1999).

There is currently no national, regulated standard for Cr in soils. Regulated standards for Cr(VI) and Cr(III) are determined and enforced at the state level. Due to extensive soil contamination from COPR disposal on and in soils of Hudson County, NJ, the New Jersey Department of Environmental Protection (NJDEP) has set the allowable

Cr(VI) level in soils at 20 mg/kg based on a risk assessment analysis reviewed by a NJDEP-established Chromium Workgroup (NJDEP, 2010). This is the lowest standard set by any state. In order to successfully apply a remediation strategy that could meet a standard of 20 mg Cr(VI)/kg soil, a thorough understanding of the dissolution, solubility, reduction, and potential oxidation of Cr from Cr-containing minerals in COPR and COPR-contaminated soils is essential.

Chromite Ore Processing Residue (COPR)

In oxidizing insoluble Cr(III) and extracting Cr(VI) from chromite ore ($FeO \bullet Cr_2O_3$) in a high-temperature lime roasting process, chromite ore processing residue (COPR) is produced. This process separates metal impurities, such as Fe, Mg, and Al from Cr and isolates Cr as soluble sodium chromate (Na_2CrO_4) (Lioy et al., 1992). Added lime (CaO) forms Cr(III) and Cr(VI) minerals with a highly alkaline pH approximately 11-12, and total Cr levels up to 46,000 mg/kg (Lioy et al., 1992).

Although each sample of COPR varies in mineralogical and chemical properties from location to location and depending on how much CaO was added, some commonalities of mineralogical properties important to understanding the chemical behavior of COPR during reduction processes have been investigated (Chrysochoou et al., 2010; Hillier et al., 2003; Tinjum et al., 2008). The most abundant metals other than Cr found in COPR samples are Ca, Mg, Fe, and Al (Chrysochoou et al., 2010). Additionally, Hillier et al. (2003) rationalized that there are three main categories of mineral compositions in COPR samples. The first is chromite, a relic of the chromite ore. The second category consists of minerals formed at the high temperatures during the roasting process, such as brownmillerite and periclase, and the third category of minerals includes ones that are presumed to have formed after COPR has been deposited and exposed to more natural conditions, such as the leaching of elements with the influx of water and uptake of CO_2. Although there are many different minerals that can be assigned to these three categories, there are four common minerals in COPR that have been found to incorporate Cr(VI) by substitution for Fe or Al in their structures: brownmillerite ($Ca_2(Fe,Al)_2O_5$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$), hydrocalumite ($Ca_2(Al,Fe)(OH)_6(OH)\cdot 3H_2O$), and hydrogarnet ($Ca_3(Al,Fe)_2(H_4O_4)_3$) (Chrysochoou et al., 2010; Hillier et al., 2003). Additionally, up to 30% of the mineralogical makeup of COPR can be paracrystalline in structure (Hillier et al., 2003).

Column studies assessing the reduction of COPR with the influx of $FeSO_4$-H_2SO_4 or polysulfides (CaS_x) demonstrated that the hydraulic conductivity of the COPR decreased following reduction treatment due to formation of precipitates in the pores (Tinjum et al., 2008). One of the main issues with COPR reduction is ensuring that the reductant is able to reach Cr(VI) entrained in Cr(VI)-bearing minerals. The addition of SO_4^{2-} with the reductant, such as $FeSO_4$ enhances the amount of Cr(VI) reduced through anion exchange; SO_4^{2-} is able to displace CrO_4^{2-} in Cr(VI)-bearing minerals (Geelhoed et al., 2003). Once displaced and leached from COPR, soluble Cr(VI) can be reduced and once reduced, Cr(III) will precipitate, but also possibly oxidized back to Cr(VI) if sufficient levels of Mn(III,IV)(hydr)oxides are present (Bartlett and James, 1979).

Hexavalent Chromium

Remediation-by-reduction strategies in soils aim to reduce Cr(VI) to Cr(III),which can be done either *in situ* with the soil or *ex situ* (James, 1996). This dissertation will focus on the reduction of Cr(VI) by tartaric acid, which is a four-carbon, α-hydroxy organic acid with two hydroxyl and two carboxylic acid groups: (COOH(CHOH)$_2$COOH). The oxidation of tartaric acid by Cr(VI) can be negligible if pH is above 5.0; however, an isopropyl alcohol-water solution will enhance oxidation due to an interaction between Cr(VI), the organic acid, and the alcohol, resulting in reduction of Cr(VI) to Cr(III) and co-oxidation of the alcohol to acetone.

Westheimer and Novick (1943) first presented the mechanism for the oxidation of isopropyl alcohol by chromic acid. Several important concepts needed for understanding aqueous Cr(VI) solutions and its oxidation of isopropyl alcohol were put forth in this early paper. First, Westheimer and Novick demonstrated that $HCrO_4^-$ is more important in oxidation reactions than $Cr_2O_7^{2-}$ (Westheimer and Novick, 1943). Equation 1 illustrates the equilibrium between $Cr_2O_7^{2-}$ and $HCrO_4^-$; however at high Cr concentrations and/or low pH values, $Cr_2O_7^{2-}$ increases in importance.

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \leftrightarrow CrO_4^- + 2H^+ \qquad (1)$$

These authors also showed that as concentrations of $HCrO_4^-$ were lowered, the rate constants increased, and that kinetically the rate of isopropyl alcohol oxidation was pseudo-first order with respect to Cr(VI). The rate constant also increased as the concentration of isopropyl alcohol increased. An investigation of interferences in the reaction showed that Fe^{3+} and Al^{3+} did not affect the oxidation of the alcohol; however, Mn^{2+} added as $MnCl_2$ lowered the rate of oxidation by half (Westheimer and Novick, 1943). In a solution of Cr(VI) and Mn^{2+}, but no isopropyl alcohol, no oxidation of Mn^{2+} was observed, and so the authors hypothesized that an intermediate Cr(VI)-isopropyl alcohol compound formed and enhanced the reactivity with Mn^{2+}.

Further work by Westheimer and colleagues supported monoisopropyl chromate as the intermediate species, and proposed that tetravalent chromium Cr(IV) was the intermediate Cr species produced following the 2-electron transfer from isopropyl alcohol to Cr(VI) in the oxidation of isopropyl alcohol to acetone (Holloway et al., 1951; Watanabe and Westheimer, 1949). The authors proposed a monoisopropyl chromate ester as the activated complex (Figure 1-1). The formation of the ester is necessary for the electron transfer to occur, but it was determined that it is the decomposition or cleavage of the ester bond that is the rate-limiting step in determining the overall rate of oxidation. Kwart and Francis (1959) working with secondary alcohols further demonstrated that the ester decomposition step was the rate limiting step in the reaction.

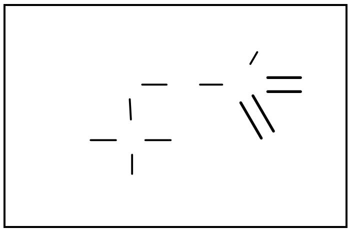


Figure 1-1
Monoisopropyl-Cr(VI) ester

From these studies, the two electron transfer from isopropyl alcohol to Cr(VI) to form acetone and Cr(IV) via a monoisopropyl chromate ester is summarized in equations 2 and 3.

$$CH_3CHOHCH_3 + H_2CrO_4^- \rightarrow (CH_3)_2CH\mathbf{O}CrO_3H + H_2O \qquad (2)$$

$$(CH_3)_2CH\mathbf{O}CrO_3H + OH^- \rightarrow (CH_3)_2CO + HCrO_3^- + H_2O \qquad (3)$$

The overall oxidation-reduction reaction for Cr(VI) being reduced to Cr(III) is illustrated in equation 4.

$$1.5CH_3CHOH\ CH_3 + HCrO_4^- + 2H^+ \rightarrow 1.5CH_3COCH_3 + Cr(OH)_3 + H_2O \qquad (4)$$

Rahman and Rocek (1971) used acrylamide as a free-radical scavenger to provide insight into the reactions that occur in equations 2 and 3 by presenting the following mechanistic scheme:

Cr(VI) + isopropyl alcohol → Cr(IV) + acetone (5)

Cr(IV) + isopropyl alcohol → Cr(III) + ketyl free-radical (6)

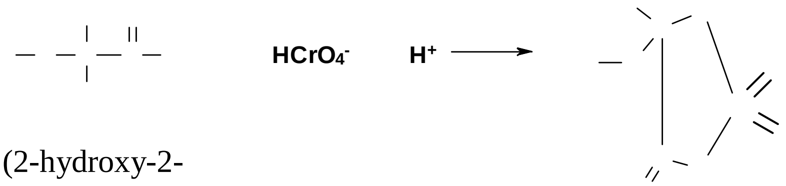
Cr(VI) + ketyl free-radical → Cr(V) + acetone (7)

Cr(V) + isopropyl alcohol → Cr(III) + acetone (8)

These authors suggested that the full reduction from Cr(VI) to Cr(III) requires both transitional oxidation states Cr(V) and Cr(IV) as well as the production of a ketyl free-radical.

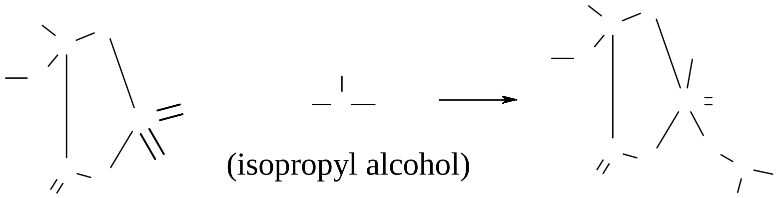
Further work done by Hasan and Rocek (1972) showed an increase in the oxidation rate with 1×10^{-4} to 1.0 M isopropyl alcohol, 4.2×10^{-4} to 4.2×10^{-2} M H_2CrO_4, 1.9×10^{-5} to 0.2 M oxalic acid, and in up to 0.5 M perchloric acid. The rates ranged from 1.7×10^{-4} to 4.8×10^{-2} (sec^{-1}), and the reaction (total average reaction time was under 20 mins) increased with increasing oxalic acid concentrations until the reaction became zero order in oxalic acid. The authors proposed that Cr(VI), isopropyl alcohol, and oxalic acid formed an intermediate complex that allowed for a three-electron transfer resulting in the reduction of Cr(VI) to Cr(III) (Hasan and Rocek, 1972). In addition to being the first work completed with these unique constituents, this is also the first time a three-electron oxidation step involving Cr(VI) had been proposed.

The mechanistic scheme for the intermediate complex was further described by Mahapatro et al. (1980) using 2-hydroxy-2-methylbutyric acid and isopropyl alcohol. The proposed reaction is illustrated in equations 9 - 13:



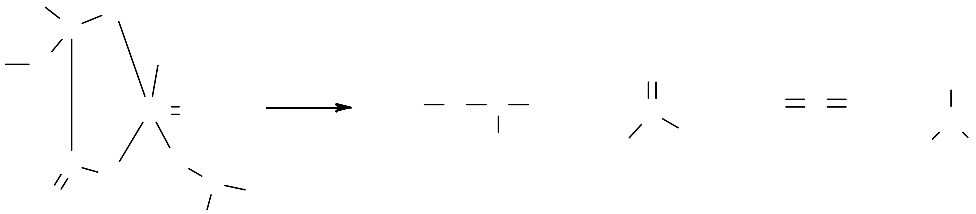
(2-hydroxy-2-
methylbutyric acid)

(9)



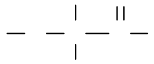
(isopropyl alcohol)

(10)



(11)

$$CH_3CH_2C{\bullet}OHCH_3 + Cr(VI) \rightarrow CH_3CH_2COHCH_3 + Cr(V) \qquad (12)$$



$$+ Cr(V) \rightarrow CH_3CH_2COHCH_3 + CO_2 + Cr(III) \qquad (13)$$

(2-hydroxy-2-
methylbutyric acid

Equation 9 shows the first step of the mechanism, which is the formation of a bimolecular cyclic complex between Cr(VI) and the 2-hydroxy-2-methylbutyric acid. In equation 10, this complex reacts with isopropyl alcohol to form a termolecular complex. Equation 11 shows the oxidative decomposition of this complex to yield acetone, carbon dioxide, trivalent chromium, and the free radical formed from the partial oxidation of 2-hydroxy-2-methylbutyric acid. This α-hydroxy free radical reacts with a molecule of Cr(VI) in equation 12 to form Cr(V), which can react with 2-hydroxy-2-methylbutyric acid in equation 13 to yield carbon dioxide and trivalent chromium (Hasan and Rocek, 1973a; Mahapatro et al., 1980). At concentrations of 2-hydroxy-2-methylbutyric acid at 0.1 M, Cr(VI) at $5x10^{-4}$M, and isopropyl alcohol at 0.05 M, these authors showed the reaction rate varied as a function of acidity, ranging from 0.30 sec^{-1} at $5x10^{-3}$ M perchloric acid to 62 sec^{-1} at 1.9 M perchloric acid.

Other work by Hasan and Rocek (1973b) demonstrated that in addition to 2-hydroxy-2-methylbutyric acid, this reaction occurs with other α-hydroxy carboxylic acids, such as maleic, malic, tartaric, and citric acid. Kabir-ud-Din et al. (2002) showed the reduction of Cr(VI) by tartaric acid in the three-electron transfer pathway, with the intermediate production of Cr(V) and free radicals. As earlier studies have shown, the ephemeral Cr(V) species is important as an intermediate Cr species involved in the oxidation of tartaric acid and of isopropyl alcohol. Sun et al. (2009) demonstrated the reduction of Cr(VI) in the presence of Fe(III) with tartaric, citric, malic, and n-butyric acids. The authors showed that the extent of reaction increased as the number of hydroxyl groups increased, due to the electron withdrawing nature of the hydroxyl group increasing the tendency of the carboxyl group to leave the molecule in a reductive decarboxylation step (Houghton, 1979).

Chromium Redox in Soils

Soils are a key medium for terrestrial ecosystems, and provide nutrients, water, and physical space for plants and animals to reside. Microorganisms and macrofauna that reside in the rhizosphere, or root zone of soils, are diverse and interact with their environment in dynamic processes that alter that environment both physically and chemically. The organic and inorganic solid phases of the soil matrix are also chemically dynamic, and can consist of redox active species, such as Fe(II)/Fe(III)- and Mn(II, III, IV)(hydr)(oxides), sulfur compounds, nitrogen compounds, soil organic matter, and organic acids. The interaction of these chemical species with microorganisms, as well as with each other, often with fluctuations in dissolved O_2 concentrations due to the rise and fall of water tables, can make soil redox processes and Cr redox cycling in soils dynamic and challenging to study.

Solubility Hexavalent Cr forms tetrahedral, oxo(compounds) in aqueous solution, whereas Cr(III) forms many stable, amphoteric compounds of which many are octahedral, kinetically inert complexes (Niki, 1985). Chromium(III), when not complexed by an organic chelating (or complexing) agent, will form $Cr(OH)_3$ and precipitate out of solution at approximately pH 5.5 and higher. Equation 14 shows the formation of the Cr(III) hydroxide with Ksp = 10^{-12} (mol/L) at pH 7 given (James and Brose, *In press*):

$$Cr(OH)_{3(S)} \leftrightarrow Cr^{3+} + 3OH^- \tag{14}$$

The low Ksp value indicates that the hydroxide will be stable thermodynamically and precipitate out of solution. In the presence of excess hydroxide ions, the formation of the hydroxo-chromite ion $Cr(OH)_4^-$ is possible, and is represented by equation 15.

$$Cr(OH)_4^- \leftrightarrow Cr(OH)_3 + OH^- \tag{15}$$

Other precipitated forms for Cr(III) include chromium arsenate ($CrAsO_4$) and chromite ($FeO·Cr_2O_3$) with Ksp values (pH 7) of 10^{-10} and 10^{-20} mol/L, respectively (James and Brose, *In press*). Also contributing to solubility is the ability of Cr(III) to form both organic and inorganic complexes (Cotton and Wilkinson, 1980; James and Bartlett, 1983a; Mandiwana et al., 2007; Puzon et al., 2008). If complexed with organic acids such as fulvic or citric acid, Cr(III) will remain soluble at pH values up to 6.7 depending in part on the pKa of the organic acid and the COOH-Cr(III) ratio (James and Bartlett, 1983b). The complexation of Cr(III) with organic ligands allows for organic-Cr(III) complexes to remain soluble and resistant to biodegradation in soils and natural waters, because complexed Cr inhibits the ligand serving as a carbon and energy source for microbial growth (Puzon et al., 2008).

Relative to Cr(III) cationic compounds, Cr(VI) anionic compounds are more soluble over the pH range of natural environments, i.e. 4.0 to 8.0, leading to a greater concern about the potential mobility of Cr(VI) in soils and natural waters; however, chromium (VI) salts, such as $PbCrO_4$ and $BaCrO_4$ with Ksp values (pH 7) of 1.8×10^{-6} and 1.7×10^{-3} mol/L, respectively, are only sparingly-soluble (James and Brose, *In press*).

Iron oxides are one of the most common minerals found in soils, with goethite (α-FeOOH) existing in almost every soil in all climate regimes, with greater concentrations occurring in wetter and cooler climates (Essington, 2004). Other Fe(III)(hydr)oxides relevant to the current research are hematite (α-Fe_2O_3) and ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$).

Mn(hydr)oxides in +III or +IV oxidation states are generally microcrystalline, poorly-ordered (non-stoichiometric), and often occur as coatings on ped faces and pore surfaces as concretions or nodules (Essington, 2004). Because of the paracrystalline nature of naturally-occurring Mn(III,IV)(hydr)oxides, they are challenging to characterize, especially in soils. Birnessite is one of the most common soil Mn minerals and has a mixed +III/IV oxidation state and layered structure that commonly forms surface coatings on clay and other mineral surfaces (Oze et al., 2007; Sparks, 2003).

Sorption In colloidal environments, such as soils and sediments with clays and metal (hydr)oxides, sorption processes (cation exchange, precipitation, and surface-induced hydrolysis) can immobilize cationic metals. Generally, the most important parameters affecting sorption of metals in soils are other metal hydroxides, clay, organic matter, oxidation state, concentration, solid-to-solution ratio, contact time, and most importantly soil pH (Bradl, 2004). There are two main interactions between solute and solid phases relevant to the current research that can be used to understand metal sorption in soils. The first are inner-sphere surface complexes between the metal and surface site, and second are electrostatic interactions, which consist of outer-sphere complexes where the metal is at a distance from the surface site. The number of surface sites available imparts cation exchange capacity (CEC) to the soil; the amount of negative charge of a soil determines CEC and comprises of a constant charge component and a variable charge (Sparks, 2003). The constant charge is due to isomorphic substitution in secondary minerals, such as phyllosilicate clay minerals that result in a permanent negative charge. Variable charge is attributed to the deprotonation and protonation of functional groups on hydroxide groups on exposed edges of octahedral sheets of clays, metal (hydr)oxides, silicates coated with metal oxides, and soil organic matter (Sparks, 2003).

Although CrO_4^{2-} and $HCrO_4^-$ can adsorb to positively-charged surfaces similarly to SO_4^{2-}, the net negative charge of soils relevant to the current research will make sorption of cations, such as Cr^{3+} more likely; however, under low pH conditions, some surfaces sites can be protonated and allow for electrostatic adsorption of $HCrO_4^-$. This sorption may be reversible and will allow anions to again be solubilized, or via chemisorption, sorbed $HCrO_4^-$ can potentially be incorporated into the structure of a mineral surface (James and Bartlett, 1983c). Kantar et al. (2008) demonstrated the "ligand-like" behavior of Cr(VI) in a soil column study, with maximum sorption of Cr(VI) at acidic pH values and decreasing rapidly with an increase in pH.

Cr(III) was shown to be rapidly adsorbed by Fe(III) and Mn(III,IV)(hydr)oxides and clay minerals, with adsorption increasing with increasing pH (Bradl, 2004). Adsorption of Cr(III) decreased in the presence of competing anions for sorption sites. Han et al. (2004) demonstrated the importance of contact time in that Cr(III) in undisturbed and unpolluted soils was strongly bound to solid mineral phases, whereas Cr(III) in newly contaminated soils was less strongly bound and was more associated with soil organic matter making this form of Cr(III) potentially more labile.

Oxidation Soluble Cr(III) salts and freshly-precipitated hydroxides oxidize rapidly to Cr(VI) in the presence of Mn(III,IV)(hydr)oxides in moist soils (Bartlett and James, 1979). Mn(III,IV)(hydr)oxides, such as birnessite and todorokite have a low point of zero charge (PZC) in the range of pH 1-2, resulting in their being negatively charged in near-neutral, natural environments, and capable of attracting cations such as Cr^{3+} and $CrOH^{2+}$ (Kim et al., 2002). Cr(III) oxidation followed a first-order reaction dependent on Cr(III) concentration with four Mn(III,IV)(hydr)oxides: todorokite, birnessite, lithiophorite, and pyrolusite, with more Cr(III) being oxidized at pH 4 than pH 7 (Kim et al., 2002).

The enhanced oxidation at lower pH values may be attributed to the proton consuming nature of Mn(III,IV) reduction and also the decreased solubility of Cr(III)(hydr)oxides at higher pH values. Additionally, the electron transfer between Mn(III,IV) surfaces and Cr(III) species was shown to occur rapidly at pH 3, but was inhibited at higher pH values, possibly due to a change in the charge on the mineral surface induced by initial Cr(III) concentrations (Fendorf and Zasoski, 1992). Higher initial Cr(III) concentrations resulting in the surface becoming less negatively charged, resulted in the Mn(III/IV)(hydr)oxide being less able to adsorb Cr(III) in solution. Alternately, Negra et al. (2005) demonstrated that the strongest oxidizing forms of Mn had the greatest Mn(IV)/Mn(III) ratio, and that more Cr(III) oxidation was associated with higher soil pH due to a greater proportion of Mn being in the +IV oxidation state.

Reduction In aerobic soils, Fe is predominantly immobile and found in the oxidation state Fe(III) (Lemanceau et al., 2009). In a reducing environment, such as a flooded soil, Fe(III) can be reduced to Fe(II) and migrate with moving water. The reduction of Fe(III) to Fe(II) has a standard potential of +0.771 V and is illustrated in equation 16 (Heusler and Lorenz, 1985).

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \qquad (16)$$

The addition of a reducing agent to a soil with Fe(III) and Cr(VI) may result in the reduction of Fe(III) to Fe(II), and in Fe(II) reducing Cr(VI) (Yang et al., 2008). Citric acid was shown to effectively reduce Cr(VI) in the presence of “red soil”, and also in the presence of Fe(III), which yielded a catalytic effect by being reduced to Fe(II) which then reduced Cr(VI). It was also shown that the extent of reduction decreased as the pH was raised from 3.3 to 5.1 (Yang et al., 2008).

Hug et al. (1997) demonstrated the complexity involved in the reduction of Cr(VI) in natural environments having oxalate and Fe(III). A mechanistic kinetic model was presented to explain both dark and photochemical reactions with oxalate where superoxide ($O_2^{\bullet -}$), hydroperoxyl radical (HO_2), and Fe(II) were formed, which were likely reductants for intermediate Cr(V) and Cr(IV) species. Following reduction, the main product formed was a soluble Cr(III)-oxalate compound (Hug et al., 1997). Kantar et al. (2008) also demonstrated the enhanced reduction of Cr(VI) by Fe(II) in adding the organic acids galacturonic and glucuronic acids to systems with or without soil. The reduction of Cr(VI) with these organic acids resulted in a delay in the breakthrough of Cr in column studies, due to sorption of the newly formed Cr(III) to the soil.

In addition to Fe(II) as a reducing agent in soils, soil organic matter can also contribute significantly to redox pathways. Generally, soil organic matter can be considered to consist of humin, humic acids, and fulvic acids (Sparks, 2003). Soil humin is regarded as the (paracrystalline) organic material that is neither soluble in acid nor base. Soil humin has several distinct qualities, such as aromatic rings with carboxyl, hydroxyl, carbonyl, and alkyl groups; significant amounts of C-1 to C-20 alkyl chains; aromatic rings and alkyl groups with C-to-C bonds; and simple and polymeric proteinaceous and carbohydrate groups associated along a randomly ordered backbone (Baldock and Broos, 2012).

Humic and fulvic acids have many of the functional groups that contribute to many of the chemical characteristics of a soil; these include carboxyl, phenolic, quinone, alcoholic, ketone, amine, and amide groups (Sparks, 2003). Phenolic groups are important in complexation reactions with metals, and can also be further oxidized to produce quinones, which are considered to be the major electron donor and acceptor moieties of humic material (Tan, 2003). Under aerobic conditions, humic acids express significant reducing capacity, and although Fe(II) bound to humic acids can also contribute electrons in reduction reactions, relative to humic acids its contribution can be considered negligible (Peretyazhko and Sposito, 2006).

Thermodynamics

The redox reactions involving Cr(VI) and Cr(III) are not only dependent on pH, but are also dependent on the pe, or "electron activity", of the system. Electron activity, or the potential for the electron to do electrical work, is measured as a voltage, Eh, and is often expressed in Nernstian form as pe, where pe = Eh (V)/0.059. Although its activity (related to concentration) is dimensionless due to the electron having negligible mass, it is analogous to pH as the measure of proton activity (James and Brose, 2012). The large charge-to-size ratio of the electron, again similar to the proton, (charge-to-size ratio for H^+ is small relative to e^-) makes it ephemeral in free form, however, it is a strong reducing agent with a potential of -2.7 V relative to hydrogen (James and Brose, 2012).

In soils and natural waters, the range for pH is approximately 3 to 12, and -10 to 17 for pe (Stumm and Morgan, 1996). These pe values correspond to Eh values of -591 to 1005 mV, where the more positive a value, the lower the electron activity. In soils, the higher the Eh value the more the soil can be considered oxic. The pe and pH of a system can be thought of as being in balance on a see-saw where a rise in one value corresponds to a fall in the other, and vice-versa (James, 1996). One use of pe and pH data is to represent which species of an element predominates, and is thermodynamically favorable, at given electron and proton conditions. The pe-pH relationships for different species of Cr(VI) and Cr(III) are illustrated with a pe-pH diagram, as shown in Figure 1-2.

Cr(VI) and Cr(III) redox reactions in soils and natural waters can also be predicted using thermodynamic data and reduction half-reactions for Cr, Mn, anthraquinone-2,6-disulfonate (AQDS), tartaric acid, and citric acid (Table 1-1). Although the oxidized species of tartaric and citric acids were not indicated in the reference, standard electron potentials (relative to SHE) were given (Milazzo et al., 1978). The compound AQDS is a chemical analog for dissolved humic substances in soils and natural waters (Lovley, 1996). The log K values of these equations can be compared to predict which species may be oxidizing and which ones may be reducing.

The protonation of the chromate ion is important in considering the thermodynamics of reduction and oxidation reactions of Cr. Take for example the ΔG_r values for the reduction reactions of $HCrO_4^-$ and CrO_4^{2-} by tartaric acid. For the reaction with $HCrO_4^-$ reduced by tartaric acid, the ΔG_r value is -95.3 kJ/eq, whereas for the reaction involving tartaric acid and CrO_4^{2-} the ΔG_r value is -107.3 kJ/eq. The reduction of CrO_4^{2-} by tartaric acid is more favorable than that for $HCrO_4^-$. The standard electron potentials for these values are determined at pH 0, and referring back to the pe-pH diagram for Cr(VI) and Cr(III), as pH decreases Cr(VI) reduction may occur at higher Eh values. Neither the pe-pH diagram nor Table 1-1 allow inference into the rate of

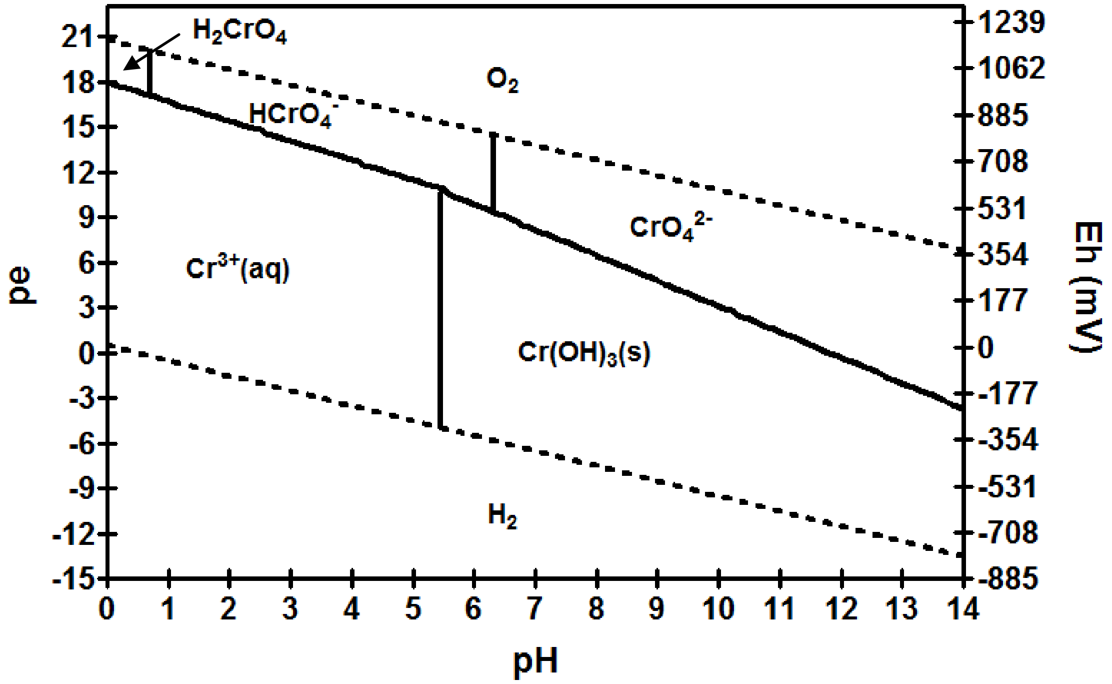


Figure 1-2 A pe-pH diagram for Cr(VI)-Cr(III) redox transitions. Calculations made with ion activities at 10^{-4} M.

Table 1-1 Reduction half reactions for Cr(VI) and other species likely to be present in soils (AQDS= anthraquinone-2,6-hydroxy acid). These reactions can be combined to form redox reactions, many of which are energetically favorable as indicated by negative ΔG_r values. Data from James and Brose, *In press*; Milazzo et al., 1978;

Species		Equation	E^0 (V)	Log K	ΔG_r^0 (kJ/mol)
A	γ-MnOOH	$\gamma\text{-MnOOH} + e^- + 3H^+ \rightarrow Mn^{2+} + 2H_2O$	1.50	25.4	-145.0
B	CrO_4^{2-}	$1/3CrO_4^{2-} + e^- + 5/3H^+ \rightarrow 1/3Cr(OH)_3 + 1/3\ H_2O$	1.24	21.0	-119.9
C	γ-MnO_2	$1/2\ \gamma\text{-}MnO_2 + e^- + 2H^+ \rightarrow 1/2Mn^{2+} + H_2O$	1.23	20.8	-118.8
D	$HCrO_4^-$	$1/3HCrO_4^- + e^- + 4/3H^+ \rightarrow 1/3Cr(OH)_3 + 1/3\ H_2O$	1.11	18.9	-107.9
E	$Fe(OH)_3$	$Fe(OH)_3 + e^- + 3H^+ \rightarrow Fe^{2+} + 3\ H_2O$	0.93	15.8	-90.1
F	AQDS	$1/2AQDS + e^- + 2H^+ \rightarrow 1/2\ AH_2DS$	0.22	3.9	-22.3
G	Lactic acid	$1/2$ pyruvate $+ e^- + H^+ \rightarrow 1/2$ lactate	0.23	3.9	-22.3
H	Citric acid	Oxidized species not indicated	0.19	3.2	-18.3
I	Tartaric acid	Oxidized species not indicated	0.13	2.2	-12.6
J	CH_2O	$1/4CO_2 + e^- + H^+ \rightarrow 1/4\ CH_2O + 1/4H_2O$	-0.07	-1.9	6.9

reduction of Cr(VI), but instead only indicate if a reaction could be thermodynamically favorable.

Another important soil constituent regarding Cr redox is Mn(III,IV)(hydr)oxides. The log K value for γ-MnO_2 (20.8) is greater than the log K for $HCrO_4^-$ (18.9) indicating that the oxidation of Cr(III) to Cr(VI) is thermodynamically favorable (Table 1-1). There is great uncertainty in the exact composition of Mn(III,IV)(hydr)oxides and due to their being non-stoichiometric, the thermodynamic predictions towards redox behavior are also uncertain (James, 2002).

The thermodynamic predictions derived from this table have been explored experimentally and were found to hold true (Brose, 2008; Brose and James, 2010). In the presence of anthraquinone-2,6-disulfonate (AQDS), lactic acid reduced 0.18 mM soluble Cr(VI) in 14 days with an initial pH value of 5.5, initial Cr concentration of 0.2 mM, and under aerobic conditions (22 ± 2º C). Using the same initial conditions, but conducted with a soil sampled from the Ap horizon of a Watchung series mapping unit (Typic Albaqualf), reduction was complete in 11 days. Both of these results showed more reduction of Cr(VI) occurred in samples with AQDS than those without, indicating its contribution to Cr(VI) reduction by acting as an electron shuttle. In the absence of AQDS and soil, lactic acid did not reduce any Cr(VI) over the course of 14 days (Figure 1-3, Brose and James, 2010). The results are presented in net reduction terms due to the possible re-oxidation of Cr(III) by Mn(III,IV)(hydr)oxides. In fact, soluble Mn, assumed to be Mn(II) but measured as total soluble Mn, increased with time during the 14 day trial. The reducing ability of the lactic acid-AQDS system was non-selective towards Cr(VI) and also appeared to be reducing Mn(III,IV)(hydr)oxides. The co-reduction of Mn suggests strong reducing conditions, which inhibited any potential re-oxidation of freshly-reduced Cr(III) back to Cr(VI).

This interaction among organic acids, Cr(VI), and soils leads to the current work that investigated the use of tartaric acid and isopropyl alcohol in the reduction of Cr(VI) in aqueous solutions, in the presence of five Maryland soils, and with chromite ore processing residue (COPR)-derived Cr(VI) in aqueous solutions and with the same Maryland soils.

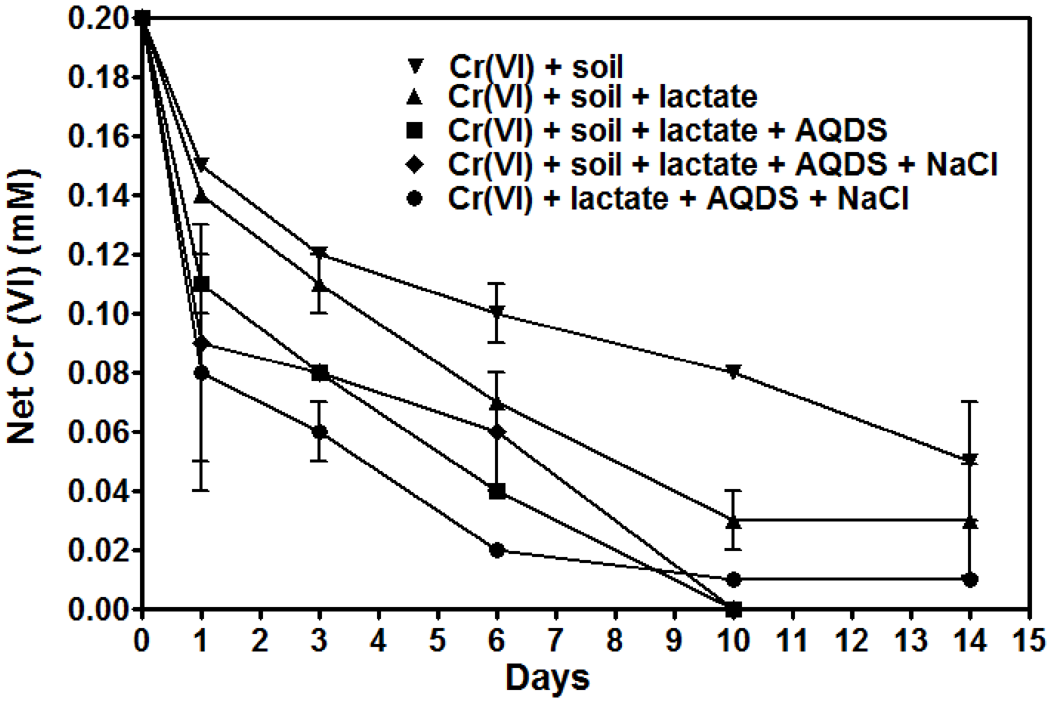


Figure 1-3 Reduction of 0.2 mM Cr(VI) in Watchung A horizon, and enhanced reduction by addition of 15 mM lactate and 10 mM AQDS, over 14 days. Error bars are SEM (n=3) (Brose and James, 2010).

This work addressed the following research questions:

- How does the rate of reduction vary with the addition of tartaric acid and isopropyl alcohol to aqueous solutions of Cr(VI) at environmentally relevant pH values, i.e. 3-6?
- Does the addition of tartaric acid and isopropyl alcohol enhance the effect of reduction of Cr(VI) in Maryland surface soil samples?
- Can a novel *in-situ* remediation strategy be employed in which tartaric acid and isopropyl alcohol can be applied in the reduction of Cr(VI) from chromite ore processing residue (COPR) and COPR-contaminated soils?

The literature review on the reduction of Cr(VI) with isopropyl alcohol and 2-hydroxy-2-methylbutric acid or oxalic acid were conducted at concentrations up to 1 M perchloric acid. The rate of these reactions were in s^{-1}, with the average of the oxalic acid experiments lasting only 20 minutes. These conditions suit the purpose of that work, which was to infer mechanisms by investigating the kinetics of the reaction, but using this chemistry in environmental applications will require knowledge about how these reactions would “behave” under conditions more like what is found in soils and natural waters. The first research question is explored in Chapter 2, which explores how the rate changes under varying conditions of isopropyl alcohol, tartaric acid, Cr(VI), and importantly, pH.

Reactions in aqueous solutions may not correlate to observations in the field, and the second research question explores how reduction reactions of Cr(VI) by tartaric acid and isopropyl alcohol would vary in five Maryland soils. Previous work with a

Watchung soil A horizon soil sampled showed that reduction of Cr(VI) by lactic acid was enhanced in the presence of this soil. The five soil mapping units (Russett-Christiana, Askecksy, Annapolix, Jackland, and Ingleside) were sampled in order to capture a range of characteristics, such as texture, percent organic carbon, and levels of Fe(III)- and Mn(III/IV)(hydr)oxides. Chapter 3 explores how reduction varied with time in the presence of each of these soils.

The final research question posed addresses the remediation of chromite ore processing residue (COPR), and applying the chemistry involving the tartaric acid-Cr-isopropyl alcohol complex to the reduction of COPR-derived Cr(VI). This was the last of the three research questions explored, and as seen in Chapter 4, included the lessons learned from the work with the aqueous solutions and soils.

This dissertation research is presented in the next three chapters, with the last chapter, Chapter 5, providing concluding remarks on the research and implications of the results. Each of the next three chapters has been written to stand apart from each other and submittable individually as a journal article manuscript. Chapter 2 will provide a characterization of the reduction reaction between tartaric acid and Cr(VI) in isopropyl alcohol, Chapter 3 applies this chemistry to the reduction of Cr(VI) in five Maryland surface soil samples (see Appendix B for complete sampling details and soil characterization data), and Chapter 4 applies this chemistry to the reduction of Cr(VI) from chromite ore processing residue (COPR) in an attempt to develop a novel *in-situ* remediation strategy.

CHAPTER 2

HEXAVALENT CHROMIUM REDUCTION IN AQUEOUS SOLUTIONS: THE ROLE OF ISOPROPYL ALCOHOL AND TARTARIC ACID

Introduction

Chromium is a naturally occurring, transition metal found mostly in the trivalent state; however, concerns regarding the presence of Cr in the environment focus on the potential adverse health effects of Cr(VI)-contaminated soils, groundwater, and drinking water supplies. Regulation of Cr is currently based, not on the oxidation state of Cr, but on total chromium concentration [i.e., the sum of Cr(III) and Cr(VI)]. The U.S. Environmental Protection Agency's (USEPA) national standard for total Cr in drinking water is 100 µg/L (USEPA, 2010). Chromium(VI) is genotoxic in a number of *in vitro* and *in vivo* toxicity assays, and was found to be carcinogenic when administered in laboratory animals (IARC, 1990; Stout et al., 2009). Thus, reducing Cr(VI) in contaminated soils and natural waters to Cr(III) is a remediation strategy that would detoxify the metal.

Soluble α-hydroxy carboxylic acids have been explored as reducing agents in the treatment of Cr(VI), but alone they demonstrate negligible rates of reduction of Cr(VI). When dissolved in an isopropyl alcohol-water solution, however, the reduction of Cr(VI) will be significantly enhanced (Hasan and Rocek, 1973; Mahapatro et al., 1980). α-hydroxy carboxylic acids in isopropyl alcohol enhance the reduction of Cr(VI) due to the formation of a single termolecular complex that forms from the esterification of the alcohol and the α-hydroxy carboxylic acid with Cr (Mahapatro et al., 1980; Hasan and

Rocek, 1973; Westheimer and Novick, 1943). The work of these authors demonstrated an instantaneous three-electron transfer resulting in the oxidation of isopropyl alcohol and α-hydroxy carboxylic acids. The present work will focus on tartaric acid, a four carbon α-hydroxy carboxylic acid with two hydroxyl groups and two carboxylic acid groups. The stoichiometry of the reaction results in two moles Cr(VI) reduced for every one mole tartaric acid and isopropyl alcohol, as shown in equation 1:

$$\underset{\text{Tartaric acid}}{COOH(CHOH)_2COOH} + \underset{\text{Isopropyl alcohol}}{CH_3CHOHCH_3} + 2HCrO_4^- \rightarrow \qquad (1)$$

$$\underset{\text{Glyoxylic acid}}{HCOCOOH} + \underset{\text{Acetone}}{CH_3COCH_3} + 2CO_2 + 2Cr(OH)_3 + H_2O$$

The oxidative decomposition of the tartaric acid-Cr-isopropyl alcohol complex ultimately yields acetone, carbon dioxide, trivalent chromium, and glyoxylic acid from the decarboxylation of tartaric acid (Kabir-ud-Din et al., 2002).

Although pH was not directly reported, reactions in the literature were carried out at concentrations of perchloric acid ranging from 0.1 to 0.9 M, corresponding to pH values < 2.0 (Kabir-ud-Din et al., 2002; Mahapatro et al., 1980). The use of tartaric acid and isopropyl alcohol could be an effective reductant in the treatment of Cr - contaminated soils and natural waters; however, there currently are no data for this reaction at conditions more relevant to environmental applications, i.e., in the pH range of 3 to 6. The current work investigates the variation in the rate of the reaction with variations in the concentrations of tartaric acid, isopropyl alcohol, Cr(VI) concentrations, and acidity in aqueous solutions. Thermodynamic inferences are drawn from oxidation-reduction potential (ORP) measurements, and the application of this reaction to the treatment of Cr(VI) in soils and aqueous solutions is discussed.

Methods

Hexavalent chromium stock solutions at 1000 mg Cr(VI)/L were prepared from DILUT-IT® Analytical Conc. Std, 1g Cr^{6+} (J.T. Baker, Inc.) or from reagent grade K_2CrO_4 (J.T. Baker, Inc.) and stored at room temperature (22 ± 2º C). Concentrations of 2 mM (104 mg/L) Cr(VI) were used to represent drainage water or groundwater concentrations subjacent to chromite ore processing residue (COPR) -enriched soils. Chromium(VI) concentrations in such soil-water systems have been reported up 58 mM (3,000 mg/L) (Yalcin and Unlu, 2006). Thus, 2 mM would be a low-to-medium concentration representing Cr(VI) solutions leached from such soil-water systems.

Isopropyl alcohol was reagent grade (99.9% purity) and stored at room temperature (22 ± 2º C). Tartaric acid (J.T. Baker, Inc.) solutions were made fresh at the start of each experimental setup from reagent grade solids. All sample solutions included 0.01 M $NaNO_3$ as a background electrolyte to control for ionic strength, and sample solution pH was adjusted with µL volumes of reagent grade NaOH (J.T. Baker) or HNO_3 (J.T. Baker) solutions. The solution pH values 3.0 to 6.0 were chosen as representative of Mid-Atlantic soil and surface water pH values, and in part, from the reduction of Cr(VI) occurring most readily at pH 3.3 to 5.1 (Yang et al., 2008). Solution pH was measured potentiometrically using a glass electrode, and oxidation-reduction potential (ORP) was measured using a combination platinum electrode with a Ag/AgCl reference electrode.

Eh values (mV) were reported relative to the standard hydrogen electrode (SHE), and used to calculate pe values (pe = Eh/0/059).

The experiments were run under four conditions. The first was with tartaric acid added to 50 mL Erlenmeyer flasks in concentrations of 0.29, 2.9, 5.8, 12, 23, 29, and 58 mM, corresponding to stoichiometric amounts of 0.5 to 20 times the stoichiometric amount needed to fully reduce 2 mM (104 mg/L) Cr(VI) in a two-electron transfer (equation 1). At each level of tartaric acid, isopropyl alcohol was added at 0.29 M and pH was adjusted to 4.0. The second condition was with isopropyl alcohol added to separate flasks in concentrations of 0.03, 0.29, 0.58, 1.2, 1.7, 2.4 and 2.9 M, corresponding to stoichiometric amounts of 5 to 500 times the amount needed for full reduction of 2 mM Cr(VI) in an two-electron transfer to Cr (equation 1). At each level of isopropyl alcohol, tartaric acid was added at 23 mM and pH adjusted to 4.0. The third condition included 2 mM Cr(VI), 23 mM tartaric acid, and 0.29 M isopropyl alcohol at initial pH values of 3.0, 4.0, 5.0, and 6.0. The fourth condition included initial concentrations of 0.2, 0.5, 1.0, 1.5, and 2.0 mM Cr(VI) with 23 mM tartaric acid, 0.29 M isopropyl alcohol, and adjusted to pH 4.0.

All samples had 0.01 M $NaNO_3$ as a background electrolyte and were brought to initial pH values of 3.0, 4.0, 5.0 or 6.0 with HNO_3 or NaOH. After all reagents except Cr were added to the flask, 2.6 mL Cr(VI) stock solution was added to initiate the reaction, which also brought the total volume to 25 mL. Flasks were capped with foam plugs, and shaken at 100 cycles min^{-1} on an orbital shaker. Samples were taken at 2, 4, 8, 24, and 48 h, and then ongoing every 24 h until 240 h (10 d) for increasing isopropyl alcohol concentrations, 312 h (13 d) for increasing pH and initial Cr(VI) samples, and 336 h (14

d) for samples with increasing tartaric acid concentrations. Sampling times up to 336 h (14 d) were allowed in order to allow at least one of the treatments in each setup to fully reduce Cr(VI).

At each sampling time, a 0.25 mL aliquot was removed from the flask, diluted to 10 mL with distilled water, and analyzed for Cr(VI) using a modified diphenylcarbazide (DPC) method that combines an acidification step (pH 1.5-2) with the reduction reaction between DPC and Cr(VI). In this method, the rapid reduction of Cr(VI) by DPC under acidic conditions is coupled simultaneously with the immediate complexation of newly-reduced, unhydrated Cr^{3+} cations by the oxidized form of DPC, diphenylcarbazone (Bartlett and James, 1979). This reduces the likelihood that any organic C in the sample will reduce Cr(VI) during analysis.

Results and Discussion

The reduction of Cr(VI) was examined by conducting the reaction with one of the reagents (tartaric acid or isopropyl alcohol) in excess of the other at pH 4.0 (Figures 2-1A and 2-2A). The reaction was also conducted with increasing pH from 3.0 to 6.0, while tartaric acid and isopropyl alcohol were held constant (Figure 2-3A), and lastly the reaction was conducted with increasing initial Cr(VI) concentrations at pH 4 with tartaric acid and isopropyl alcohol concentrations constant (Figure 2-4A). The data from these varying conditions provide insight into whether tartaric acid or isopropyl alcohol is the limiting reagent, and into the sensitivity of the reaction to changes in pH and initial Cr(VI) concentration. These data showed that reduction of 2.0 mM Cr(VI) was complete within 48 h in samples that had 1.7 M or higher isopropyl alcohol concentrations in 23

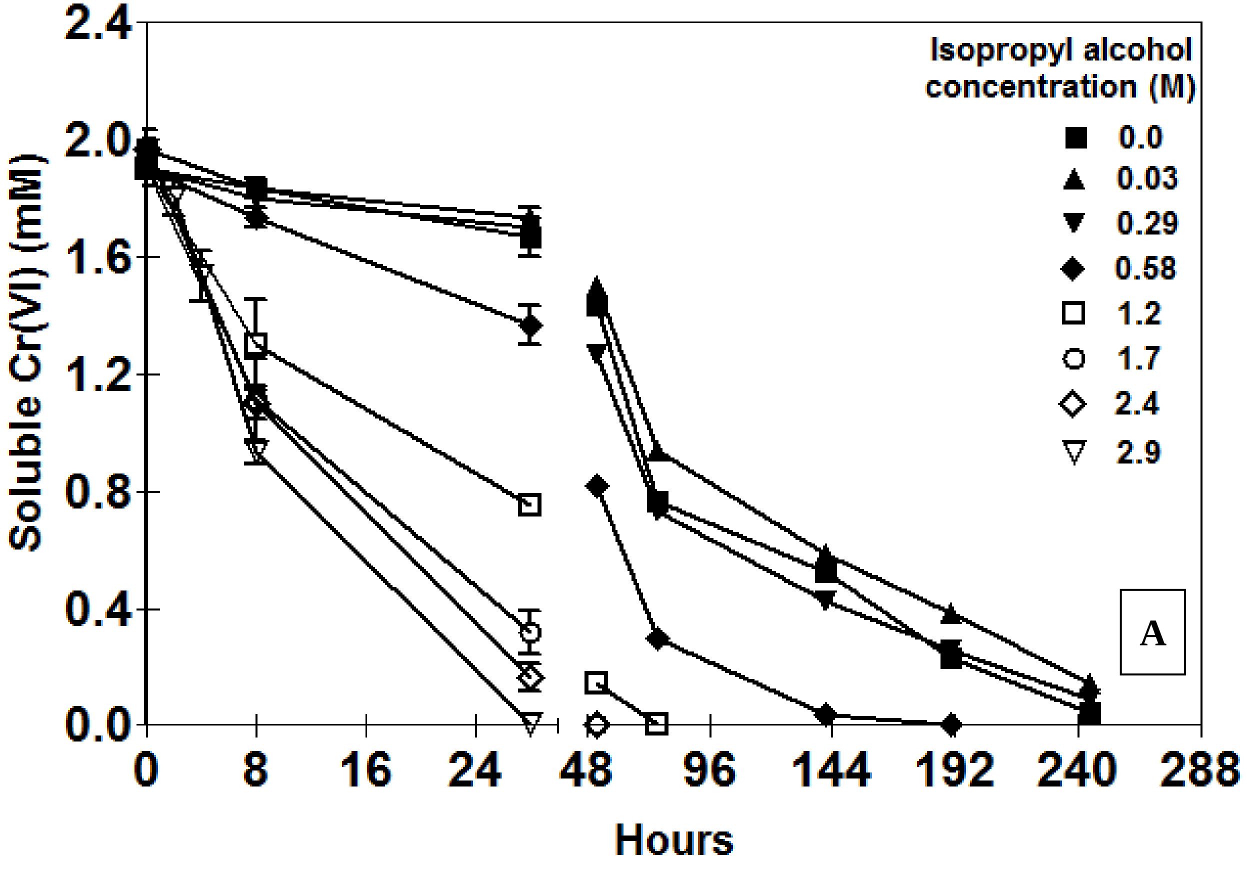


FIGURE 2-1 (A) Reduction of 2.0 mM soluble Cr(VI) at pH 4.0 in 23 mM tartaric acid and increasing concentration of isopropyl alcohol, from 0.03 to 2.9 M (5x to 500x stoichiometric ratio). No data points fall in the approximately 20 h break in x-axis. Error bars are SEM (n=3).

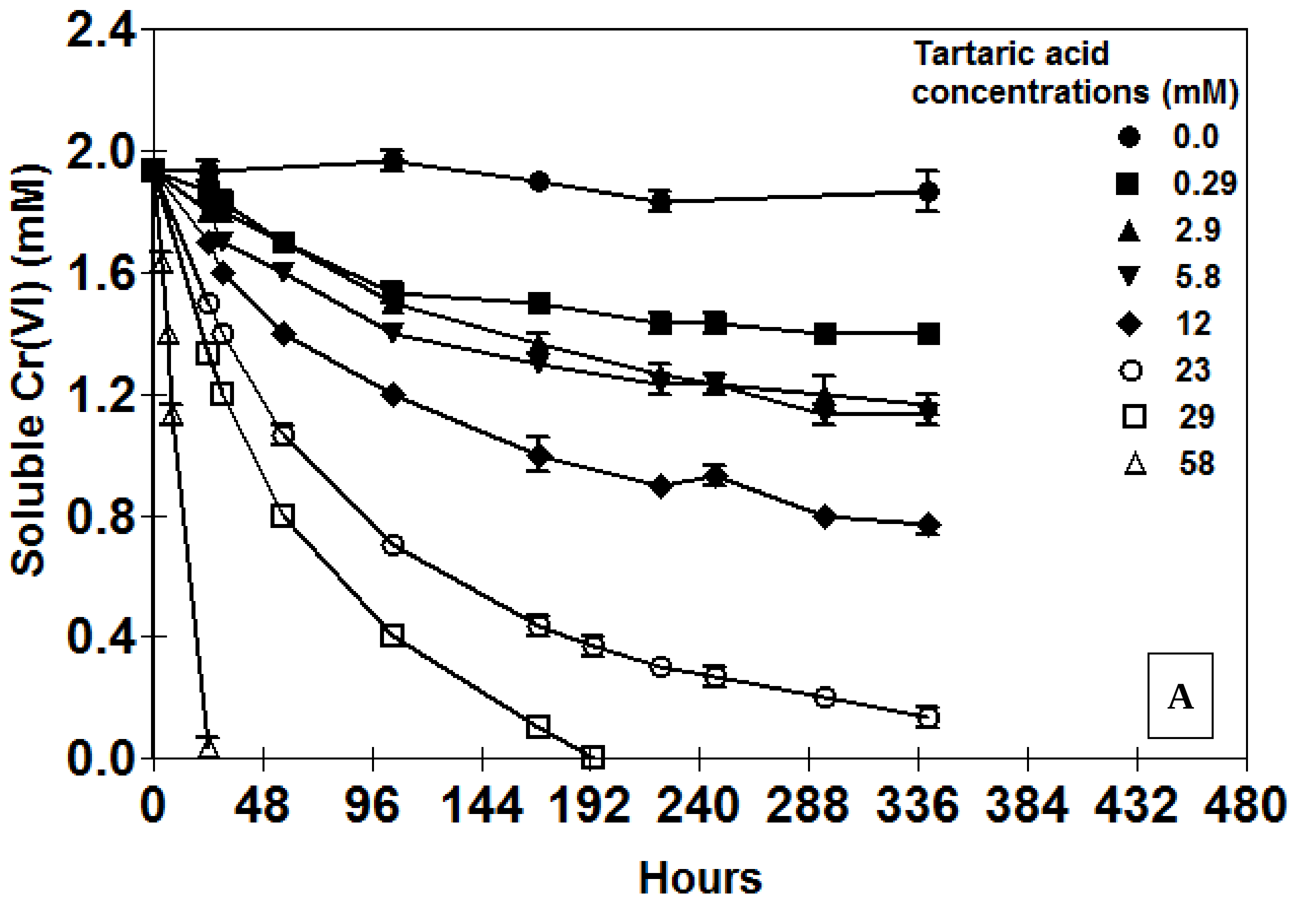


FIGURE 2-2 (A) Reduction of 2.0 mM soluble Cr(VI) at pH 4.0 in 0.29 M (2.2% v/v) isopropyl alcohol and increasing concentrations of tartaric acid from 0.29 to 58 mM (0.5x to 20x the stoichiometric ratio). Error bars are SEM (n=3).

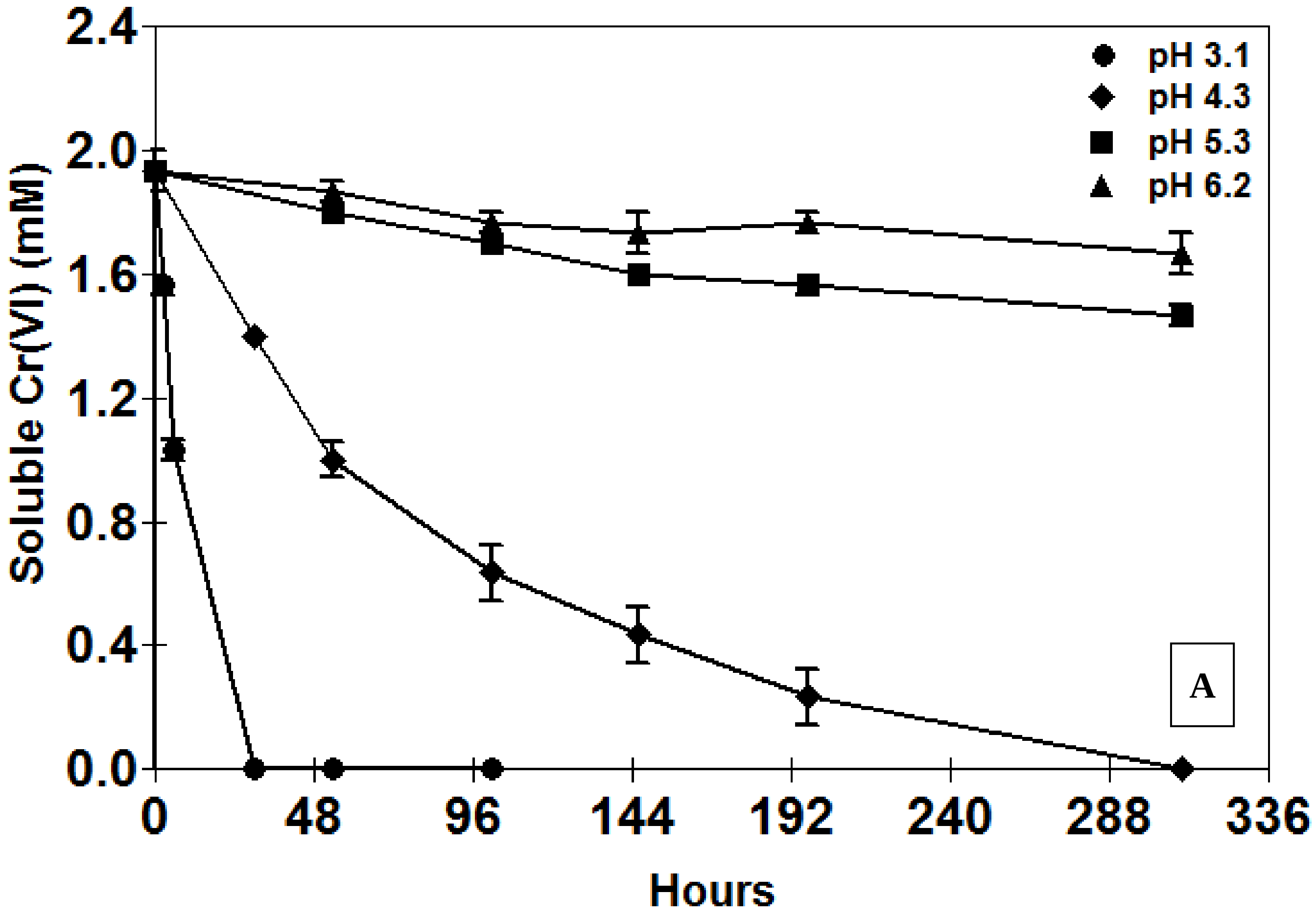


FIGURE 2-3 (A) Reduction of 2 mM soluble Cr(VI) in 23 mM tartaric acid and 0.29 M (2.2%) isopropyl alcohol with increasing initial pH from 3.0 to 6.0 (final pH values labeled on graph). Error bars are SEM (n=3).

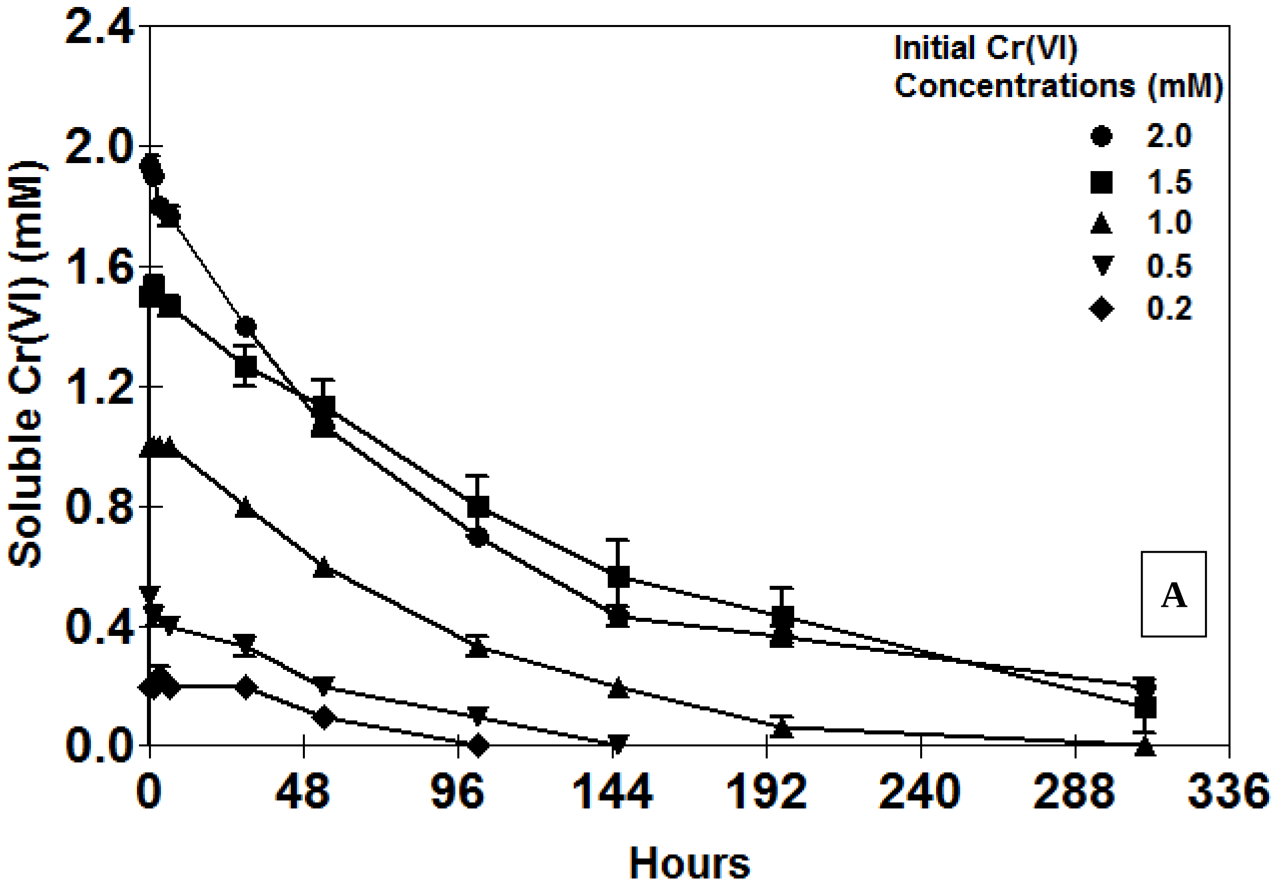


FIGURE 2-4 (A) Reduction of 0.2, 0.5, 1.0, 1.5, and 2.0 mM soluble Cr(VI) in 23 mM tartaric acid and 0.29 M (2.2% v/v) isopropyl alcohol. Error bars are SEM (n=3).

mM tartaric acid (Figure 2-1A), or with 58 mM tartaric acid in 0.29 M isopropyl alcohol (Figure 2-2A).

Reduction was greatest at pH 3.0, having reduced 2.0 mM Cr(VI) within 48 h; however, at pH 6.0 only 0.3 mM Cr(VI) (15%) was reduced at 312 h (13 d) (Figure 2-3A). For samples ranging in tartaric acid concentrations, 23 mM tartaric acid reduced 1.87 mM (93%) Cr(VI) and 0.29 mM tartaric acid reduced 0.6 mM Cr(VI) (29%). All but the two lowest levels of isopropyl alcohol fully reduced Cr(VI) within 192 h (8 d), although the sample at 0.03 M isopropyl reduced 1.85 mM (93%) Cr(VI) at 240 h (10 d). The rate constants of these reactions under each of the four conditions (increasing alcohol, tartaric acid, pH, or initial Cr concentration), were taken as the slopes of linear regression best fit lines on first-order rate plots – natural log of Cr(VI) concentrations over initial concentrations (ln C/C_o) plotted as a function of time. Regression lines for zero-order and second-order rate plots were also determined, but statistically fit less well than regressions with first-order plots.

The negative first-order rate constants (-k) for each condition were plotted as a function of the change in constituent of that condition: increasing isopropyl alcohol (Figure 2-1B), tartaric acid (Figure 2-2B), pH (Figure 2-3B), and initial Cr concentration (Figure 2-4B). The rate constants increased linearly with increasing isopropyl concentration, but the rate constant increased exponentially with increasing tartaric acid concentration and decreased exponentially with increasing pH. There is a greater sensitivity of the reaction to tartaric acid concentrations and changes in pH then with isopropyl alcohol. The slope of the line for the linear regression of the rate constant on

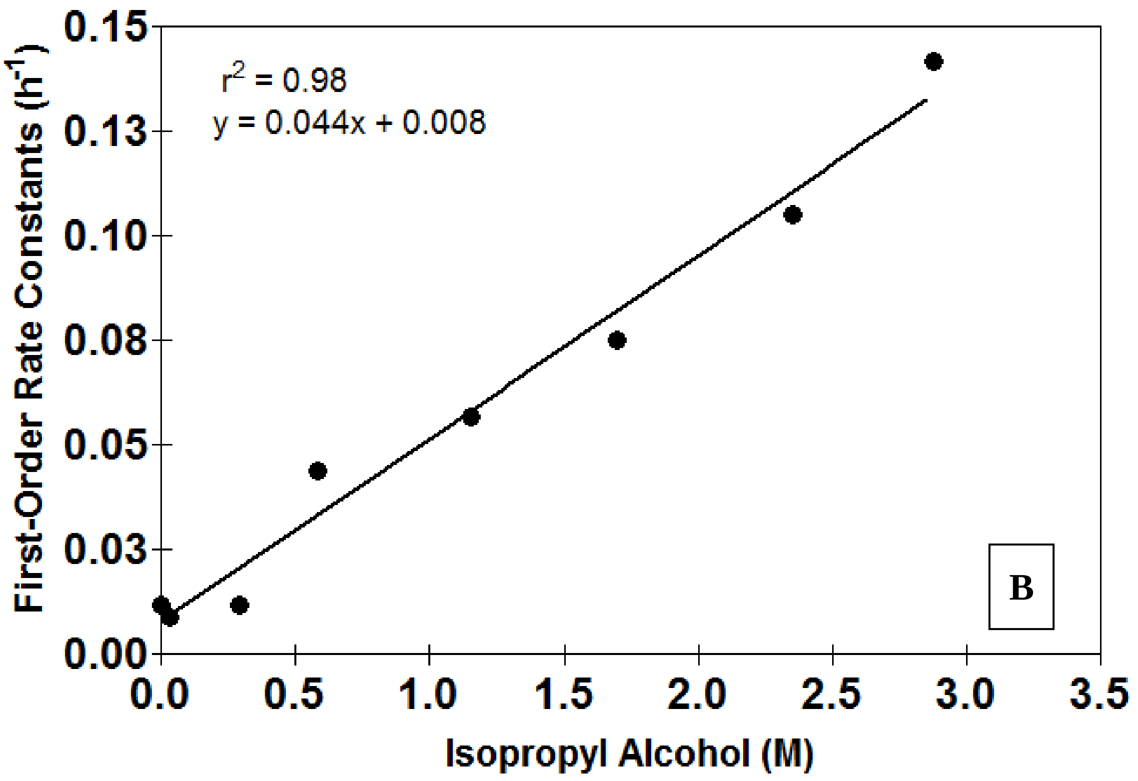


FIGURE 2-1 (B) First-order rate constants (h^{-1}) as a function of isopropyl concentration for data in (A).

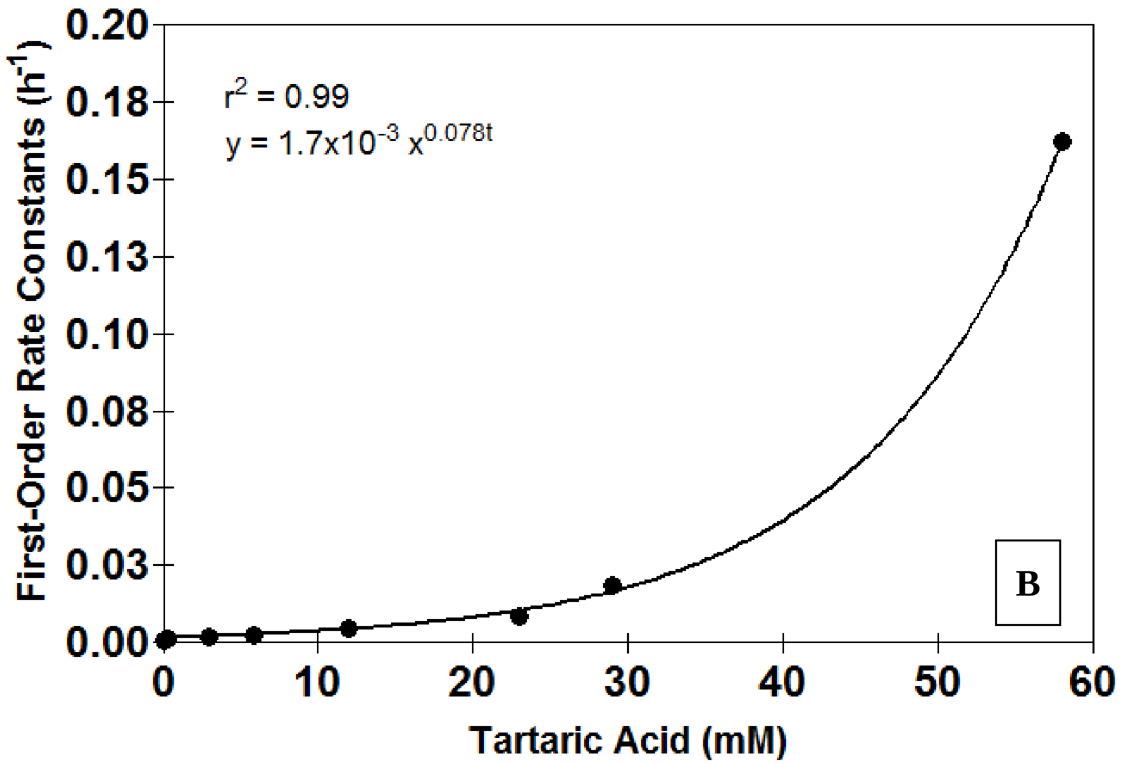


FIGURE 2-2 (B) First-order rate constants as a function of tartaric acid concentration from data in (A).

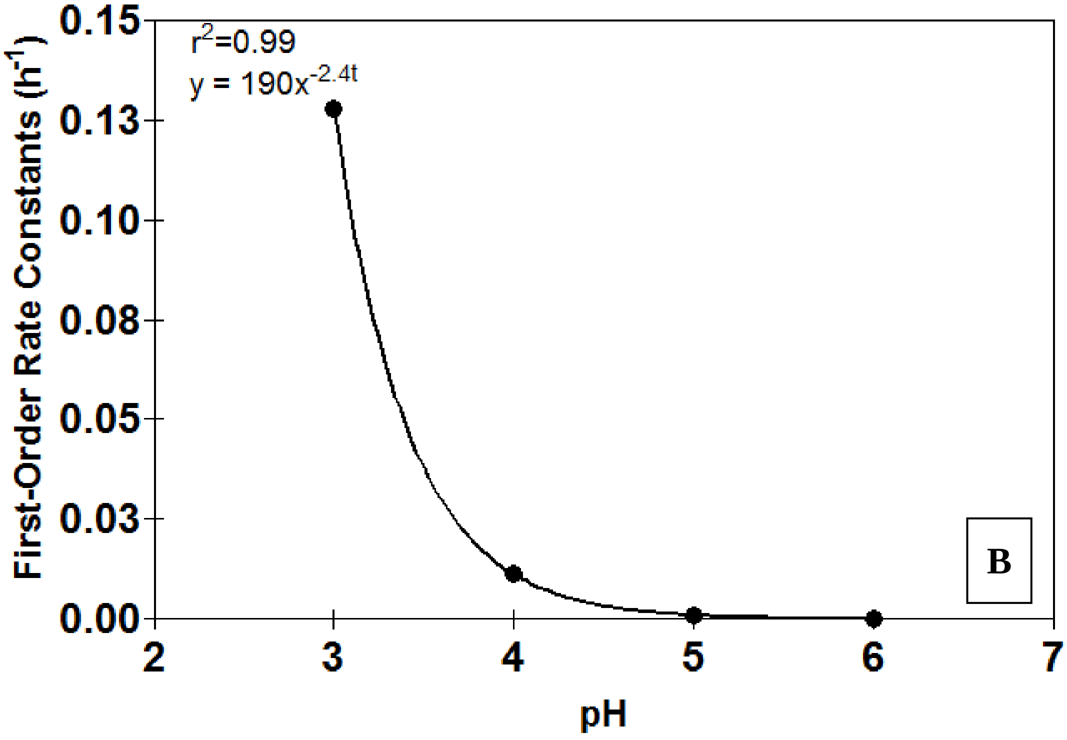


FIGURE 2-3 (B) First-order rate constants as a function of pH from data in (A) with increasing pH.

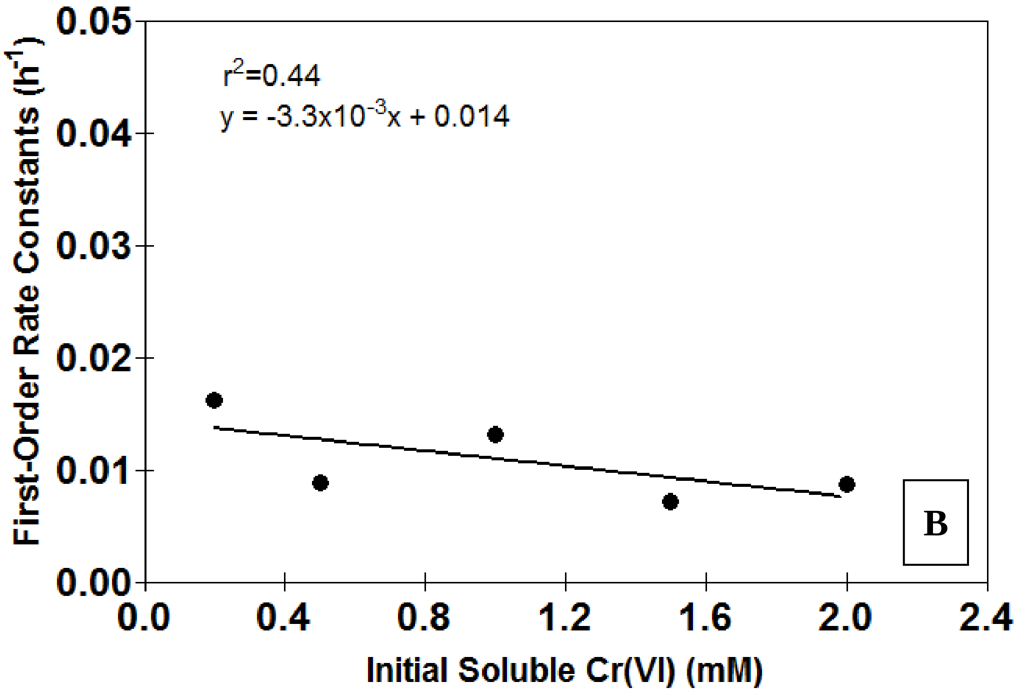


FIGURE 2-4 (B) First-order rate constants as a function of initial soluble Cr(VI) concentration from data in (A). The slope of the regression line is not significantly different than zero (p=0.22), indicating that there is no effect of initial concentrations on the rate coefficient.

initial concentrations of Cr(VI) was not significantly different than zero ($p=0.22$), thus indicating that there is no change in the rate constant regardless of initial Cr(VI) concentration.

Because of the ability for tartaric acid to buffer pH due to the presence of two carboxylic acid groups ($pKa_1=2.9$, $pKa_2=4.4$), the pH of the samples remained close to 4.0 over the approximately 12-14 d sampling period, with some drifting upwards by 0.1 to 0.2 units. Overall, there is a correspondence of decreasing pe values as Cr(VI) was reduced, with initial pe values at approximately 11 to 12 and dropping to 8 to 9 (Figures 2-5A and B). For samples with 1.2 M isopropyl alcohol or higher in 23 mM tartaric acid, pe values initially dropped to approximately 8; however, for lower alcohol concentrations, pe values increased and then drifted back to approximately 11 (Figure 2-5). Higher tartaric acid concentrations did not necessarily result in low pe values, as 0.29 mM tartaric acid had the lowest pe value at 8.5 yet 5.8 mM had the highest pe value at 11 with the remaining concentrations falling in between these two points (Figure 2-5).

These data indicate that initially the presence of tartaric acid, more so than isopropyl alcohol, increased solution pe, but with time, the system became more reducing as indicated by the drop in pe values. The time at which the curves of these pe values leveled off corresponded with the approximate time that full reduction of Cr(VI) was reached in those samples. Thermodynamically, when these values are compared with a pe-pH diagram, it would be expected that the reduction of Cr(VI) would occur under these conditions since they fall below the Cr(VI)-Cr(III) line (Figure 2-6). However, the extent of reduction would be expected to decrease or not occur when conditions are in the region of the box shown in Figure 2-6 that extends above the solid Cr(VI)-Cr(III) line.

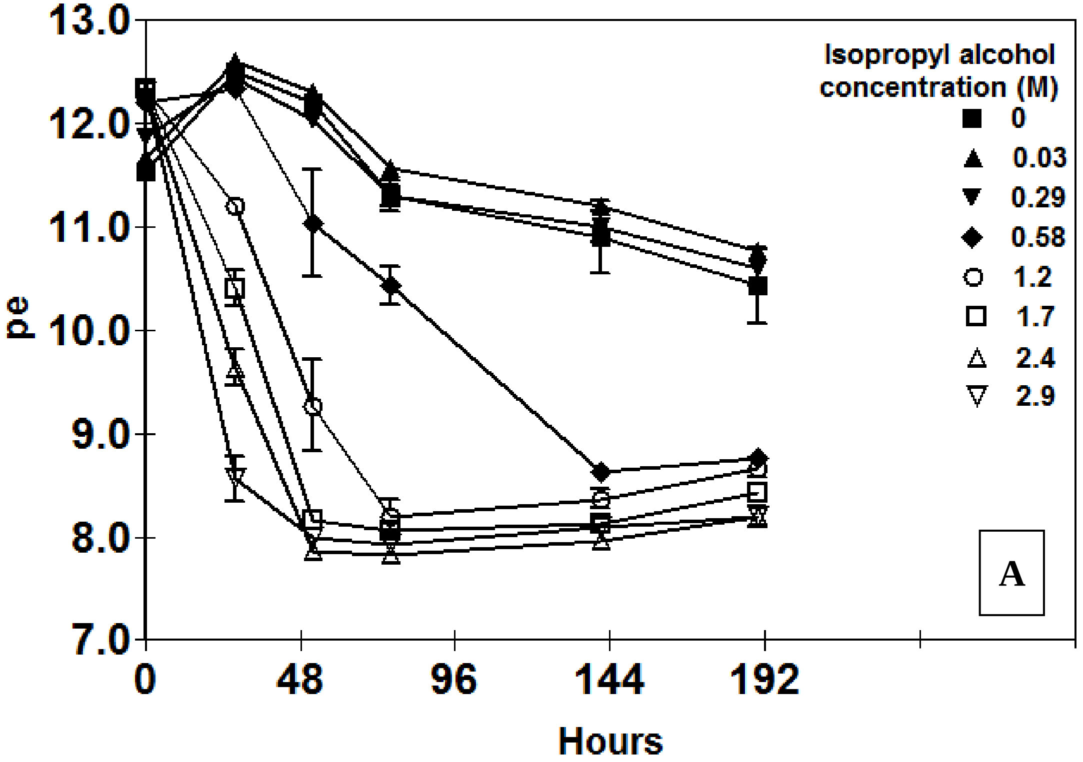


FIGURE 2-5 (A) Decrease in pe from reduction of 2.0 mM soluble Cr(VI) in 23 mM tartaric acid, increasing isopropyl alcohol, and pH 4. Isopropyl alcohol ranges from 0.03 to 2.9 M, which is 5-500x stoichiometric ratio for full reduction Cr(VI). Error bars are SEM (n=3).

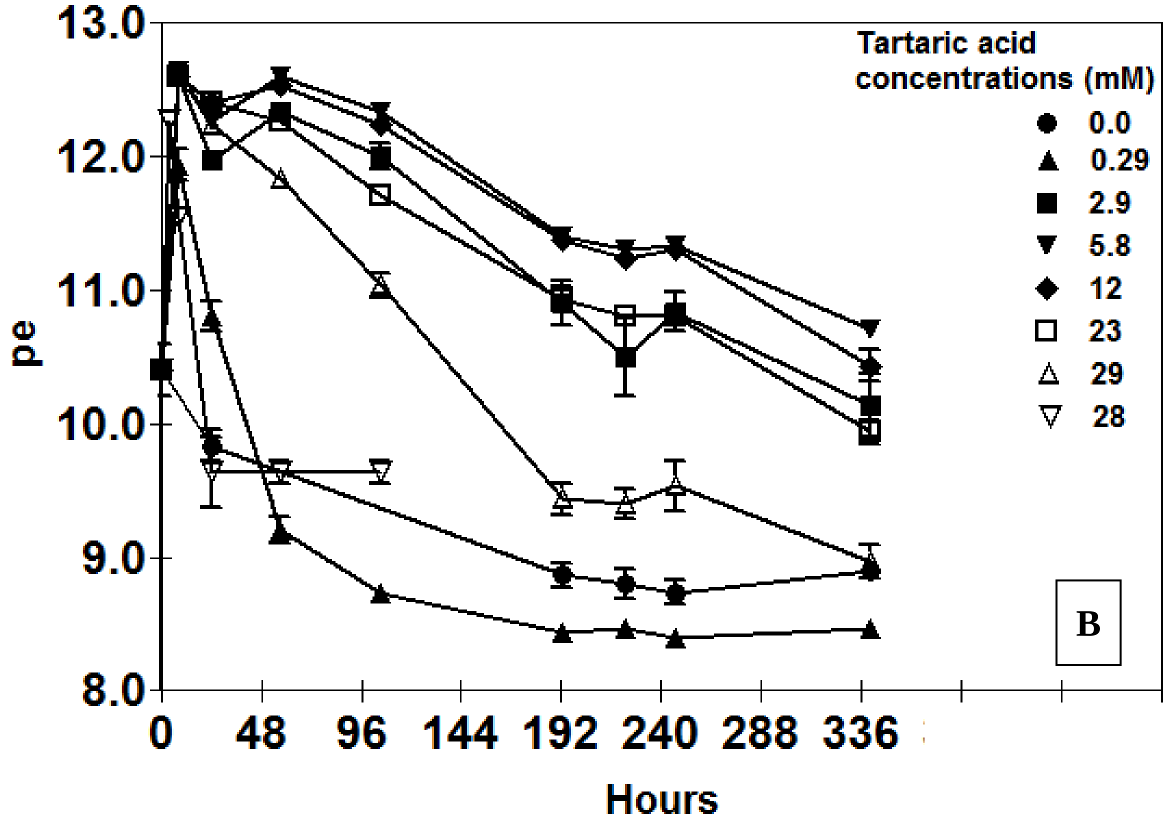


FIGURE 2-5 (B) Decrease in pe from reduction of 2.0 mM soluble Cr(VI) in 0.29 M (2.2%) isopropyl alcohol, increasing tartaric acid, and pH 4. Tartaric acid ranges from 0.29 to 58 mM, which is 0.5-20x stoichiometric ratio for full reduction Cr(VI). Error bars are SEM (n=3).

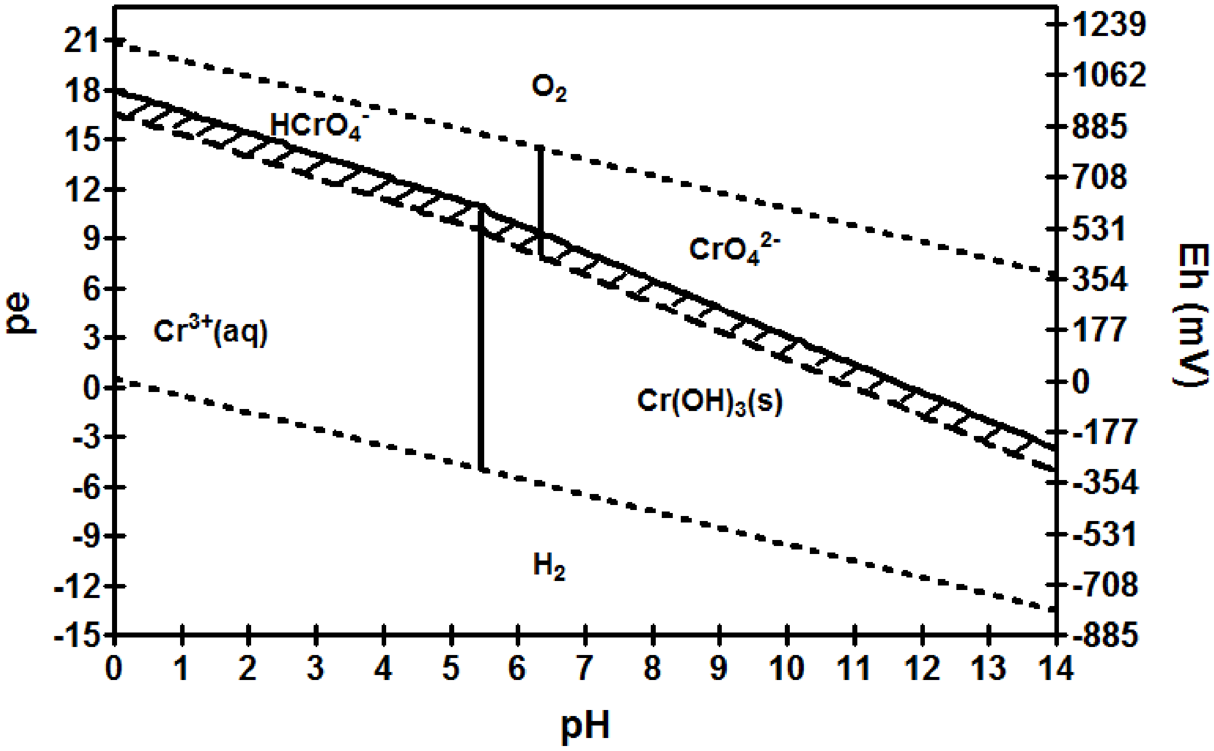


FIGURE 2-6 A pe-pH diagram for Cr(III) and Cr(VI) showing the region for experimental conditions in Figures 2-1 to 2-4 with the shaded box. Thermodynamically, Cr(VI) reduction at initial conditions of 2 mM Cr(VI) would be expected in the region below the solid Cr(VI)-Cr(III) line, whereas reduction at conditions when Cr(VI) has mostly been reduced (10^{-4} mM) would occur below the dashed Cr(VI)-Cr(III) line. The cross-hatched area between the lines is a transition zone during experimental conditions.

This was demonstrated when the amount of Cr(VI) reduced decreased as pH increased (Figure 2-3A), with only 0.3 mM (15%) Cr(VI) reduced at pH 6.0 at 312 h. The solid line on the pe-pH diagram represents the initial 2.0 mM Cr(VI) concentration, but as reduction occurs with time and Cr(VI) concentrations decrease, the line would shift lower on the diagram. The dashed line is calculated at concentrations of 10^{-7} mM Cr(VI), representing conditions after most of the Cr(VI) was reduced. The cross-hatched area between the solid and dashed Cr(VI)-Cr(III) line would represent a transition zone during the experimental period when Cr(VI) concentrations are decreasing. This transition zone is approximately from pe 11.8 to 12.4, and as pe values of the treatment solutions passed through this transitional zone, as most did as seen in Figures 2-5A and B, then depending on the Cr(VI) concentration of the sample, the reduction reaction may be less thermodynamically favorable until the pe dropped to below 11.8.

The highest rate constants in the present work were for the following three conditions 1) pH 3, 23 mM tartaric acid, and 0.29 M isopropyl alcohol; 2) pH 4, 23 mM tartaric acid, and 2.9 M isopropyl alcohol; and 3) pH 4, 58 mM tartaric acid, and 0.29 M isopropyl alcohol, which corresponded to rates of 0.128, 0.142, and 0.162 h^{-1}, respectively. Mahapatro et al. (1980) found rates ranging from 504 to $3.5x10^{3}$ h^{-1} , corresponding to concentrations of 2-hydroxy-2-methylbutyric acid (HMBA) from 1 to 500 mM in 0.045 M isopropyl alcohol. The reduction of Cr(VI) by HMBA and isopropyl alcohol have the same stoichiometric relationship as tartaric acid and isopropyl alcohol; however, these experiments were conducted in 0.5 to 0.02 M perchloric acid, likely resulting in pH values < 2.0 (pH not reported).

Based on the results presented by these authors, and in the present work, the reduction of Cr(VI) by a tartaric acid and isopropyl alcohol complex at conditions relevant to Cr-contaminated soils and natural waters will be most dependent on tartaric acid concentrations, but more importantly, the pH of the system. Although the rates presented here are much lower than what can be accomplished at a very low pH, these rates, and the environmentally-relevant pH values at which they were determined, suggest an application of the tartaric acid and isopropyl alcohol complex in a Cr(VI) treatment scheme would still result in successful reduction of Cr(VI) to Cr(III).

CHAPTER 3

THE ROLE OF TARTARIC ACID, ISOPROPYL ALCOHOL, AND MANGANESE IN THE REDUCTION OF HEXAVALENT CHROMIUM IN Cr(VI)-CONTAMINATED SOILS

Introduction

Remediation-by-reduction is a soil clean-up strategy that can be used in an attempt to mitigate the toxic effects of Cr(VI) and to clean up Cr-contaminated sites to meet regulatory standards and protect human health (James, 1996). Chromium is a naturally occurring, transition metal, but the potential adverse health effects of Cr(VI) has led to concern over contaminated soils, groundwater, and drinking water supplies.

Soils naturally contain chemical species capable of carrying out reduction and oxidation reactions (redox active species), and many capable of reducing Cr(VI) to Cr(III). For, example quinone and phenol functional groups and humic and fulvic acids within soil organic matter (James and Bartlett 1983a, Wittbrodt and Palmer 1997, Nakayasu et al. 1999, Rendina et al. 2011), α-hydroxy carboxylic acids (Deng and Stone 1996, Brose and James 2010, Tian et al. 2010), Fe^{2+} (Ludwig et al. 2008, Jagupilla et al. 2009, Qafoku et al. 2010), and H_2S and HS^- (Pettine et al. 1998, Chrysochoou and Ting 2011) have demonstrated the reduction of Cr(VI) to Cr(III). In this sense, soils, as natural bodies on the landscape, have a tendency towards reducing or detoxifying Cr(VI) to Cr(III).

Of particular interest is the reduction of Cr(VI) by α-hydroxy carboxylic acids, such as lactic, tartaric, or citric acid. Although not strong reducing agents on their own, in the presence of isopropyl alcohol, the ability of these organic acids to reduce Cr(VI) is enhanced (Hasan and Rocek, 1972, Mahapatro e t al. 1980). The mechanism involved is the esterification of Cr with the α-hydroxy carboxylic acid and with isopropyl alcohol, forming a termolecular complex that allows for a three-electron transfer to Cr(VI), reducing it to Cr(III). The oxidation of the alpha-hydroxy carboxylic acid is a decarboxylation step that releases two electrons with CO_2. Tartaric acid has two carboxylic acid groups and two hydroxyl groups, allowing for two decarboxylation steps that results in glyoxylic acid (Kabir-ud-Din et al., 2002). The stoichiometry of the reaction is two moles Cr(VI) reduced for every one mole tartaric acid and isopropyl alcohol, as shown in equation 1:

$$\underset{\text{(Tartaric Acid)}}{COOH(CHOH)_2COOH} + \underset{\text{(Isopropyl Alcohol)}}{CH_3CHOHCH_3} + 2HCrO_4^- \rightarrow \tag{1}$$

$$\underset{\text{(Glyoxylic Acid)}}{HCOCOOH} + \underset{\text{(Acetone)}}{CH_3COCH_3} + 2CO_2 + 2Cr(OH)_3 + H_2O$$

In the presence of isopropyl alcohol and low pH values, tartaric acid has been demonstrated to be an effective reducing agent for Cr(VI); however, there has not been any application of this chemistry to Cr(VI)-contaminated soils and natural waters at environmentally relevant pH values, i.e., pH 4.0-6.0. The present work investigates the application of the tartaric acid-Cr-isopropyl alcohol complex to the reduction of Cr(VI) in five Mid-Atlantic soils sampled from Maryland, USA.

Materials and Methods

Soils Soils samples from Maryland, USA were taken from profiles located in delineations of five different mapping units as part of a larger sampling scheme to collect soil profiles for research purposes. The horizons sampled from the profile in the

Askecksy soil mapping unit were similar to the Atsion series (sandy, siliceous, mesic, Aeric Alaquod), the profile from the Russett- Christiana Complex unit was similar to the Russett series (fine-loamy, mixed, semiactive, mesic Typic Hapludult), the profile from the Annapolis unit was similar to the Collington series (fine-loamy, mixed, active, mesic Typic Hapludult), the profile from the Ingleside unit was similar to the Downer series (coarse-loamy, siliceous, semiactive, mesic Typic Hapludult), and the profile from the Jackland unit was similar to the Jackland series (fine, smectic, mesic Aquic Hapludalf). At each location a hole was dug to at least the first B horizon, although many of the pits extended down to the second B and C horizons, which ranged from 80 to 140 cm in depth. From each horizon exposed in the profile, approximately 20 L of soil was taken.

The sampling was conducted when soil matric water potentials were approximately -5 to -10 kPa (field capacity moisture). The soil was brought into the laboratory, passed through a 4-mm polyethylene sieve, mixed thoroughly by hand, and stored in the dark at 22 ± 2º C in a plastic bucket lined with 1-mm thick plastic garbage bags to minimize soil drying while maintaining the aerobic status of the soil.

The Ap or A horizon (surface horizon) of each soil was used, except for the Atsion soil, a Spodosol, where the E horizon (eluviated horizon) was used instead. This E horizon was overlain by an O/A horizon, which consisted of partially degraded and fresh forest litter. Soil characterization data are summarized in Table 3-1 and full sampling information and characterization data are available in Appendix B.

Table 3-1 Characterization data for soils. CBD refers to a citrate-dithionite extraction.

Soil	**Texture** **(% sand, silt, clay)**	**Field pH**	**Eh (mV)**	**Organic Carbon (g/kg)**	**CBD Fe (g/kg)**	**CBD Mn (g/kg)**
Russett	Sandy loam (58, 37, 5.8)	5.0	577	25 ± 0.1	4.1 ± 0.3	0.3 ± 0.0
Atsion	Sandy (94, 5.9, 0.1)	3.5-4.0	524	20 ± 0.4	0.1 ± 0.0	0.0 ± 0.0
Collington	Loamy sand (83, 14, 3)	4.0	606	37 ± 0.0	3.0 ± 0.4	0.0 ± 0.0
Jackland	Silt loam (35, 57, 8)	6.0	470	9.0 ± 0.1	6.3 ± 0.3	1.0 ± 0.0
Downer	Loamy sand (75, 21, 4)	5.5	490	3.1 ± 0.1	1.5 ± 0.4	0.1 ± 0.0

Reagents Hexavalent chromium stock solution at 1000 mg Cr(VI)/L was prepared from reagent grade K_2CrO_4 (J.T. Baker, Inc.) and stored at room temperature (22 ± 2° C). Isopropyl alcohol was reagent grade (99.9% purity) and stored at room temperature (22 ± 2° C). Tartaric acid (J.T. Baker, Inc.) solution was made fresh at the start of each experimental setup from reagent grade solids. All sample solutions in all experiments included a final concentration of 0.01 M $NaNO_3$ as a background electrolyte to control for ionic strength, and sample solution pH was adjusted with µL volumes of reagent grade NaOH or HNO_3 (J.T. Baker).

Cr(VI) Reduction Treatments The field-moist equivalent of 5.0 g oven-dried soil (105°C) of each soil was weighed into 50-mL polycarbonate Oak Ridge-type centrifuge tubes. Tartaric acid salt was dissolved in 5 mM NaOH to approximately pH 4.0. Then to each centrifuge tube with soil, 12 mM tartaric acid, 0.29 M isopropyl alcohol, and 0.01 M $NaNO_3$ were added. Samples were adjusted to pH 4.0, if necessary, with µL volumes of NaOH. After all solutions were added, 2.6 mL of the 1,000 mg/L Cr(VI) stock solution and nanopure water (18 MΩ) was added for a final concentration of

2 mM Cr(VI), which initiated the reaction and brought the final volume to 25 mL. Another set was repeated with all five soils, but with no tartaric acid or isopropyl alcohol added.

The centrifuge tubes were capped and shaken at 50 cycles min^{-1} on an orbital shaker. Destructive sampling was conducted in that at each sampling time, one set of centrifuge tubes was removed from the shaker and processed. Sampling was done at 2, 24, 51, 75, and 99 h (approx. 4 d). At each time, sample solution pH was measured with one hour left, at which point 0.25 mL of a 1 M KH_2PO_4/K_2HPO_4 buffer solution (pH 7.2) was added and the centrifuge tubes were re-capped and shaken for the remainder of the hour. The P buffer displaces exchangeable Cr(VI) from the soil to ensure that any loss of Cr(VI) can be attributable to reduction processes, and not to sorption to colloidal surfaces.

Samples were centrifuged (10 minutes, 10,000 x *g*, 24^{o} C), and 0.25 mL aliquots of centrifugate were diluted to 10 mL with distilled water and analyzed for Cr(VI) using a modified diphenylcarbazide (DPC) method that combines an acidification step (pH 1.5-2) with the reduction reaction between DPC and Cr(VI). In this method, the rapid reduction of Cr(VI) by DPC under acidic conditions is coupled simultaneously with the immediate complexation of newly-reduced, unhydrated Cr^{3+} cations by the oxidized form of DPC, diphenylcarbazone (Bartlett and James, 1979). Total soluble Cr, Mn, and Fe remaining in solution were determined by flame atomic absorption spectroscopy. Data were analyzed and statistical differences reported with analysis of variance or analysis of covariance using Statistical Analysis Software (SAS) v9.2.

Three trials were conducted based on results from the tartaric acid and soil treatments. The first trial examined was the reduction of Cr(VI) in the five soils with added Fe^{3+} and Mn^{2+} to assess the effect of these metals on the reduction of Cr(VI) by tartaric acid. Solutions of $Fe(NO_3)_3$ and $MnCl_2$ were made from reagent grade solids (J.T. Baker, Inc.) and added to 50-mL polycarbonate Oak Ridge-type centrifuge tubes with the field-moist equivalent of 5.0 g oven-dried soil (105^oC) of each soil so that final concentrations of Fe^{3+} and Mn^{2+} were 0.2 mM. Then, 2.6 mL of 1,000 mg/L Cr(VI) stock solution and nanopure water was added for a total volume of 25 mL. The soils were shaken for 23 h, the P-buffer added and shaken for 1 h, and then 0.25 mL aliquots of centrifugate were diluted to 10 mL with distilled water and analyzed for Cr(VI) using the modified DPC method. Total soluble Cr, Fe, and Mn were determined by flame atomic absorption.

The second trial examined was with a synthetic Mn oxide-coated sand to evaluate possible reductive dissolution of Mn(III,IV)(hydr)oxides by tartaric acid. The synthetic Mn-oxide coated sand was prepared by using a wet oxidation procedure modified to precipitate the colloidal oxide onto a sand surface (Golden et al., 1986). The oxide was precipitated by adding 78 mL of 0.5 M $MnCl_2$ and 97 mL of 5.5 M NaOH to 500 g of acid-washed quartz sand in a crystallization dish. The mixture was placed in a drying oven at 44 °C for 120 h. Sand/salt solution mixtures were stirred periodically to prevent wicking of salts to the surface of the sand mixture. Prior to oxide synthesis, the quartz sand was acid washed in 1.0 M HNO_3 for 24 h. Tartaric acid, at pH 4.0, was added to centrifuge tubes containing 0, 10, 50 and 100 mg of the Mn-oxide coated sand. Then, 2.6 mL of 1,000 mg/L Cr(VI) stock solution and nanopure water was added for a total volume of 25 mL, and shaken for 48 h. Samples were centrifuged (10 minutes, 10,000 x *g*, 24^o C), and 0.25 mL aliquots of centrifugate was diluted to 10 mL with distilled water and analyzed for Cr(VI) using the modified DPC method. Total soluble Cr and Mn were determined by flame atomic absorption.

The third trial was the reduction of Cr(VI) by tartaric acid at pH 4.0 in aqueous solutions in the presence of Al^{3+}, Cr^{3+}, Ca^{2+}, Zn^{2+}, and Cu^{2+}. These metals represent trivalent and divalent metals found in soils, and were tested to see if they had an effect on the reduction of Cr(VI) by tartaric acid. Solutions for all metals were made from reagent grade solids to a concentration of 0.5 mM in 50 mL Erlenmeyer flasks. The samples were adjusted to pH 4.0, and 2.6 mL Cr(VI) stock solution and nanopure water was added to 50 mL Erlenmeyer flasks for a total volume of 25 mL. The samples were shaken for 144 h, and 0.25 mL aliquots of sample were diluted to 10 mL with distilled water and analyzed for Cr(VI) using the modified DPC method.

Results and Discussion

The control treatment (no soil) reduced 0.37 mM (19%) of the Cr(VI) in 99 h. This amount of Cr(VI) reduction was enhanced by addition of the soil samples, which ranged from 0.87 mM (44%) in the Atsion soil to 1.97 mM (99%) with the Russett soil (Figure 3-1A). The Atsion and Downer soils were significantly different from the no soil treatment ($p < 0.05$), but not from each other. Russett significantly reduced more Cr(VI) than Jackland, which reduced more than Collington. With no tartaric acid added, the Russett soil reduced 0.47 mM (25%) of the Cr(VI) at 99 h. The Collington reduced

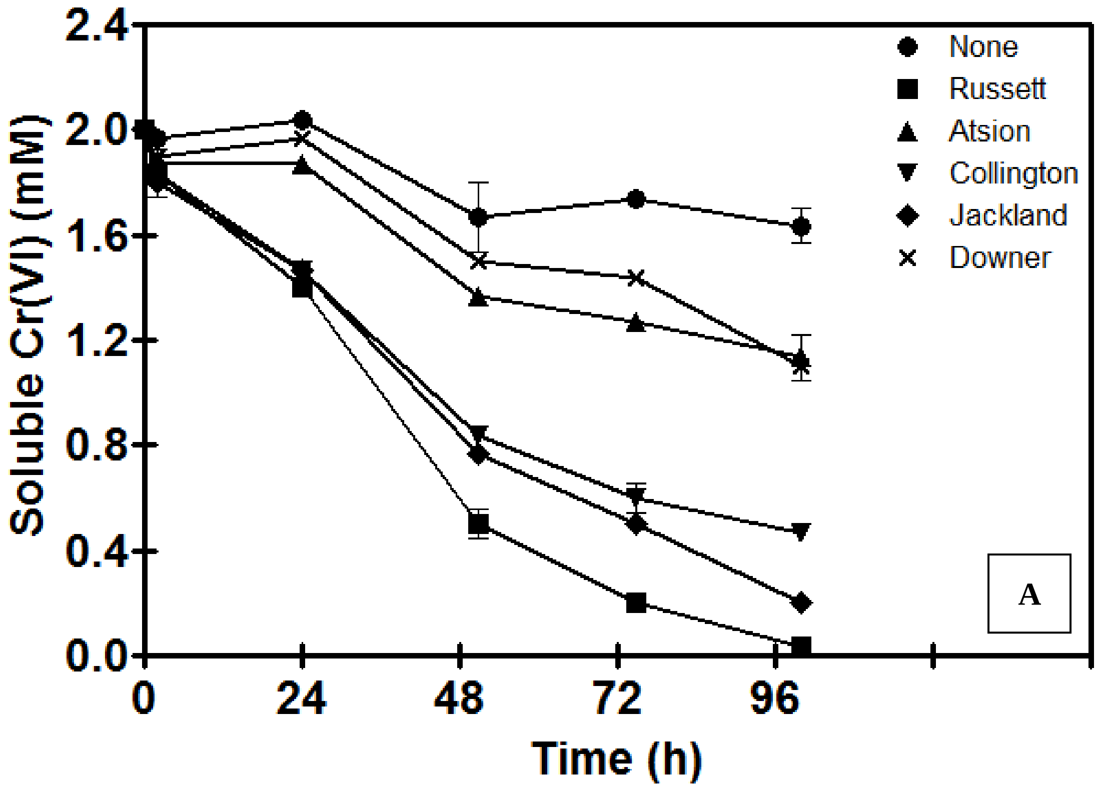


Figure 3-1 (A) Reduction of 2 mM soluble Cr(VI) by 12 mM tartaric acid and 0.29 M isopropyl alcohol (2% v/v) at pH 4 in the presence of five Maryland soils and one treatment without soil. With no tartaric acid or isopropyl alcohol added, the five soils (in same order presented in graph legend) reduced 0.47, 0.51, 0.77, 0.63, and 0.34 mM Cr(VI), respectively, after 99 h. Error bars are SEM (n=3).

the most Cr(VI) in the absence of tartaric acid and isopropyl alcohol at 0.77 mM (39%). The addition of tartaric acid and isopropyl alcohol enhanced the reduction of Cr(VI) over that which would occur with just the soil sample.

First-order rate constants were determined by fitting a linear regression through the natural log of the Cr(VI) concentrations over initial concentrations (C/C_o) against time for each soil with tartaric acid and isopropyl alcohol added. To determine if the differences between the slopes of these regression lines were statistically significant, analysis of covariance was conducted using SAS v9.2 with estimate statements to determine differences between each slope (Figure 3-1B).

Correspondingly, the differences in slopes corroborated the analysis of variance for differences between the soil effects at 99h, and so half-lives for Cr(VI) reduction from each of these soil treatments were calculated from the first-order rate constant ($t_{1/2} = 0.693/k$). The following ranking of the soils from most reducing to least with their half-lives resulted: Russett (18.7 h) > Jackland (34.1 h) > Collington (46.8 h) > Atsion (126 h) = Downer (140 h) > No Soil (371 h). As seen by the half-lives, the rate of reduction of Cr(VI) in the Russett soil sample was 20 times the rate of the sample with no soil.

If the pH of an aqueous solution containing tartaric acid, isopropyl alcohol, and Cr(VI) but with no soil is raised from 4.0 to 5.0, reduction is inhibited and the amount of Cr(VI) reduced would be negligible. In the present soil systems, however, reduction was not inhibited when pH reached as high as 5.3 in the Jackland soil sample (Figure 3-2). The pH of the Russett soil sample rose to 5.0, and yet 99% of the Cr(VI) was reduced by 99 h. Although the rate of reduction of Cr(VI) by the tartaric acid-Cr-isopropyl alcohol

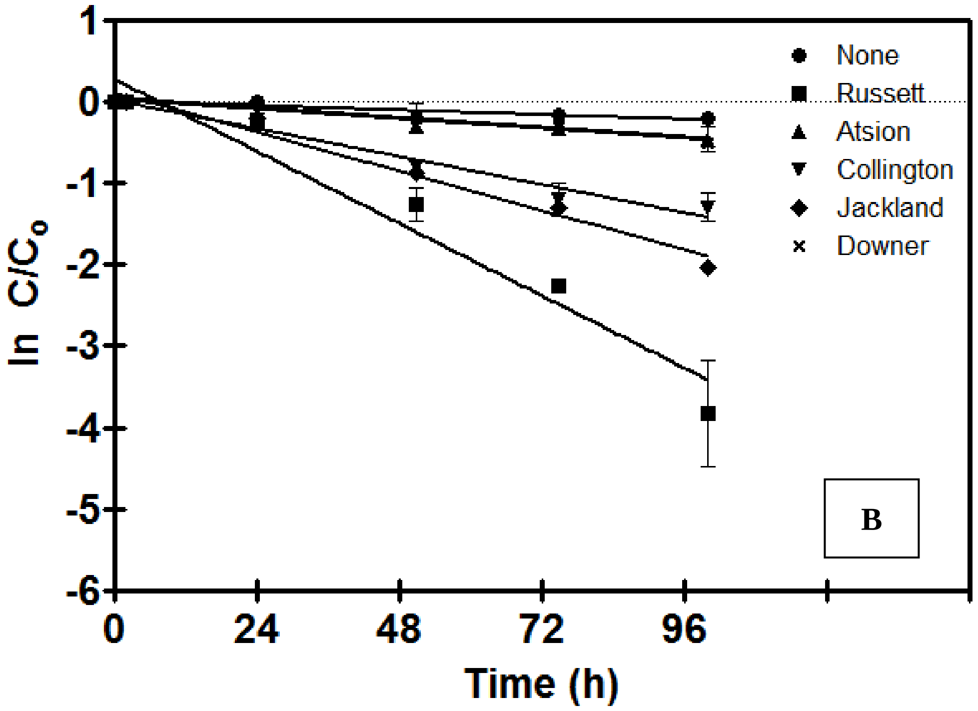


Figure 3-1 (B) Natural log of soluble Cr(VI) concentrations over initial concentrations (C/C$_o$) fit with linear regressions to determine first-order rate constants as slope of regression line.

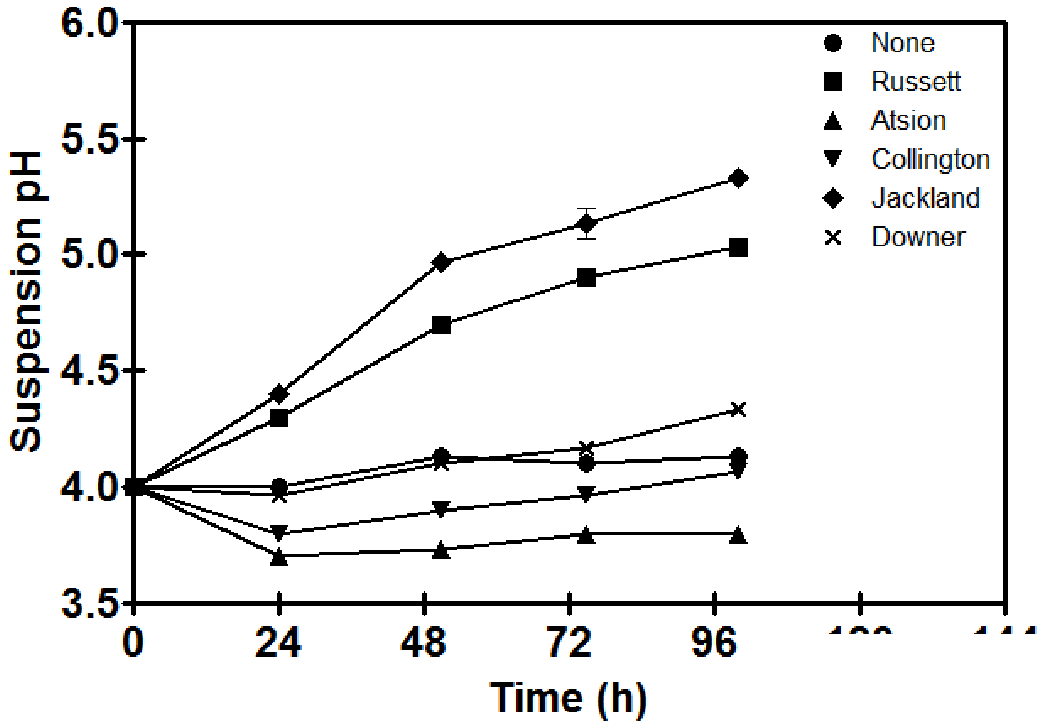


Figure 3-2 Change in pH with reduction of 2 mM Cr(VI) by 12 mM tartaric acid and 0.29 M isopropyl alcohol (2% v/v) at pH 4 in the presence of five Maryland soils and a no soil treatment. Error bars are SEM (n=3).

complex is fastest at low pH values, the reaction continued to proceed in the presence of the Russett and Jackland soils, even while pH values approached or exceeded 5.0.

This high pH inhibitory effect may have been overcome by Fe^{2+} or Mn^{2+} solubilized from Fe(III)- and Mn(III)(IV)hydroxides in the soil samples by addition of the tartaric acid and isopropyl alcohol (Figure 3-3A and B). The Russett and Jackland samples had the greatest amount of Mn solubilized with 98 and 90 µM, respectively, at 99 h. The Downer sample had considerably lower soluble Mn at the end of the trial period with only 14 µM. Soluble Mn from the Atsion and Collington samples were negligible, each having less than 10 µM. Samples that did not have tartaric acid and isopropyl alcohol added had lower amounts of soluble Mn from the samples, with the Russett having the most at 5.7 µM and the Atsion soil having no soluble Mn after 99 h shaking.

Fe(III)(hydr)oxides were solubilized to an even greater extent, with the Collington and Russett samples having the most solubilized with 550 and 427 µM, respectively. Downer had lower soluble Fe with 207 µM. Samples that did not have tartaric acid and isopropyl alcohol added had lower amounts of soluble Fe from the samples, with Jackland having the most at 87 µM and the Atsion soil having the least at 7.7 µM. The solubilization of these metal(hydr)oxides may play a role in the enhanced soil effect and increase in pH seen in these samples. Equations 2-7 and corresponding log K values illustrate the thermodynamic potential for the reductive dissolution of soil Fe(III)- and Mn(III/IV)(hydr)oxides (James and Brose, 2012). The reduction of Cr(VI), for reference, falls between the Fe and Mn values:

Reduction Half Reaction	Log K	
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	13.0	(2)
$FeOOH + e^- + 3H^+ \longrightarrow Fe^{2+} + 2H_2O$	13.0	(3)
$1/2Fe_2O_3 + e^- + 3H^+ \longrightarrow Fe^{2+} + 3/2H_2O$	13.4	(4)
$1/2MnO_2 + e^- + 2H^+ \longrightarrow 1/2Mn^{2+} + H_2O$	20.8	(5)
ϒ-$MnOOH + e^- + 3H^+ \longrightarrow Mn^{2+} + 2H_2O$	25.4	(6)
$1/3HCrO_4^- + e^- + 4/3H^+ \longrightarrow 1/3Cr(OH)_3 + 1/3H_2O$	18.9	(7)

These equations show that protons are consumed in the reduction reactions and that the reduction of Mn(III/IV)(hydr)oxides would be more thermodynamically favorable than the reduction of Fe(III)(hydr)oxides. Taking equation 6 as an example, if tartaric acid and isopropyl alcohol reduce ϒ-MnOOH by the same complex as Cr(VI), then the overall reaction would consume 1.7 mol H^+ for every mol Mn(III) reduced (equation 8):

$$\underset{\text{(Tartaric Acid)}}{COOH(CHOH)_2COOH} + \underset{\text{(Isopropyl Alcohol)}}{CH_3CHOHCH_3} + 6\Upsilon\text{-}MnOOH + 10H^+ \rightarrow \quad (8)$$

$$\underset{\text{(Glyoxylic Acid)}}{HCOCOOH} + \underset{\text{(Acetone)}}{CH_3COCH_3} + 6Mn^{2+} + 2CO_2 + 11\,H_2O$$

The Russett soil resulted in 97.6 µM soluble Mn at 99 h, and attributing this reduction to the reaction in equation 8, as an example, would result in 1.6×10^{-1} mM H^+ consumed from solution. Unbuffered, this level of proton consumption would result in a pH close to 10; however, both tartaric acid and soil organic matter can contribute protons and buffer against increased alkalinity. This suggests, however, that the increase in pH may be

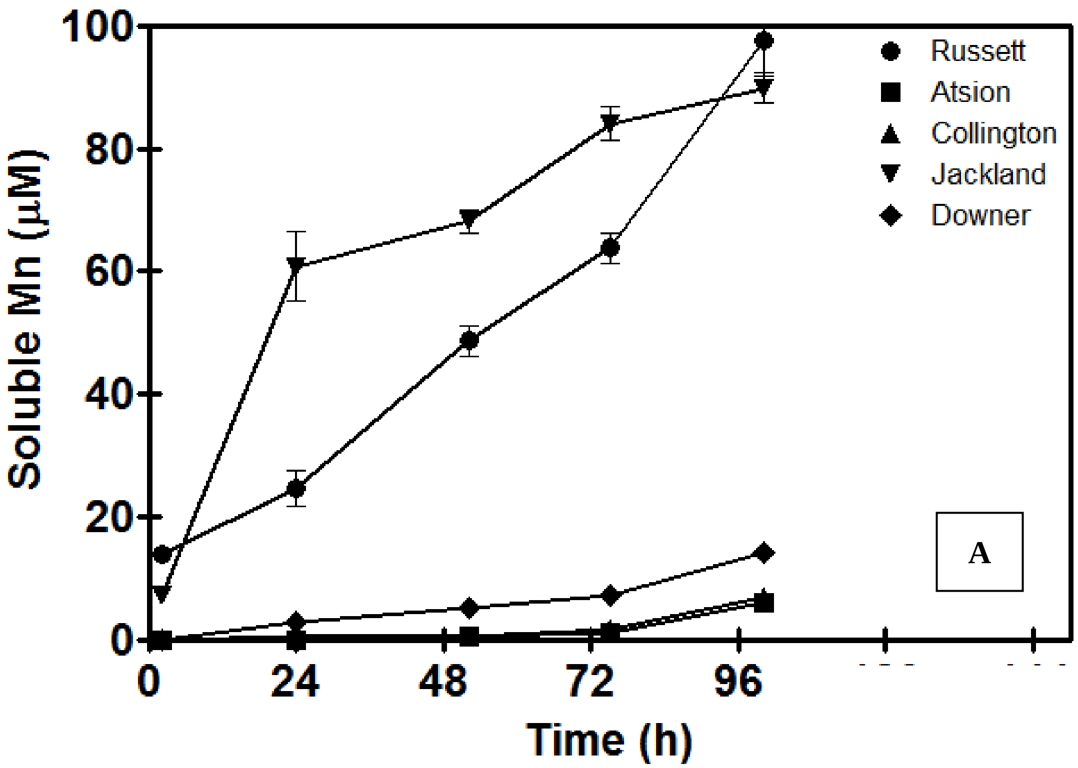


Figure 3-3 (A) Solubilization of Mn(III,IV)(hydr)oxides from five Maryland soils with reduction of 2 mM soluble Cr(VI) by 12 mM tartaric acid and 0.29 M isopropyl alcohol (2% v/v) at initial pH 4.0. Soil samples with no tartaric acid and isopropyl alcohol solubilized less Mn (in order presented in graph legend) at 5.6, 0.0, 1.2, 1.5, and 1.2 µM, respectively, at 99 h. Error bars are SEM (n=3).

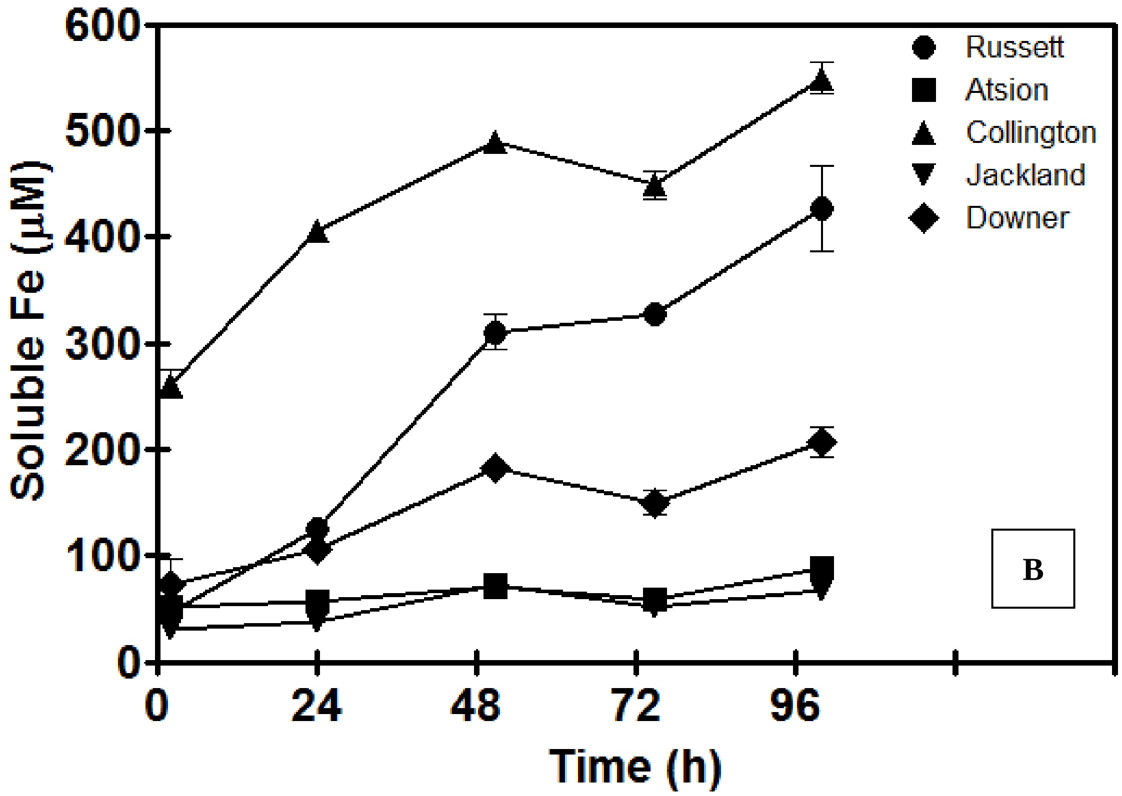


Figure 3-3 (B) Solubilization of Fe(III)(hydr)oxides from five Maryland soils with reduction of 2 mM soluble Cr(VI) by 12 mM tartaric acid and 0.29 M isopropyl alcohol (2% v/v) at initial pH 4.0. Soil samples with no tartaric acid and isopropyl alcohol solubilized less Fe (in order presented in graph legend) at 54, 7.7, 59, 87, and 22 µM, respectively, at 99 h. Error bars are SEM (n=3).

attributed to the dissolution of Fe(III)- and Mn(III/IV)(hydr)oxides, and that the resulting Mn(II) and to some extent, Fe(II), continued to enhance the reduction of Cr(VI).

When 200 µM Fe(III) was added to the five soil samples with 12 mM tartaric acid, 0.29 M isopropyl alcohol, and at pH 4.0, there was enhanced reduction seen in all soils, with Russett and Collington soils having the greatest enhanced effect over the soil effect, reducing an additional 0.57 mM and 0.58 mM Cr(VI), respectively (Table 3-2). When 200 µM Mn(II) was added to the soils under the same conditions (12 mM tartaric acid, 0.29 M isopropyl alcohol, and at pH 4.0), there was more of an enhanced reduction for all soils from the Mn treatment than the Fe treatment, with Russett and Downer reducing an additional 1.03 mM and 1.46 mM Cr(VI), respectively, more than the soil effect (Table 3-2). The Jackland and Russett soils have naturally higher levels of Mn(III,IV)(hydr)oxides than the other soils, which is illustrated when 2 mM Cr(III) is added to the soils and Cr(VI) is measured after 24 h shaking (Table 3-2). The Jackland Ap horizon soil samples oxidized 0.52 mM (27%) Cr(III) to Cr(VI). It does not appear that the Jackland soil oxidized the added Mn(II), as there was 200 µM soluble Mn still left in solution (data not shown); however, the Atsion sample had only 26 µM soluble Mn remaining in solution, suggesting that most of the added Mn oxidized as Cr(VI) was reduced and precipitated out of solution or else was removed from solution by sorption processes with the soil.

Table 3-2 Soluble Cr(VI) concentrations (mM) after 24 h shaking with no Mn^{2+} or Fe^{3+} added, with 0.20 mM Fe^{3+}, 0.20 mM Mn^{2+}, or 2.0 mM Cr^{3+} (conducted in separate experiment). Asterisks indicate significant treatment effects between the no added Fe^{3+} or Mn^{2+}, Fe^{3+}, and Mn^{2+} treatments within each soil (comparisons not made across soils) Errors are SEM (n=3).

Soil	**No added Mn or Fe**	**0.20 mM Fe^{3+}**	**0.20 mM Mn^{2+}**	**From 2.0 mM Cr^{3+}**
None	2.04 ± 0.01*	1.96 ± 0.03*	0.89 ± 0.00**	0.0 ± 0.0
Russett	1.40 ± 0.02*	0.83 ± 0.02**	0.37 ± 0.02***	0.04 ± 0.01
Atsion	1.84 ± 0.02*	1.68 ± 0.02**	0.97 ± 0.11***	0.0 ± 0.0
Collington	1.47 ± 0.03*	0.89 ± 0.05**	0.57 ± 0.02***	0.0 ± 0.0
Jackland	1.46 ± 0.02*	1.34 ± 0.02**	1.19 ± 0.02***	0.52 ± 0.18
Downer	1.96 ± 0.02*	1.67 ± 0.06**	0.50 ± 0.02***	0.0 ± 0.0

Further evidence is seen for the role of Mn(III/IV)(hydr)oxides enhancing the reduction of Cr(VI) by tartaric acid with the addition of 12 mM tartaric acid to Mn-oxide coated quartz sand (Figure 3-4). The total amount of Mn on the coated sand, assuming all added Mn^{2+} in solution oxidized and precipitated, was 1.8 x 10^{-1} µmol Mn/mg sand. The concentration of Cr(VI) decreased as soluble Mn increased linearly as the amount of sand increased from 10 to 100 mg. With 100 mg sand, 1.24 mM (62%) of the Cr(VI) was reduced and 41 µM soluble Mn remained in solution at the end of 48 h. If all Mn(III/IV)(hydr)oxides on 100 mg sand were to be solubilized, 720 µM soluble Mn would be present; thus, only 5.7% of the total amount of Mn came into solution. Total Cr remained relatively constant at 2 mM; however, at 100 mg sand there is a slight tapering

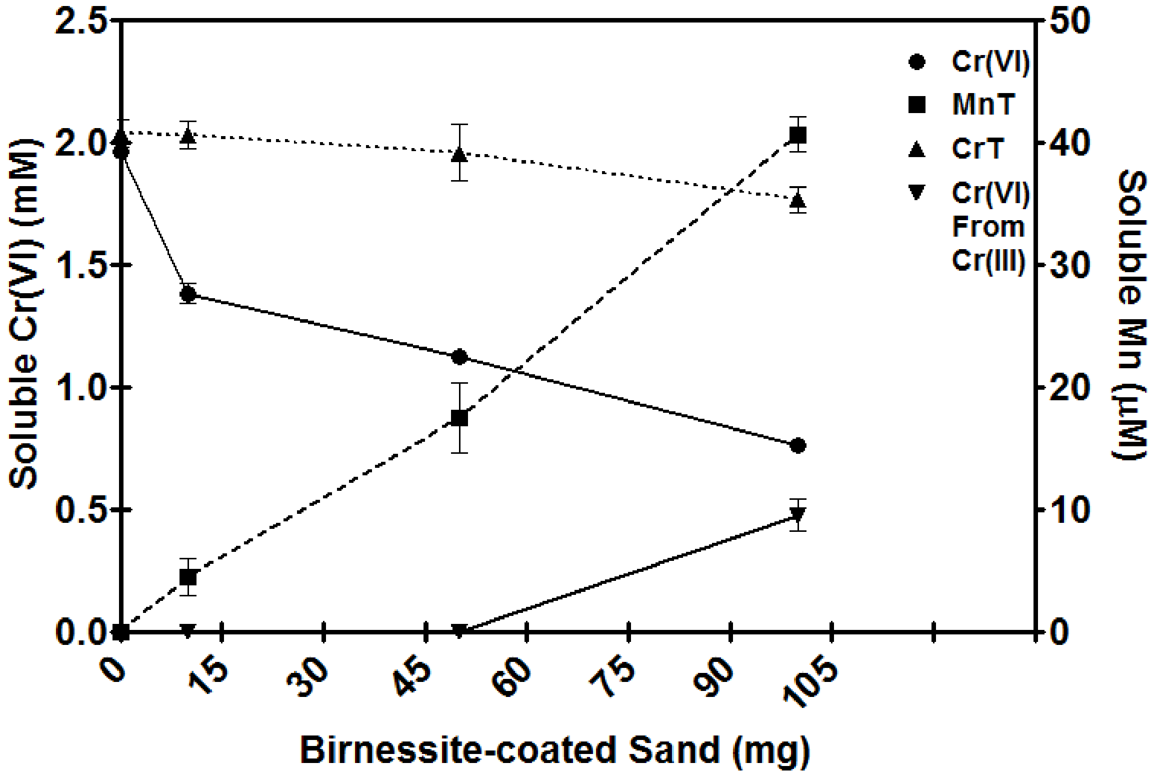


Figure 3-4 Reduction of 2 mM soluble Cr(VI) by 12 mM tartaric acid at pH 4.0 added to increasing amounts of Mn-oxide coated sand. Samples shaken for 24 h. Error bars are SEM (n=3).

in total Cr, likely due to the sorption of Cr(VI) or Cr(III)-organic complexes to the Mn-oxide coated sand.

The enhanced reduction of Cr(VI) by tartaric acid with the addition of Mn(II) was shown by Kabir-ud-Din et al. (2002) to be due to a complex formed by the esterification of tartaric acid with Cr(VI) and Mn(II) being bound to the tartaric acid. The bound Mn(II) donates one electron in an overall three-electron transfer process (equation 9):

$$\underset{\text{(Tartaric Acid)}}{\mathrm{COOH(CHOH)_2COOH}} + 2\mathrm{Mn^{II}} + 2\mathrm{HCrO_4^-} + 2\mathrm{H^+} \rightarrow \tag{9}$$

$$\underset{\text{(Glyoxylic Acid)}}{\mathrm{HCOCOOH}} + 2\mathrm{Mn^{III}} + 2\mathrm{CO_2} + 2\mathrm{Cr(OH)_3} + \mathrm{H_2O}$$

Tartaric acid donates four electrons and goes through two decarboxylation reactions, as it does when complexed with Cr and isopropyl alcohol, but in this case, two moles of Mn are required in the reduction of two moles Cr(VI). Manganese(II) was also demonstrated to be a catalyst in the reduction of Cr(VI) by citric acid (Li et al., 2007).

To assess the effect that other metals, other than Mn(III/IV)(hydr)oxides and Fe(III)(hydr)oxides, have on the reduction of Cr(VI) by tartaric acid and isopropyl alcohol, 0.5 mM Al^{3+}, Cr^{3+}, Ca^{2+}, Zn^{2+}, and Cu^{2+} was added to the tartaric acid and isopropyl alcohol system. These results showed that Cu^{2+} was the only other of these metals to also enhance the reduction of Cr(VI) (Figure 3-5). The addition of Cu^{2+} reduced 1.1 mM (55%) Cr(VI) in 144 h, which was less effective than Mn^{2+}, which reduced all 2 mM soluble Cr(VI) in 48 h.

The role of Cu^{2+} in the enhanced reduction of Cr(VI) is likely a different mechanism than through an organic-Cu complex. Pettine et al. (1998) showed the enhanced effects of different metals on Cr(VI) reduction by H_2S, including Cu^{2+}. It was

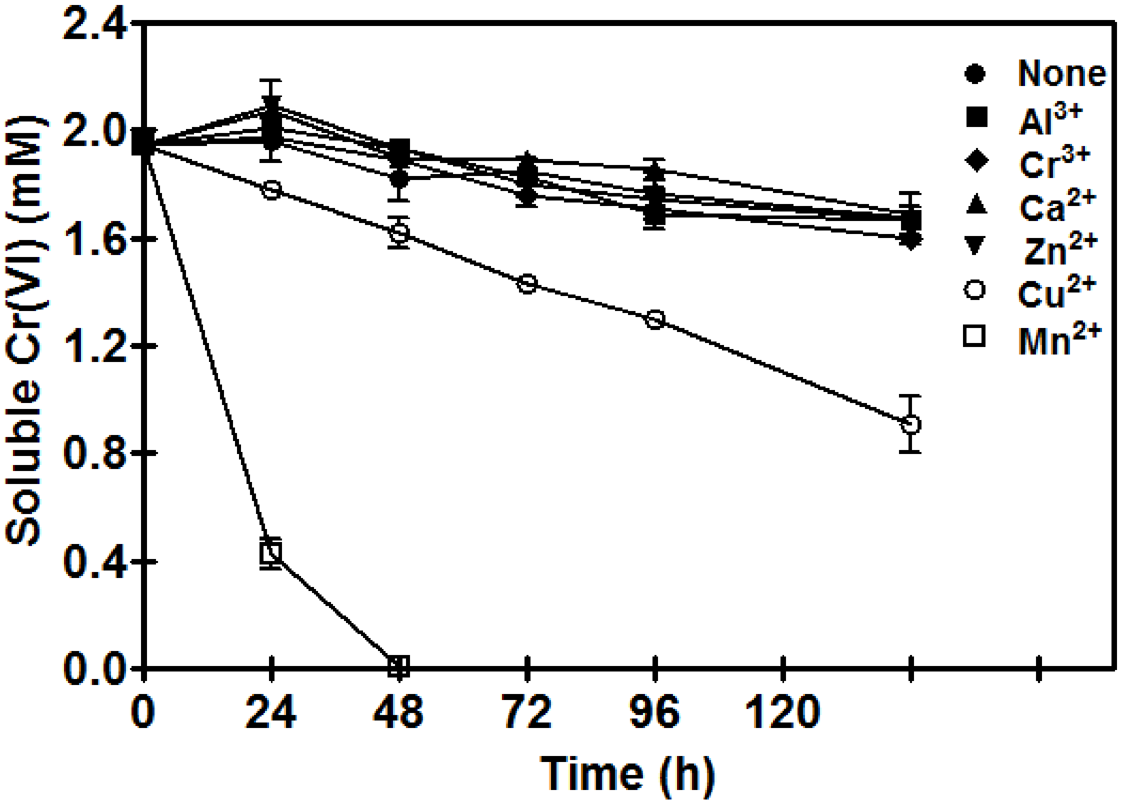


Figure 3-5 Reduction of 2 mM soluble Cr(VI) by 12 mM tartaric acid in the presence of different metals at pH 4.0. The only metals to enhance reduction were Cu^{2+} and Mn^{2+}. Error bars are SEM (n=3).

shown that Cu^{2+} and CrO_4^{2-} complexed to form $CuCrO_4$ and that this metal complex increased the availability of Cr(VI) to receive electrons from H_2S. In this same study, Mn^{2+} had no effect on enhancing reduction of Cr(VI) by H_2S, due to the weak formation of a Mn-Cr(VI) complex. This sheds light on the reaction in this study, due to the necessity for Mn^{2+} and tartaric acid to form a metal-ligand complex in order to be a reducing agent for Cr(VI). Furthermore, although some Cu^{2+} would be complexed by tartaric acid, the oxidation of Cu(II) to Cu(III) does not readily occur under ambient temperatures and pressure (Cotton and Wilkinson, 1980). Neither Al^{3+} nor Fe^{3+}, which are readily complexed by organic ligands, enhanced reduction of Cr(VI). The lack of enhanced reduction in the presence of these trivalent cations suggest that it is not just the complexation of tartaric acid with Mn^{2+} that is important, as it is also the donation of one electron from Mn^{2+}.

The addition of isopropyl alcohol to tartaric acid enhances the ability of this α-hydroxy carboxylic acid to reduce Cr(VI), but when applied to soils, this reduction is further enhanced. Tian et al. (2010) treated soils with hydrogen peroxide to destroy soil organic matter to demonstrate that the enhanced reduction from soils is related to a mineral phase in soils and not to reducing functional groups or organic acids in the soil organic matter, and postulated this enhanced reduction is attributable to the presence of Mn(III,IV)(hydr)oxides.

The favorable thermodynamic predictions and demonstration of catalytic behavior of Mn(II) suggests a mechanism where Mn(II) is solubilized by tartaric acid from easily reducible Mn(III,IV)(hydr)oxides in the soil and the resulting Mn(II) is able to complex with tartaric acid and Cr(VI) to enhance reduction. Additionally, the effectiveness of

Mn(II) in this system appears to be unique to Mn(II); although Cu(II) also enhances reduction, the effectives of Cu(II) is much less, and by a different mechanism, than that demonstrated by Mn(II). Complexation of metals to organic reducing agents will result in stronger acting reducing agents; for example, the reduction half reaction for Fe^{3+} to Fe^{2+} has a pe at pH 7 of 13.0, but when complexed to EDTA, this same reaction has a pe of 2.0 (James and Brose, 2012). This same reaction when complexed with ferritin, a ubiquitous, intracellular protein, has a pe of -3.2.

The complexation of Mn^{2+} with tartaric acid acts similarly in making tartaric acid a more effective reductant of Cr(VI). In remediation by reduction strategies in soils, there is concern that the reduction of Cr(VI) may be compromised by the presence of Mn(III/IV)(hydr)oxides, due to their ability to re-oxidize Cr(III) to Cr(VI). By this Mn(II)-tartaric acid complex and mechanism, the inherent ability of Mn(II) to enhance the effectiveness of reduction of Cr(VI) by tartaric acid would be beneficial to the treatment of Cr(VI)-contaminated soils. As a solution of tartaric acid and isopropyl alcohol is applied to Cr(VI) contaminated soil, either *in-situ* or removed for treatment, the tartaric acid and isopropyl alcohol would reduce Cr(VI) to Cr(III), while at the same time reduce Mn(III/IV)(hydr)oxides to Mn(II), which will further enhance reduction of Cr(VI).

As seen in this work, the total amount of Cr remained soluble at pH values close to 5.0, indicating that newly reduced Cr^{3+} was not precipitating out of solution. The continued solubility of Cr in solution suggests that tartaric acid is complexing with the Cr^{3+} upon reduction, and remaining soluble as an organic-metal complex. Kantar et al. (2008) showed that new reduced Cr^{3+} was bound by galacturonic and glucuronic acids added to soil columns as reducing agents, and that sorption processes delayed breakthrough of the Cr from the columns. This suggests that as tartaric acid reduces Cr(VI), it is complexing Cr^{3+} and in the presence of soil, will immobilize the movement of Cr in the environment, further making the use of tartaric acid and isopropyl alcohol a potential soil remediation strategy.

CHAPTER 4

REDUCTION OF HEXAVALENT CHROMIUM FROM CHROMITE ORE PROCESSING RESIDUE (COPR) WITH TARTARIC ACID, ISOPROPYL ALCOHOL AND DIVALENT MANGANESE

Introduction

Chromite ore processing residue (COPR), the remaining solid waste product from the processing of ferrochromite ($FeO{\bullet}Cr_2O_3$), contains variable amounts of unreacted ore and soluble and insoluble forms of Cr(VI), and is a persistent source of Cr(VI) contamination in notable locations such as Baltimore, Maryland; Hudson County, New Jersey; and Glasgow, Scotland (Burke et al., 1991; Darrie, 2001; Deakin et al., 2001). COPR has also been used as fill material for construction purposes because of its resemblance to a sandy soil; however, residual Cr(VI) can persist as a potential pollutant of soils, air, and groundwater from this soil-like material. For example, in Hudson County, New Jersey it was used to fill wetlands and poorly-drained landscapes for use in industrial activity and development during the twentieth century (James, 1996).

Although COPR will vary in mineralogical and chemical properties from location to location, there are some commonalities of mineralogical properties important to understanding the chemical behavior of COPR during reduction processes. For example, the most abundant metals other than Cr found in COPR samples are Ca, Mg, Fe, and Al (Chrysochoou et al., 2010). Additionally, Hillier et al. (2003) described three main categories of mineral compositions in COPR samples. The first is chromite, a relic of the chromite ore. The second category consists of minerals formed at the high temperatures during the roasting process, such as brownmillerite and periclase, and the third category of minerals includes ones that are presumed to have formed after COPR has been deposited and exposed to more natural conditions, such as the leaching of elements with the influx of water. Although there are many different minerals that can be assigned to these three categories, there are four common minerals in COPR that have been found to substitute Cr(VI) for Fe or Al in their structures: brownmillerite ($Ca_2(Fe,Al)_2O_5$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\bullet}26H_2O$), hydrocalumite ($Ca_2(Al,Fe)(OH)_6(OH)\ {\bullet}3H_2O$), and hydrogarnet ($Ca_3(Al,Fe)_2(H_4O_4)_3$) (Chrysochoou et al., 2010; Hillier et al., 2003). Additionally, up to 30% of the mineralogical makeup of COPR can be paracrystalline in structure (Hillier et al., 2003).

Current remediation practices for COPR use either an Fe- or S-based reducing agent, with the former resulting in concretions or clogging of pores with oxidized Fe minerals formed as Cr(VI) is reduced to Cr(III), and the latter resulting in delayed ettringite ($Ca_6Al_2(SO_4)_3{\bullet}32H_2O$) formation, which results in extensive swelling and buckling of paved surfaces when used as fill material for roads (Dermatas et al., 2006; Ludwig et al., 2008). In contrast to these reducing agents, this research will investigate for the first time the potential use of tartaric acid in combination with Mn(II) and isopropyl alcohol as an effective alternative to Fe- or S-based reducing agents in the reduction of COPR derived Cr(VI).

The reduction of Cr(VI) by tartaric acid at pH 5.0 or greater is negligible over the course of several days to weeks; however, in the presence of Mn(II) or isopropyl alcohol, reduction is enhanced to hours. The enhanced reduction of tartaric acid by the addition of Mn(II) was shown by Kabir-ud-Din et al. (2002) to be due to a complex formed by an esterification reaction with tartaric acid and Cr(VI) while Mn(II) is bound to tartaric acid.

The bound Mn(II) donates one electron to the single step three-electron transfer to Cr(VI). The full reaction is shown in equation 1:

$$\underset{\text{(Tartaric Acid)}}{COOH(CHOH)_2COOH} + 2Mn^{II} + 2HCrO_4^- + 2H^+ \rightarrow \qquad (1)$$

$$\underset{\text{(Glyoxylic Acid)}}{HCOCOOH} + 2Mn^{III} + 2CO_2 + 2Cr(OH)_3 + H_2O$$

Tartaric acid in isopropyl alcohol will also enhance the reduction of Cr(VI) due to the formation of a single termolecular complex that forms from the esterification of the alcohol and organic acid with Cr(VI) (Westheimer and Novick, 1943; Hasan and Rocek, 1973; Mahapatro et al., 1980). An instantaneous three-electron transfer results in the oxidation of both the alcohol and organic acid, yielding acetone and glyoxylic acid, respectively from the decarboxylation of tartaric acid (Kabir-ud-Din et al., 2002). The stoichiometry of the reaction results in two moles Cr(VI) reduced for every one mole tartaric acid and isopropyl alcohol, as shown in equation 2:

$$\underset{\text{(Tartaric Acid)}}{COOH(CHOH)_2COOH} + \underset{\text{(Isopropyl Alcohol)}}{CH_3CHOHCH_3} + 2HCrO_4^- \rightarrow \qquad (2)$$

$$\underset{\text{(Glyoxylic Acid)}}{HCOCOOH} + \underset{\text{(Acetone)}}{CH_3COCH_3} + 2CO_2 + 2Cr(OH)_3 + H_2O$$

The application of a treatment consisting of isopropyl alcohol and Mn(II) added to tartaric acid could be an effective remediation-by-reduction strategy, which is a soil clean-up strategy that can be used in an attempt to mitigate the toxic effects of Cr(VI) and clean up Cr contaminated sites to meet regulatory standards and protect human health (James, 1996). Neither the tartaric acid-Mn nor the tartaric acid-isopropyl alcohol complex has been applied as a reduction treatment to COPR or COPR-contaminated soils, so the current work will investigate the reduction of COPR-derived Cr(VI) by each of these complexes as well as in combination in order to assess the potential synergistic effect between the two complexes. These complexes will be assessed in solution as well as with COPR and in a soil-COPR mixture using five Maryland soils.

Materials and Methods

COPR Chromite ore processing residue (COPR) has been stored in the dark in a plastic bucket at room temperature (22 ± 2° C). This COPR material comes from Kearny, NJ at a site called Diamond Shamrock on the Belleville Turnpike, and has approximately 1,200 mg total Cr(VI)/kg COPR, 800 mg soluble Cr(VI)/kg COPR, and is alkaline with a pH of approximately 8.0.

Soils Soil horizons from Maryland, USA were sampled from profiles located in delineations of five different mapping units as part of a larger sampling scheme to collect soil profiles for research purposes. The horizons sampled from the soil profile in the Askecksy unit was similar to the Atsion series (sandy, siliceous, mesic, Aeric Alaquod), the profile from the Russett- Christiana Complex unit was similar to the Russett series (fine-loamy, mixed, semiactive, mesic Typic Hapludult), the profile from the Annapolis unit was similar to the Collington series (fine-loamy, mixed, active, mesic Typic Hapludult), the profile from the Ingleside unit was similar to the Downer series (coarse-loamy, siliceous, semiactive, mesic Typic Hapludult), and the profile sampled from the

Jackland mapping unit was similar to the Jackland series (fine, smectic, mesic Aquic Hapludalf).

The Ap or A horizon (surface horizon) of each soil was used, except for the Atsion soil, a Spodosol, where the E horizon (eluviated horizon) was used instead. This E horizon was overlain by an O/A horizon, which consisted of partially degraded and fresh forest litter. Soil characterization data are summarized in Table 4-1 and full sampling information and characterization data are available in Appendix B.

Table 4-1 Characterization data for soils. CBD refers to a citrate-dithionite extraction.

Soil	**Texture (% sand, silt, clay)**	**Field pH**	**Eh (mV)**	**Organic Carbon (g/kg)**	**CBD Fe (g/kg)**	**CBD Mn (g/kg)**
Russett	Sandy loam (58, 37, 5.8)	5.0	577	25 ± 0.1	4.1 ± 0.3	0.3 ± 0.0
Atsion	Sandy (94, 5.9, 0.1)	3.5-4.0	524	20 ± 0.4	0.1 ± 0.0	0.0 ± 0.0
Collington	Loamy sand (83, 14, 3)	4.0	606	37 ± 0.0	3.0 ± 0.4	0.0 ± 0.0
Jackland	Silt loam (35, 57, 8)	6.0	470	9.0 ± 0.1	6.3 ± 0.3	1.0 ± 0.0
Downer	Loamy sand (75, 21, 4)	5.5	490	3.1 ± 0.1	1.5 ± 0.4	0.1 ± 0.0

Solution Analysis Four sets of treatments at two acidity levels, pH 4.0 and 5.5, were established: Tartaric acid (12 mM), made fresh from reagent grade salts, with no other amendments; tartaric acid and isopropyl alcohol at 2% v/v (0.29 M) from 99% pure, reagent grade alcohol stored at room temperature; tartaric acid and 1 mM Mn^{2+} solution from reagent grade $MnCl_2$; and the fourth had tartaric acid, isopropyl alcohol, and Mn added. All samples were brought to a total volume of 25 mL with nanopure water (18 MΩ) in 50 mL Erlenmeyer flasks, and adjusted to pH 4.0 or 5.5 with 0.1M NaOH. To initiate the reaction, Cr(VI) solution was added, made up from reagent grade K_2CrO_4 for a final concentration of 1 mM Cr(VI). All sample solutions included 0.01 M $NaNO_3$ as a background electrolyte to control for ionic strength. Samples were shaken at 50 rpm on an orbital shaker, and aliquots were taken at 2, 24, 48, 72, and 96 h for Cr(VI) analysis spectrophotometrically by the DPC method (Bartlett and James, 1979) and total soluble Cr and Mn analysis on flame atomic adsorption. Solution pH was measured potentiometrically at each sampling time.

Solution and COPR Analysis Tartaric acid (12 mM) made up in 0.2 M (low acidity) or 0.5 M (high acidity) HNO_3 was added to 50 mL Oak Ridge-type centrifuge tubes containing 1.63 g COPR material (equivalent to 1 mM soluble Cr(VI)). Three sets of treatments at each level of acidity (low/high) were established; one set had isopropyl alcohol at 2% v/v (0.29 M), another had 1 mM Mn(II) solution added, and the third set had both isopropyl alcohol and Mn added to the samples. All samples were brought to a total volume of 25 mL with nanopure water. All sample solutions included 0.01 M $NaNO_3$ as a background electrolyte to control for ionic strength. Sample pH was taken potentiometrically at 2, 24, 48, 72, and 96 h, and at each sampling time an additional 10 µL concentrated HNO_3 was added to the low acidity sample set and 50 µL was added to the high acidity set in attempt to maintain the different pH levels. Samples were centrifuged (10 minutes, 10,000 x *g*, 24^{o} C) and 0.25 mL aliquots of centrifugate was diluted to 10 mL for Cr(VI) and total soluble Cr and Mn analysis as previously described.

Soil and COPR Analysis The field-moist equivalent of 5.0 g oven-dried soil (105^{o}C) of each soil was weighed into 50-mL polycarbonate Oak Ridge-type centrifuge tubes. To simulate Cr-contaminated soils, each sample had 1.63 g COPR added (equivalent to 1 mM soluble Cr(VI) in the equilibrium solution). The tartaric acid solution was made up in 0.5 M HNO_3 and added to three sets of the soil/COPR mixtures. One set had isopropyl alcohol at 2% v/v (0.29 M), another had 1 mM Mn^{2+} solution added, and the third set had both isopropyl alcohol and Mn added to the samples. All samples were brought to a total volume of 25 mL with nanopure water. All sample solutions included 0.01 M $NaNO_3$ as a background electrolyte to control for ionic strength. Samples were shaken for 48 h. Solution pH was measured at one hour remaining in the sampling time, at which point 0.25 mL of a 1 M KH_2PO_4/K_2HPO_4 buffer solution (pH 7.2) was added. The centrifuge tubes were re-capped and shaken for the remainder of time. The purpose of the P buffer was to displace exchangeable Cr(VI) from the soil and ensure that any loss of Cr(VI) can be attributable to reduction and precipitation processes, and not to sorption of Cr(VI) to colloidal surfaces. Samples were centrifuged (10 minutes, 10,000 x *g*, 24^{o} C), and 0.25 mL aliquots of centrifugate was diluted to 10 mL and analyzed for Cr(VI) and total soluble Cr and Mn as described above. Data were analyzed and statistical differences reported using analysis of variance or analysis of covariance with Statistical Analysis Software (SAS) v9.2.

USEPA SW-846 Method 3060A Following 48 h shaking for COPR/soils and 96 h for COPR, USEPA SW-846 Method 3060A was performed on all samples. This method is an alkaline digestion procedure for extracting Cr(VI) from soluble, adsorbed, and precipitated forms of chromium compounds in soils, sludges, sediments, and similar waste materials (EPA, 1982). The sample is digested using a 0.28M Na_2CO_3 /0.5M NaOH solution and heating at 90-95 °C for 60 minutes to dissolve Cr(VI) and stabilize it against reduction to Cr(III). Following the extraction, the digestate is diluted to 100 mL and mixed uniformly. A 25 mL aliquot is taken, centrifuged and diluted, as previously described, and analyzed for Cr(VI) using the DPC method and total Cr using flame atomic absorption.

Results and Discussion

Solution systems The two samples with 1 mM Cr(VI)-salt solution and tartaric acid/Mn and tartaric acid/Mn/isopropyl alcohol at pH 4 were most effective, reducing all Cr(VI) in 48 h (Figure 4-1A, Table 4-2). The corresponding treatments at pH 5.5 only reduced 0.6 mM Cr(VI) (60%) at 96 h, demonstrating that pH is a major determinant of the extent of Cr(VI) reduction. The tartaric acid/Mn and tartaric-acid/Mn/isopropyl alcohol treatments at both pH levels were not significantly different (p-value < 0.05) in analysis of variance, demonstrating that Mn contributes more to the reduction than the isopropyl alcohol, and furthermore, that having both Mn and alcohol in solution does not result in any synergistic effects. The tartaric acid/isopropyl alcohol treatments at pH 4.0 and 5.5 were significantly different from each other, with the samples at pH 4.0 reducing 0.44 mM (44%) of the Cr(VI) and at pH 5.5 reducing only 0.1 mM (10%) (Figure 4-1A, Table 4-2). The pH for the samples stayed within 0.1 unit of initial pH values, except for the treatments at pH 5.5 with isopropyl alcohol, which increased to pH 5.8 and 6.0 (Table 4-2).

The first-order rate constants were determined by fitting a linear regression through the natural log of the Cr(VI) concentrations over initial concentration (C/C_o) as a function of time for each treatment (Figure 4-1B, Table 4-2). Analysis of covariance was

Table 4-2 Values from Cr-solution and COPR samples (non-soil) for final pH, final concentration soluble Cr(VI), first-order rate constant where applicable, half-life from rate constant, r^2 for first-order regression line, significant differences between first-order slopes at $p<0.05$, and final concentration soluble Mn. Isopropyl alcohol = IPOH, low acidity = 0.2 M HNO_3 and high acidity = 0.5 M HNO_3.

Treatment	pH at 96 h	Cr(VI) at 96 h (mM)	First-order rate constant (h^{-1})	Half-life (h)	r^2	Sig. Difference between Half-lives	Mn at 96 h (mM)
pH 4	4.1 ± 0.0	0.8 ± 0.08	k=0	N/A	0.26	*	0.0 ± 0.0
pH 5.5	5.5 ± 0.0	1.1 ± 0.05	k=0	N/A	0.02	*	0.0 ± 0.0
pH 5.5/IPOH	5.8 ± 0.0	0.9 ± 0.01	k=0	N/A	0.23	*	0.0 ± 0.0
pH 4/IPOH	4.0 ± 0.1	0.5 ± 0.04	-0.008	88.6	0.79	**	0.0 ± 0.0
pH 5.5/Mn	5.4 ± 0.1	0.4 ± 0.01	-0.010	69.3	0.92	***	0.9 ± 0.01
pH 5.5/Mn/IPOH	6.0 ± 0.1	0.4 ± 0.01	-0.010	69.3	0.94	***	0.9 ± 0.03
pH 4/Mn	4.1 ± 0.0	0.0 ± 0.0	-0.067	10.2	0.97	****	0.9 ± 0.01
pH 4/Mn/IPOH	4.1 ± 0.0	0.0 ± 0.0	-0.068	10.3	0.95	****	0.9 ± 0.01
Low acidity/Mn	6.3 ± 0.1	0.9 ± 0.01	k=0	N/A	0.22	†	0.3 ± 0.01
Low acidity/IPOH	6.2 ± 0.1	0.9 ± 0.02	k=0	N/A	0.22	†	0.0 ± 0.0
Low acidity/Mn/IPOH	6.3 ± 0.1	0.9 ± 0.02	-0.001	693	0.46	††	0.3 ± 0.0
High acidity/IPOH	5.7 ± 0.1	0.7 ± 0.07	-0.005	139	0.86	†††	0.0 ± 0.0
High acidity/Mn	5.9 ± 0.2	0.7 ± 0.02	N/A	N/A	0.61	N/A	0.4 ± 0.03
High acidity/Mn/IPOH	5.8 ± 0.1	0.5 ± 0.02	N/A	N/A	0.79	N/A	0.5 ± 0.0

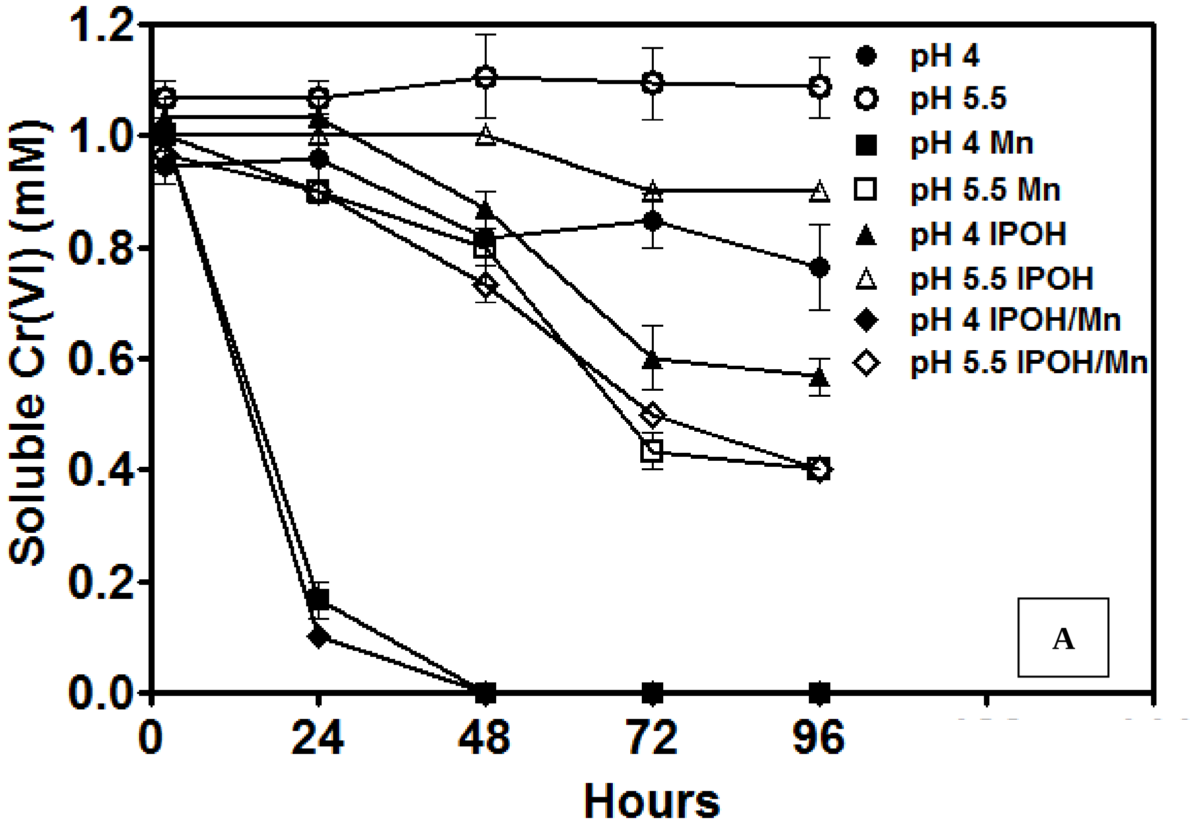


Figure 4-1 (A) Reduction of 1 mM soluble Cr(VI) with 12 mM tartaric acid and 0.29 M isopropyl alcohol (2% v/v), 1 mM Mn^{2+}, or combination of both at pH 4 or 5.5. Error bars are SEM (n=3).

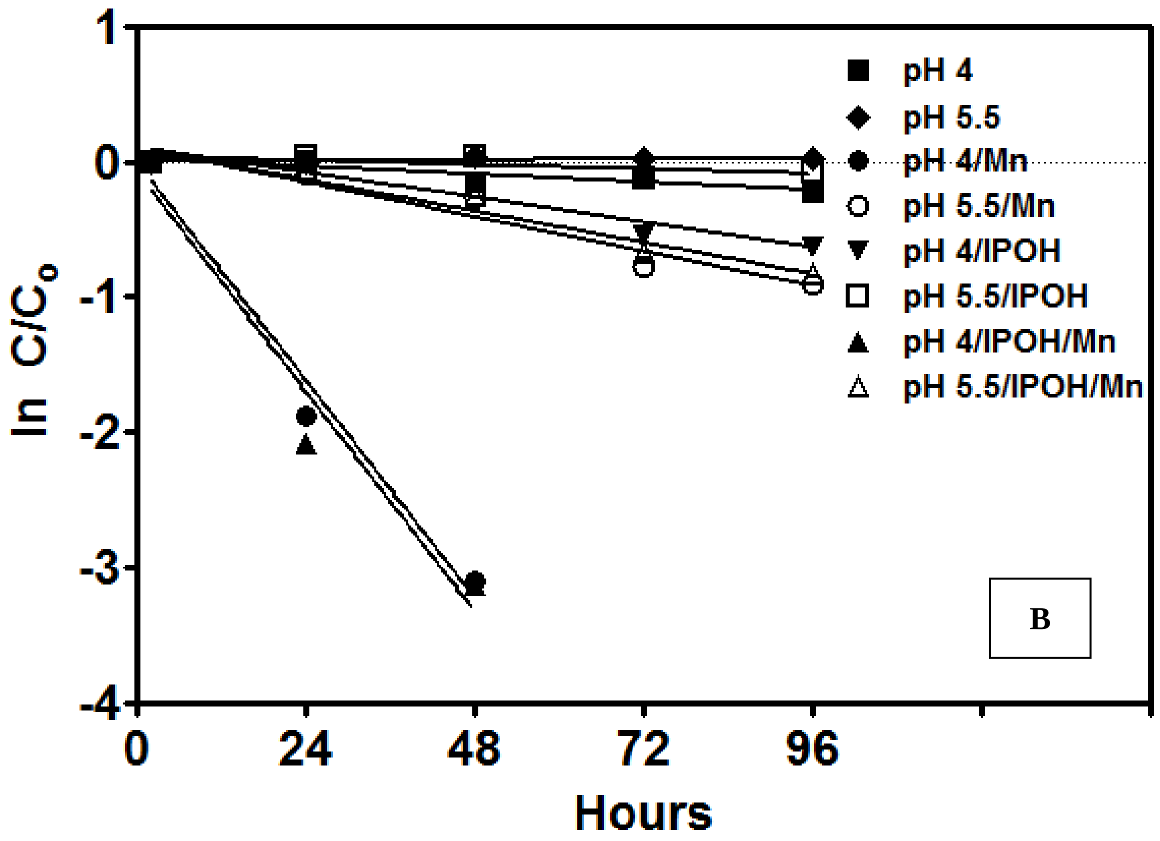


Figure 4-1 (B) Natural-log of soluble Cr(VI) concentrations over initial concentrations (C/C_o) to determine first-order rate constants as slope of the regression lines. Error bars are SEM (n=3).

used to test significant differences between slopes for each treatment. Half-lives for Cr(VI) reduction from each of the treatments were calculated from the first-order rate constants ($t_{1/2} = 0.693/k$) (Table 4-2). The Mn and Mn/isopropyl alcohol treatments at pH 4 had a half-life of 10.4 h, which was the lowest half-life. In comparison, the sample with isopropyl alcohol at pH 4 had the highest half-life at 89 h. The samples at pH 4 and 5.5 without any amendments and the isopropyl alcohol treatment at pH 5.5 all had slopes that were not significantly different than zero, and so no rate constants or half-lives were determined for these samples (Table 4-2).

COPR Systems Sample pH also played a strong role in determining the extent of Cr(VI) reduced in the samples with COPR-derived Cr(VI) . The pH increased for all sample treatments in the initial 24 h, but from 24 to 96 h, the pH decreased to approximately 5.7 for the high acidity sets and 6.2 for the low acidity sets (Figure 4-2, Table 4-2). These higher pH values resulted in less Cr(VI) being reduced than in the Cr-salt solution systems. The most Cr(VI) reduced was by the Mn/isopropyl alcohol treatment at high acidity, which reduced 0.5 mM (50%) of the soluble Cr(VI) at 96 h (Figure 4-3A, Table 4-2). This same treatment had 0.9 mM Cr(VI) at 24 h, and at 96 h had 0.9 mM total Cr in solution, indicating that nearly all the soluble fraction of Cr(VI) comes into solution within the first 24 h. COPR samples with no tartaric acid or isopropyl alcohol also solubilized 1.1 mM Cr(VI) at 96 h. The three treatment sets at low acidity were not statistically significant from each other ($p\text{-value} < 0.05$), and reduced approximately 0.1 mM (10%) of the solubilized Cr(VI) (Figure 4-3A, Table 4-2).

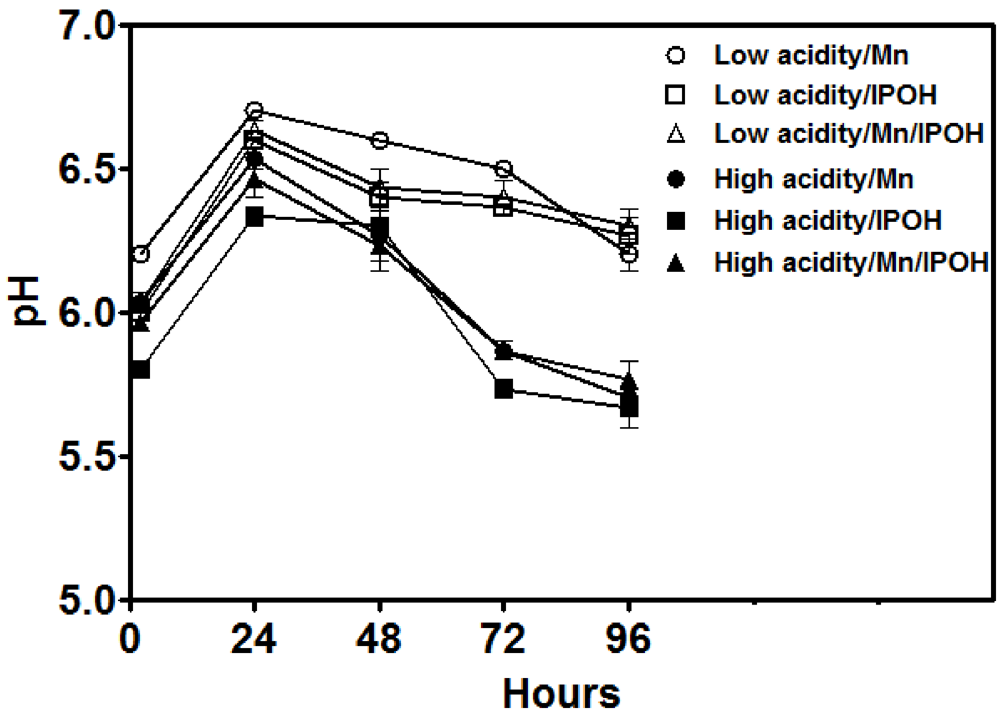


Figure 4-2 Change in pH with reduction of COPR-derived Cr(VI) at two acidity levels, 0.2 M (low) or 0.5 M (high) HNO_3 and with 12 mM tartaric acid and 0.29 M isopropyl alcohol (2% v/v), 1 mM Mn^{2+}, or combination of both. Error bars are SEM (n=3).

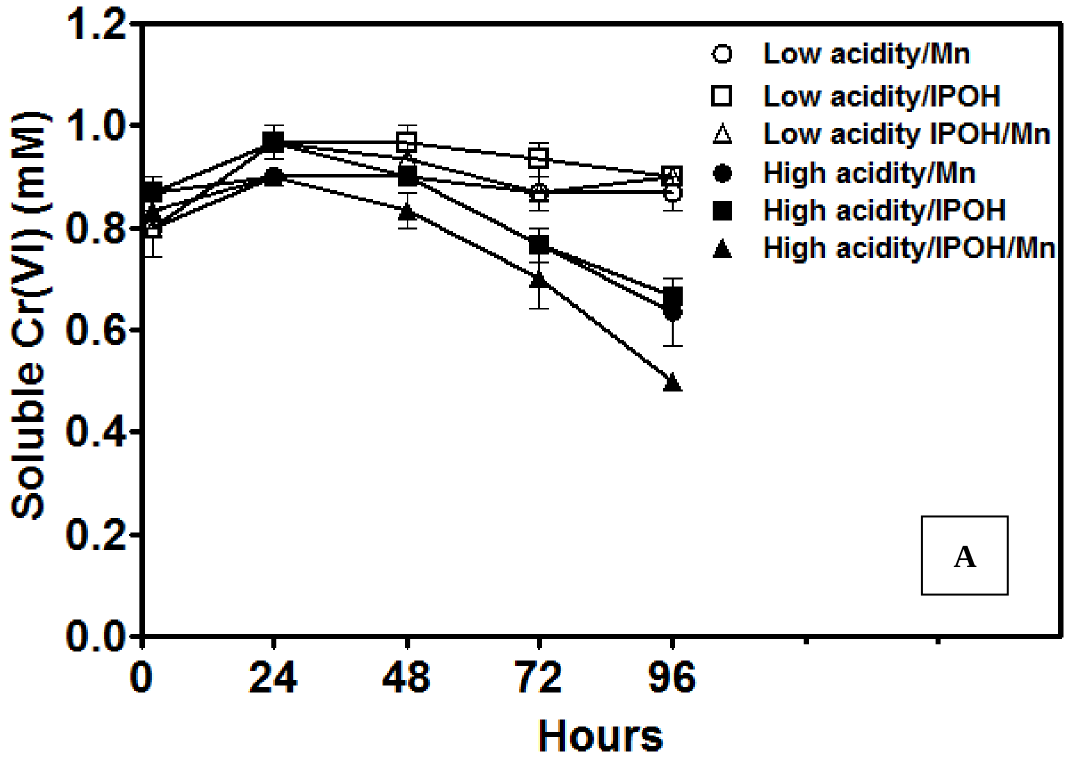


Figure 4-3 (A) Reduction of COPR-derived Cr(VI) at two acidity levels, 0.2 M (low) or 0.5 M (high) HNO_3, and 12 mM tartaric acid and 0.29 M isopropyl alcohol (2% v/v), 1 mM Mn^{2+}, or combination of both. Samples with no tartaric acid or isopropyl alcohol solubilized 1.1 mM Cr(VI) at 96 h. Error bars are SEM (n=3).

From 2 to 24 h, Cr(VI) increased for all treatments as Cr(VI) was continually solubilized. The natural log of the Cr(VI) concentrations over initial concentrations (C/C_o) as a function of time was plotted for all treatments from 24 to 96 h. Only the low acidity treatments and the high acidity treatment with isopropyl alcohol fit the first-order rate equation (Figure 4-3B). The data for the high acidity treatments with Mn and Mn/isopropyl alcohol did not fit first-order or second-order rate equations. For the samples fitted with first-order rate equations, the low acidity Mn and isopropyl alcohol treatments did not have a slope that was significantly greater than zero ($p<0.05$). Only half-lives for the low acidity treatment with Mn/isopropyl alcohol and the high acidity treatment with isopropyl alcohol were calculated, resulting in 693 and 139 h, respectively (Table 4-2). These half-lives demonstrate that although some reduction occurs in the pH range 5.0 – 6.0, the alkalinity of the system strongly contributes to the rate of Cr(VI) reduction.

Another contributing factor to the decrease in reduction in the COPR samples with added Mn^{2+} was the loss of soluble Mn (Table 4-2). There is a clear distinction between the samples in the Cr(VI)-salt solution system, which all had between 0.9 and 1 mM soluble Mn after 96 h, and the COPR samples, which were all less than 0.5 mM after 96 h shaking. The oxidation of Mn^{2+} to MnOOH or MnO_2 may have been possible with the initial, rapid increase in pH in the COPR samples, although also likely is the sorption to the remaining solid fraction of COPR in suspension.

The alkaline digestion (USEPA SW-846 Method 3060A) of the remaining COPR demonstrated that there was still Cr(VI) entrained in the solid fraction at 96 h (Figure 4-4). The remaining solid fraction in the samples ranged from 50-60% of the total amount

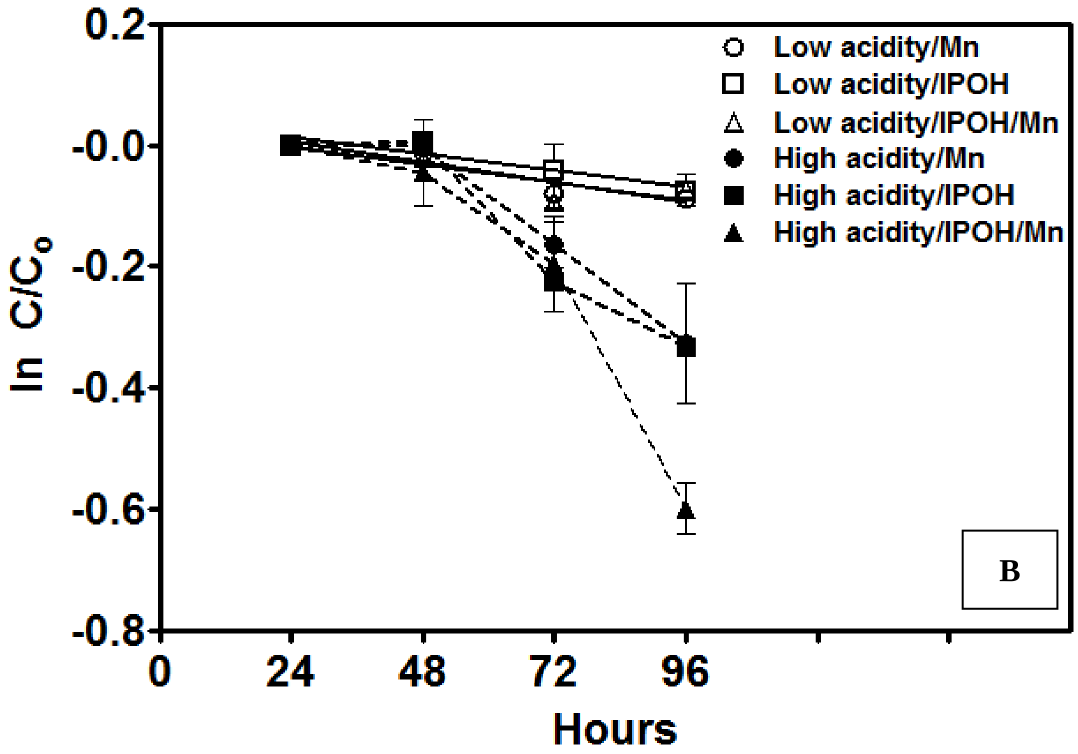


Figure 4-3 (B) Natural-log of soluble Cr(VI) concentration over initial concentration (C/C_o) to determine first-order rate constants as slope of the regression lines. High acidity samples with Mn and Mn/IPOH did not fit first- or second-order rate equations as indicated by dashed lines. Error bars are SEM (n=3).

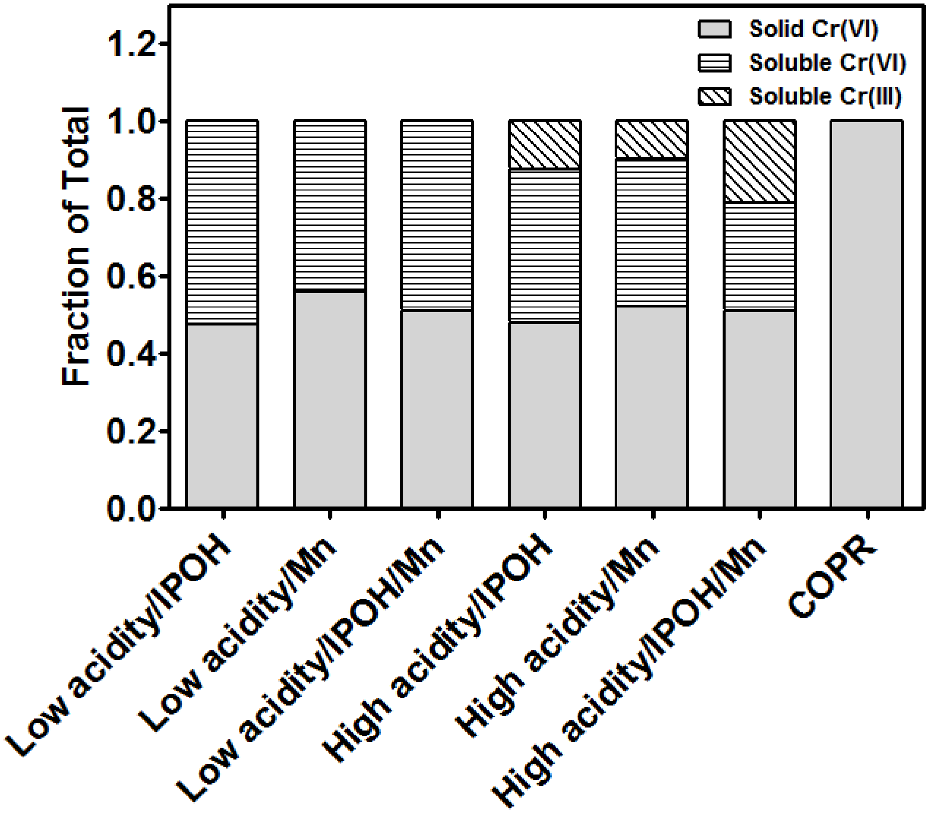


Figure 4-4 Fractions of Cr recovered from COPR samples at two different acidity levels, 0.2 M or 0.5 M HNO_3, and 12 mM tartaric acid with 0.29 M isopropyl alcohol (2% v/v), 1 mM Mn^{2+} , or a combination of both. Total fractions accounted for were the same as unreacted COPR. Samples with tartaric acid made up in 0.5 M HNO_3 reduced a fraction of the Cr(VI), whereas those in 0.2 M HNO_3 did not.

of Cr(VI), with only the high acidity treatments having reduced Cr(VI) (Table 4-2). This demonstrates that the treatments solubilized only 44 to 52% of the total amount of Cr(VI) in the COPR samples (approximately 1200 mg/kg) and that the high acidity samples were able to reduce 9.8 to 21% of the total Cr(VI) in the COPR.

COPR and Soils The solubilization of Cr(VI) from COPR and subsequent reduction was enhanced across all treatments in the presence of the five Maryland soils (Figure 4-5). The pH range across all soils and all treatments was 3.6 - 4.2, much lower than the COPR system samples that did not have soil. In the presence of the five Maryland soils, the pH was maintained, as opposed to the pH increase seen in the COPR system samples. The buffering of pH in the soils allowed for more Cr(VI) to be solubilized out of the COPR and subsequently reduced.

Also evident from Figure 4-5 is the precipitation or sorption of Cr(III) from the system. The addition of P-buffer to displace any sorbed Cr(VI) to soils is effective due to the charge and structural similarities of $H_2PO_4^-$ to $HCrO_4^-$. The difference between total soluble Cr from the COPR sample and Cr(VI) recovered from the treatments is attributed to Cr(III), which would be present as $Cr(OH)_2^+$ or $CrOH^{2+}$ and available for sorption to negative sites in the soil organic matter or on surfaces of clay and mineral surfaces. Also possible is the precipitation of $Cr(OH)_3$ from solution, although precipitation is favored at pH values greater than 5.5. The loss of Mn was also observed, and was greatest for the Russett and Atison soils (Figure 4-6). All samples had some Mn solubilized from the soil, as evident by Mn in the isopropyl alcohol treatments without added Mn. For the Jackland, Collington, and Downer soils, the amount of Mn recovered was approximately the same as the amount added.

There were no significant treatment differences between the isopropyl alcohol, Mn, and Mn/isopropyl alcohol treatments in the reduction of COPR-derived Cr(VI) in the presence of the Atsion and Christiana soils ($p<0.05$); however, for the Collington soil the Mn treatment was significantly different from the other two treatments. For the Jackland and Downer soils, the isopropyl alcohol treatment was different than the Mn and Mn/isopropyl alcohol (significant differences indicated as asterisks in Figure 4-5) Additionally, that the Mn and Mn/isopropyl alcohol treatments were not significantly different in the Russett, Atsion, Downer, and Jackland soils, indicating there were no synergistic effects observed when both Mn and isopropyl alcohol were combined.

The present work showed that the amount of Cr(VI) solubilized out of COPR by tartaric acid was greatly enhanced in the presence of the five Maryland soils. Tinjum et al. (2008) used a combination of $FeSO_4$ and H_2SO_4 solution to leach and reduce Cr(VI) from COPR and were able to solubilize up to 34% of the initial Cr(VI) due to the acid dissolution of Cr-minerals and replacement of CrO_4^{2-} with SO_4^{2-}. The acidification of COPR for reduction of Cr(VI) is necessary, whether the reductant is S, Fe, or an organic-based reductant (Jagupilla et al., 2009; Su and Ludwig, 2005). This work demonstrated that at pH values below 5.0, the addition of Mn^{2+} to tartaric acid is an effective reductant of Cr(VI) and that COPR-derived Cr(VI) would need to be acidified in order for this treatment to be used in a viable remediation strategy. This work also is the first to demonstrate that when COPR is acidified and tartaric acid and Mn^{2+} applied in the presence of soil, this treatment is effective in reducing 84% of the Cr(VI) from a COPR sample having approximately 1,200 mg total Cr(VI)/kg COPR.

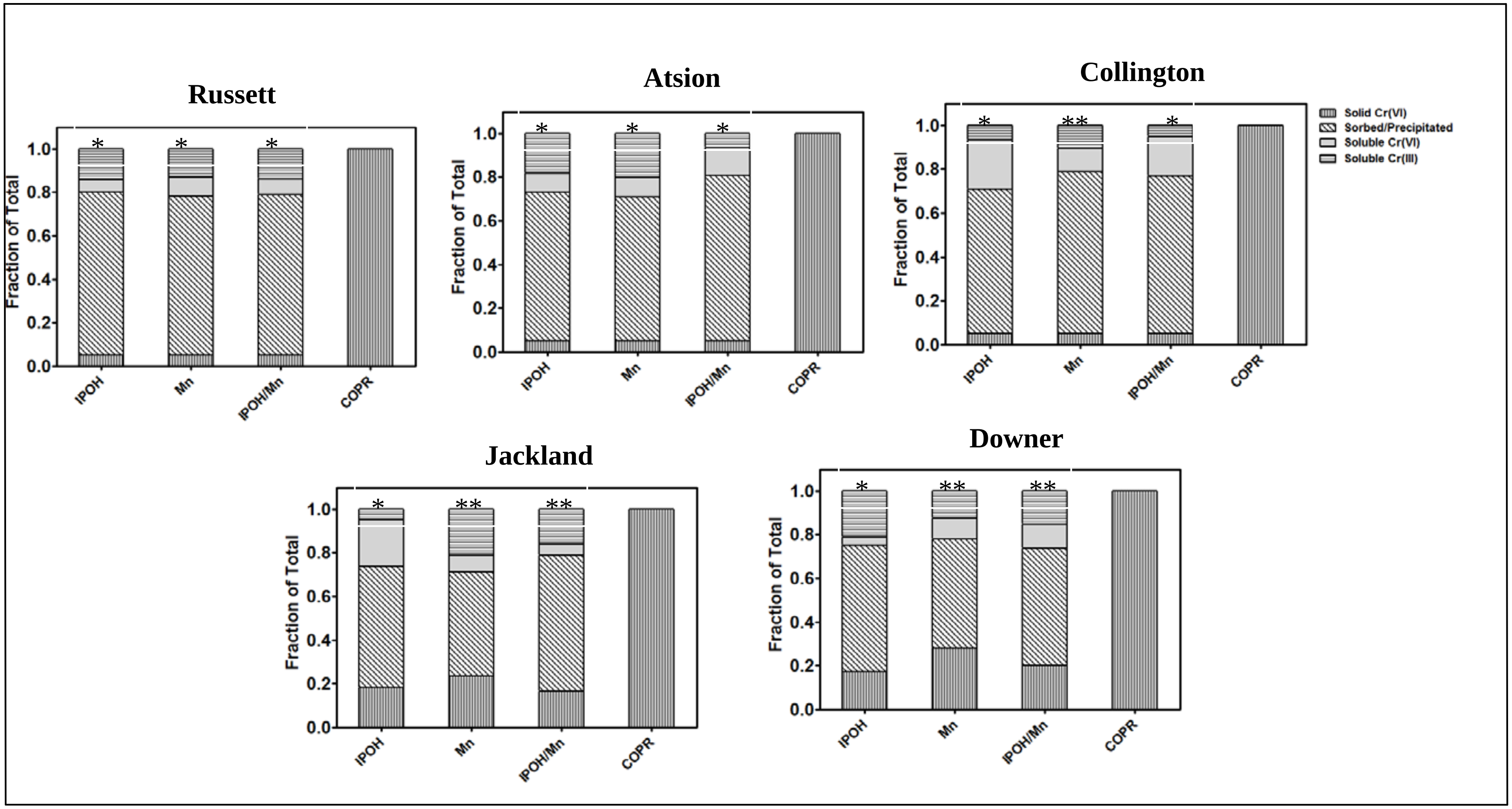


Figure 4-5 Fractions of Cr recovered from COPR and soil samples from five Maryland soils: Russett, Atsion, Collington, Jackland, and Downer. Treatments added were 12 mM tartaric acid with 0.29 M isopropyl alcohol (2% v/v), 1 mM Mn^{2+} , or a combination of both. Cross-hatched sorbed/precipitated fractions taken as non-recoverable Cr after completion of Method 3060A. Significant differences in Cr reduction from treatments indicated by asterisk above bars.

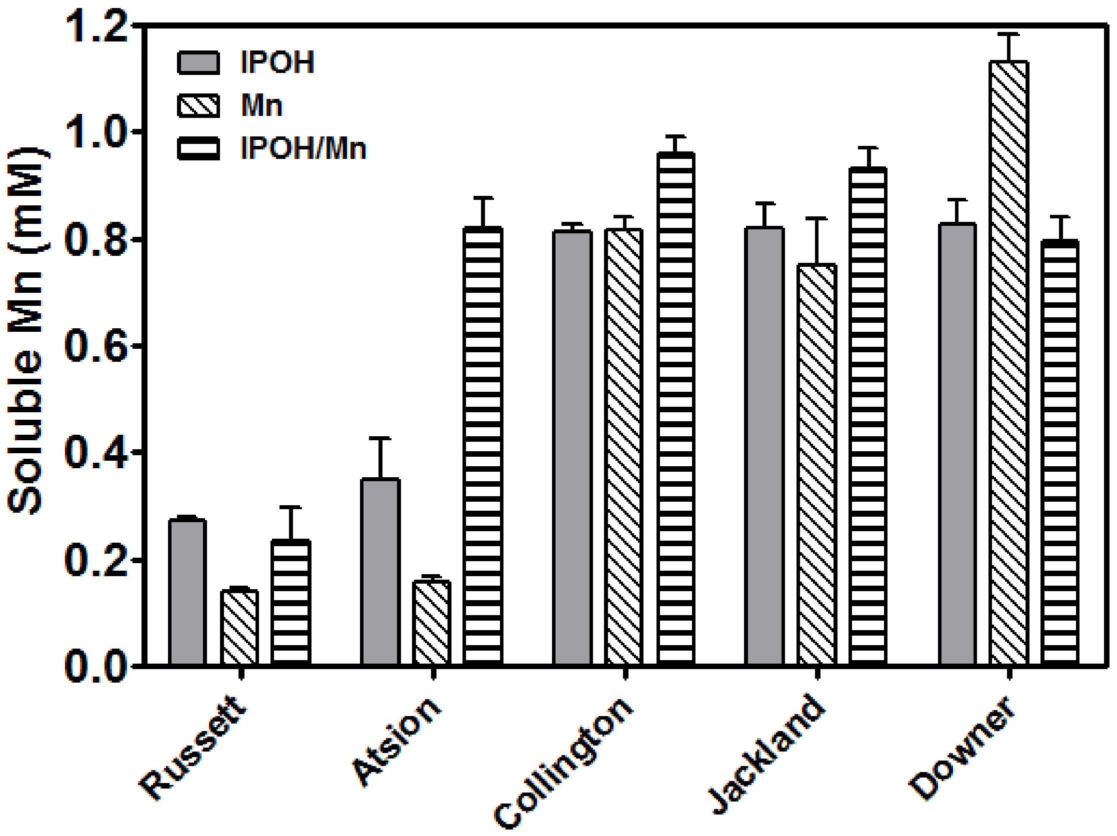


Figure 4-6 Total soluble Mn in supernatant following 48 h shaking with COPR and soil samples from five Maryland soil profiles: Russett, Atsion, Collington, Jackland, and Downer. Treatments were 12 mM tartaric acid with 0.29 M isopropyl alcohol (2% v/v), 1 mM Mn^{2+} , or a combination of both. Error bars are SEM (n=3).

CHPATER 5

Concluding Remarks

Although Cr is a naturally occurring metal, in the oxidation state +(VI) it is a health concern when present in soils and natural waters due to its demonstrated toxicity and carcinogenicity. Once Cr(VI) is reduced, organic-Cr(III) complexes can stay in solution at pH values up to 8.0, but these complexes can be rendered immobile in soils due to the presence of organic matter, which sorbs the organic component of the complex. Different reducing agents have been employed in treating COPR-contaminated soils, but the two most commonly used ones are reduced S and Fe, and although each of these reducing agents is effective in reducing Cr(VI) to Cr(III), they can be problematic in the application to a COPR-contaminated soil. When reduced S oxidizes in the presence of COPR and soils, it forms the mineral ettringite, which entraps water molecules and swells in volume, a recognized problem when COPR has been used as a fill material for asphalt paving. The oxidation of Fe^{2+} to $Fe(OH)_3$ results in the precipitation of Fe and formation of concretions that inhibit the mixing process, thus resulting in incomplete treatment of the COPR material.

This PhD dissertation presents an alternative to Fe or S for reduction of Cr(VI) in aqueous solutions and soils: the use of tartaric acid with isopropyl alcohol in the remediation of COPR-derived Cr(VI). Tartaric acid, a naturally occurring organic acid found in grapes, is oxidized to glyoxylic acid, which would be readily decomposable after treatment of COPR in a soil environment. Likewise, the oxidation of isopropyl alcohol to acetone at the concentrations used (2.2% v/v) would not pose any health or environmental risks following treatment. Concentrated isopropyl alcohol is a recognized health and flammability hazard, and the current work has taken care to use concentrations of 4% alcohol (v/v) or less.

Tartaric acid and isopropyl alcohol each form an ester with Cr(VI), resulting in a termolecular complex that greatly enhances the reduction over that which would occur with only tartaric acid. The work in Chapter 2 shows that this reaction is sensitive to changes in pH, illustrating the nature of pH as a master variable in many redox reactions that occur in soils and natural waters. The reduction of Cr(VI) was complete in less than 48 h at pH 4.0, but at pH 6.0 less than 10% of the Cr(VI) was reduced. The reaction also showed sensitivity to the concentration of tartaric acid, in that as the concentration increased, the rate of the reaction increased exponentially. The drivers of the reaction then are the concentration of tartaric acid and pH; however, application of this chemistry to artificially made Cr-contaminated soils demonstrated that the reaction was not as sensitive to pH in the presence of soils samples taken from five Maryland soil mapping units: Russett-Christiana Complex, Askecksy, Annapolis, Jackland, and Ingleside.

In Chapter 3, when tartaric acid and isopropyl alcohol were applied in the reduction of Cr(VI) in the presence of these five soils, there was a significant soil treatment effect, but also unexpected results regarding pH effects. The greatest amount of Cr(VI) reduced occurred in the presence of the Russett soil, which also had the second greatest increase in pH. The initial pH for all samples was 4.0, but by the end of 99 h (approx. 4 d), the pH increased to 5.0 for Russett and 5.3 for the Jackland soil. Both of these soils demonstrated that when applied to a soil environment, the pH effect seen in Chapter 2 is less applicable and that the reduction of Cr(VI) continues at these higher pH values.

One possible mechanism responsible for the pH and enhanced soil effects seen is attributed to Mn(III/IV)(hydr)oxides and Fe(III)(hydr)oxides in the soil. It is evident that these metal (hydr)oxides are solubilized from the soil samples, and the reactions for the reductive dissolution for both Mn(III/IV) and Fe(III) show a consumption of protons. Thus, the increase in pH seen in the Jackland and Russett soils may be attributed to the reductive dissolution of these minerals, allowing the reduced forms, Fe^{2+} and Mn^{2+}, to contribute to the reduction of Cr(VI), despite this increase in pH.

The addition of Fe(III) to samples containing tartaric acid, isopropyl alcohol, and the five soils only enhanced reduction to a great extent in the Russett and Collington soils; however, the addition of Mn(II) significantly enhanced reduction in all the soils, except the Jackland soil. Furthermore, the addition of tartaric acid and isopropyl alcohol to Mn-oxide coated sand indicated dissolution of Mn from the sand and the enhanced reduction of Cr(VI) as the amount of Mn-oxide coated sand increased. This dissertation contributes to the larger body of literature on Mn and tartaric acid interactions by showing that the tartaric acid and isopropyl alcohol solution is capable of solubilizing Mn(III/IV)(hydr)oxides and that the resulting Mn(II) is then available to further enhance the reduction of Cr(VI).

When applying this chemistry to COPR-derived Cr(VI) in Chapter 4, both the isopropyl alcohol and Mn complexes were used as reducing agents for Cr(VI). At pH values less than 5.0, the addition of Mn(II) to tartaric acid was a much more effective reducing agent than the addition of isopropyl alcohol. At higher pH values, though, this difference is not as stark. When applied to COPR-soil mixtures, both are effective at reducing Cr(VI), with the Mn treatments reducing slightly more Cr(VI) for the Downer, Collington, and Jackland soils. Often, there are synergistic effects seen when two chemicals that share a similar chemical mechanism are present together in a given reaction. There were no synergistic effects observed, however, when both Mn and isopropyl alcohol were added to the same sample; however, there were no inhibitory effects observed either. When Cr(VI) was added to the soils in Chapter 3, there were significant differences observed in Cr(VI) reduction among the five soils; however, this soil effect was not as apparent in the COPR-soil mixtures. The increase in pH observed with COPR samples was buffered in the presence of the five soils, and thus, the pH remained low enough for the added Mn and isopropyl alcohol treatments to effectively act on Cr(VI).

This dissertation presents the use of tartaric acid and isopropyl alcohol in the reduction of Cr(VI) in Cr(VI)-contaminated soils and COPR, and found that in addition to tartaric acid and isopropyl alcohol being effective at low enough pH, the addition of Mn(II) to tartaric acid was also effective as a reducing agent. Tartaric acid-isopropyl alcohol and tartaric acid-Mn complexes are effective reducing agents individually, and although there is no synergism when used in combination, this work has shown that in the presence of soil, Cr(VI) reduction is enhanced - even with the Downer soil, which is a sandy soil, low in organic C, clay, Mn(III/IV)(hydr)oxides, and Fe(III)(hydr)oxides. Soils, in the reduction of Cr(VI), contribute Mn(II) to the system from reductive dissolution processes, buffer against changes in pH, and provide surfaces for reactions to occur. Soils, as a natural body on the landscape, will naturally detoxify Cr(VI) to a limited extent, and this tendency may allow for either of the tartaric acid-isopropyl alcohol or tartaric acid-Mn complexes to complete the reduction process as a remediation strategy to clean up these polluted soils.

The experimental designs in Chapters 3 and 4 allowed for a thorough mixing of the reductants with Cr(VI), soils, and COPR material. Further work is needed to understand how these batch experiments would compare with leaching studies in order to fully evaluate the use of the solutions in an *in-situ* remediation strategy. Although effective in reducing Cr(VI), leaching a solution of tartaric acid and isopropyl alcohol through COPR-contaminated soils to depths as far down as 10 or 15 ft may not fully access all the Cr(VI) for reduction to meet regulatory standards. These batch studies do demonstrate that if the COPR and soil material were removed and treated in a batch reactor application, with thorough mixing and acidification, the treatment would be effective in reducing Cr(VI) to Cr(III) and immobilizing it either through sorption or precipitation processes. This material could then be filled back into the original location without having to be moved off-site for treatment.

There were clear differences in the reduction of Cr(VI) in the different soils in Chapter 3; however, the application of this to the COPR-soil mixtures in Chapter 4 resulted in less clear soil differences. More investigation is needed with these and additional Maryland soils to better relate Cr redox processes in soils back to inherent chemical or physical properties of these soils. Soils are a complex media for experimentation, and other authors have attempted to link Cr redox to soil properties through various kinetic and statistical studies with mixed results. This dissertation showed that Mn(III/IV)(hydr)oxides and Fe(III)(hydr)oxides are key contributors to the reduction of Cr(VI), but that pH, a master variable for many redox processes in soils and natural waters, is also a key driver.

Although this dissertation does not attribute the reduction of Cr(VI) to specific soil properties or minerals, the proposed reductive dissolution of Fe(III)- and Mn(III/IV)(hydr)oxides provides insight into natural processes involving naturally occurring α-hydroxy carboxylic acids and minerals in soils. These interactions between organic acids and minerals in natural soil bodies could influence mineral formation, illuviation of reduced Fe and Mn to lower horizons, soil organic matter formation and decomposition, and accessibility of organic compounds to microbiological communities. Lastly, this dissertation provides a basis for further investigation of leaching studies with α-hydroxy carboxylic acids through soils and Cr(VI)-contaminated soils, and for a possible field-scale application to a COPR-contaminated site.

APPENDIX A

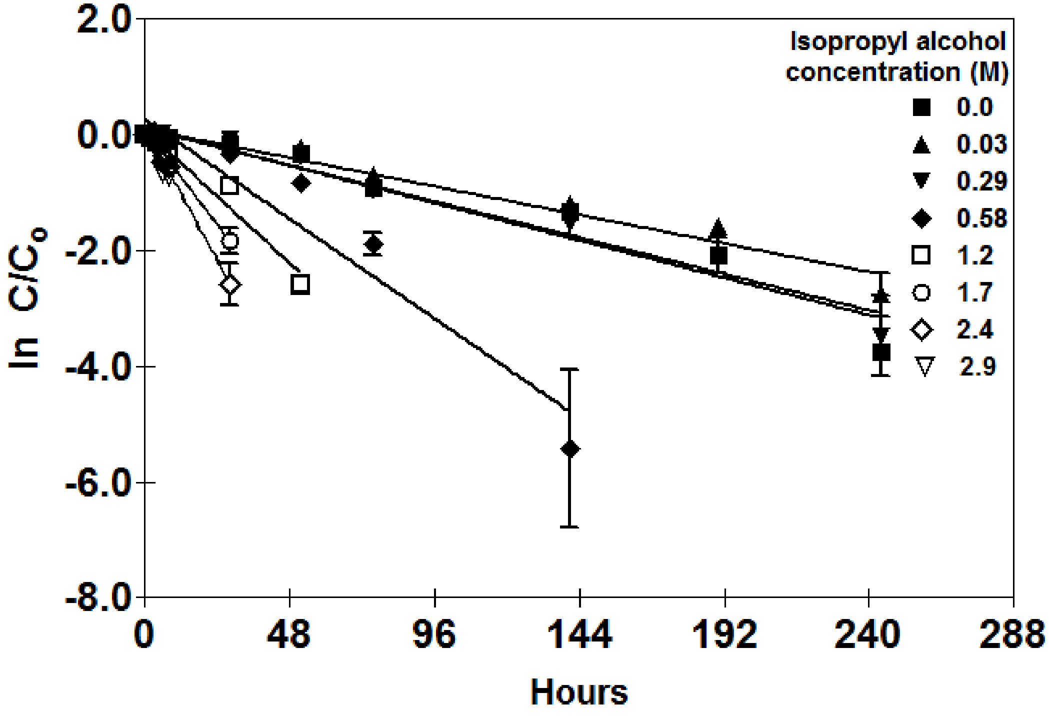


FIGURE A-1 Linear regression best fit lines for natural log concentration over initial concentration for reduction of 2.0 mM soluble Cr(VI) at pH 4.0 in 23 mM tartaric acid and increasing concentration of isopropyl alcohol. Error bars are SEM (n=3).

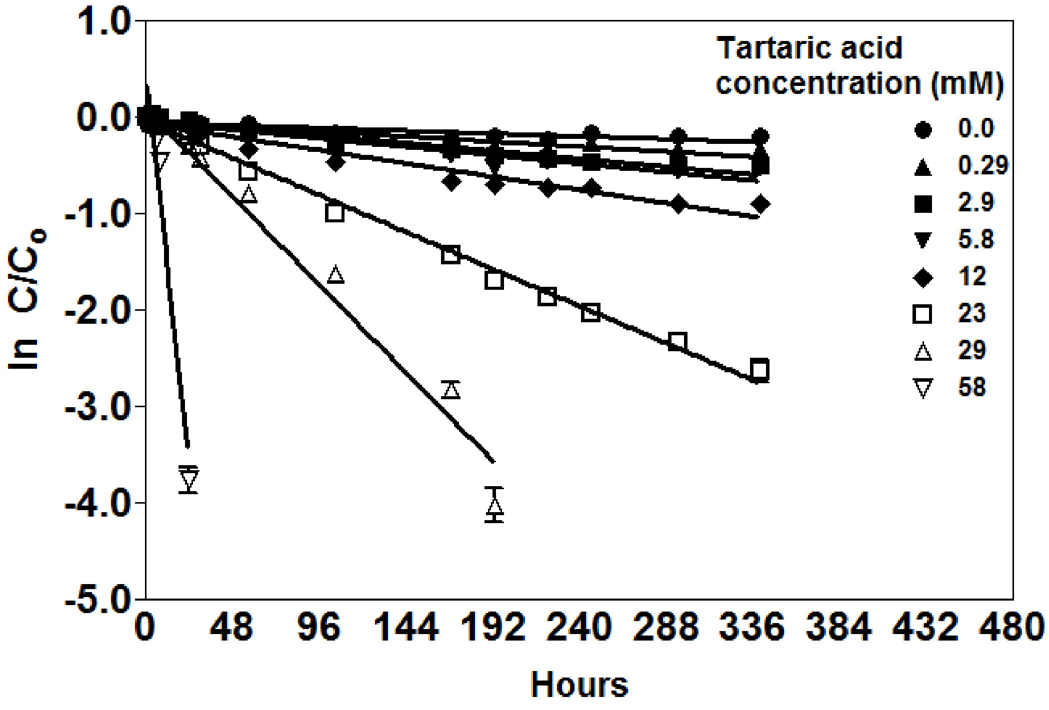


FIGURE A-2 Linear regression best-fit lines for natural log concentration over initial concentration for reduction of 2.0 mM soluble Cr(VI) at pH 4.0 in 0.29 M isopropyl alcohol and increasing concentrations of tartaric acid. Error bars are SEM (n=3).

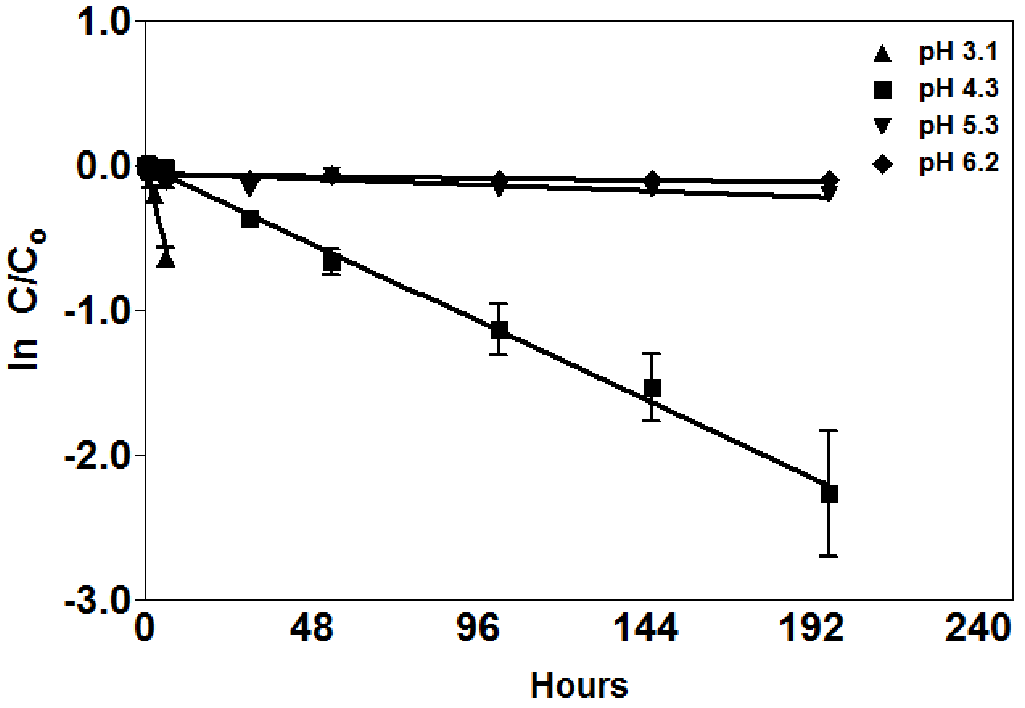


FIGURE A-3 Linear regression best-fit lines for natural log concentration over initial concentration for reduction of 2.0 mM soluble Cr(VI) in 0.29 M isopropyl alcohol and 23 mM tartaric acid with increasing pH. Error bars are SEM (n=3).

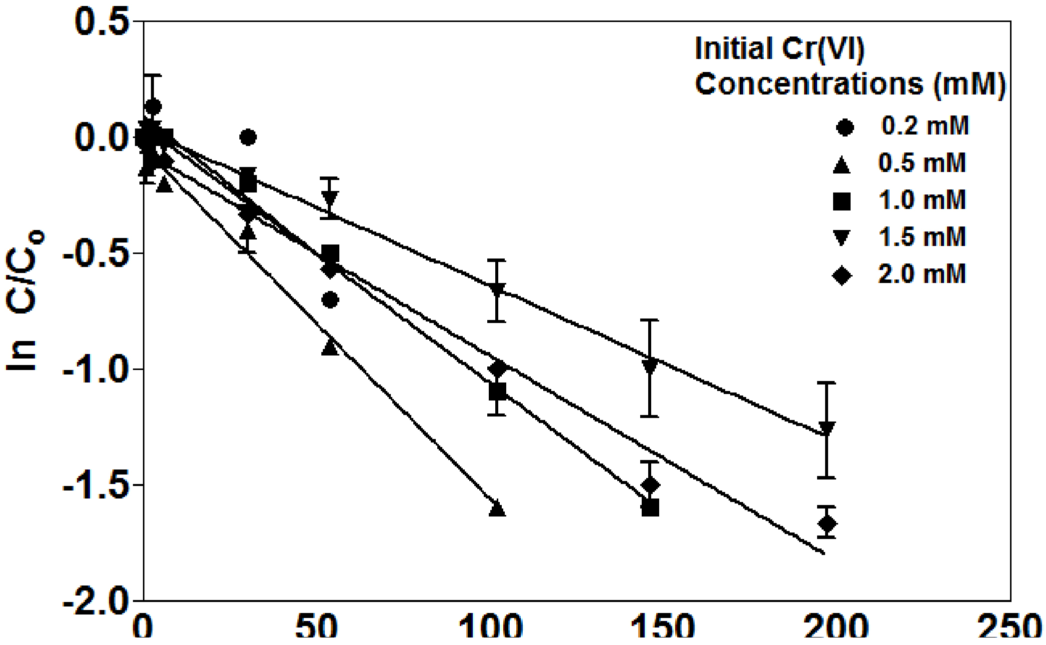


FIGURE A-4 Linear regression best-fit lines for natural log concentration over initial concentration for reduction of increasing concentrations of soluble Cr(VI) at pH 4.0 in 0.29 M isopropyl alcohol and 23 mM tartaric acid. Error bars are SEM (n=3).

APPENDIX B

OVERVIEW OF SOILS AND SAMPLING

Five soil profiles from Maryland, USA were sampled as part of a larger sampling scheme by our Soil Chemistry Laboratory to collect soil horizon samples for research and teaching purposes. The soils were sampled from delineations of five different map units: Askecksy, Russett- Christiana Complex, Annapolis, Ingleside, and Jackland.. At each location a hole was dug so that at least the upper B horizon was exposed, although many of the pits extended down to the lower B and C horizons, which ranged down from 24 to 90 cm in depth. From major horizons exposed in the profile, approximately 20 L of soil was taken by carefully excavating soil material out of the horizon with a knife and onto the head of a shovel. The sampling was conducted when soil matric water potentials were approximately -5 to -10 kPa (field capacity moisture). The soil was brought into the laboratory, passed through a 4-mm polyethylene sieve, mixed thoroughly by hand, and stored in the dark at 22 ± 2º C in a plastic bucket lined with 1-mm thick plastic garbage bags to minimize soil drying while maintaining the aerobic status of the soil.

Soil properties were analyzed for each horizon of the five profiles sampled. The soils were analyzed for water content by drying at 105º C for 24 h (Gardner, 1986), for pH by field colorimetric method, 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 from the five soils using a modified Na-citrate and $Na_2S_20_4$ extraction method (Mehra and Jackson 1960). To the field-moist equivalent of 2.5 g oven-dried soil 20 mL of 0.3 M Na-citrate and 2.5 mL of 1 M $NaHCO_3$ was added, shaken, and brought to 75-80° C in a water bath. After soil suspensions reached 75° C for five minutes, 0.5 g $Na_2S_20_4$ was added and suspensions stirred intermittently for 5 minutes. Then, an additional 0.5 g $Na_2S_20_4$ was added and stirred intermittently for another 10 minutes. To each sample, 5 mL of a saturated NaCl solution was added to flocculate the soil. Samples were centrifuged for 10 minutes at 10,000 rpm (~ 10 K RCF) and the supernatant liquid was decanted into a 200 mL flask. Samples were washed twice with remaining Na-citrate solution and decanted into the same flask. Solutions were brought to volume and Fe and Mn analyzed by flame AAS.

In addition to soil characterization data, a Soil Quick Redox Assessment was also conducted. For this, 10.0 mL of 0.2 mM $Cr(NO_3)_3$ was added to each soil in 50-mL centrifuge tubes and also separately, 10.0 mL of 0.2 mM K_2CrO_4 was added to each soil in 50-mL centrifuge tubes. This is equivalent to a concentration of 0.1 mM Cr or 5.2 mg/L. The tubes were capped and shaken on a reciprocating shaker at 110 cycles min^{-1} for 20 ± 1 hours at which point they were opened and 0.2 mL of 1.0 M phosphate buffer (K_2HPO_4/KH_2PO_4 mole ratio = 1; pH 7.2) was added. The tubes were capped and shaken one additional hour. They were then removed and centrifuged at 10,000 rpm (~ 10 K RCF) for 15 minutes. Chromium(VI) in the centrifugate was then measured by adding 1.0 mL of diphenylcarbazide (DPC) reagent to 10 mL of a 1-to-5 dilution of each centrifugate. The values represent “net Cr(VI) reduction” and “net Cr(III) oxidation” by each soil.

The following descriptions summarize the soil characterization and redox assessment data for the five soils sampled and used in the current work.

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 (Figure B-1). The profile was similar to the Russett soil series (fine-loamy, mixed, semiactive, mesic Typic Hapludult).

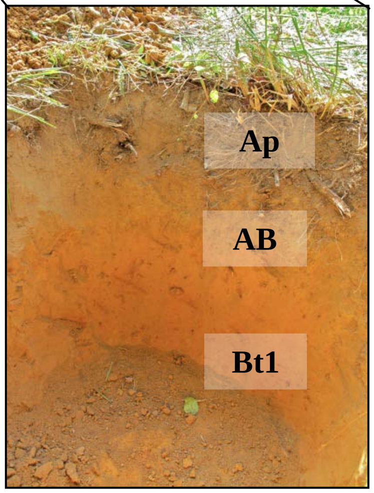


Figure B-1 Profile sampled from the Russett soil to a depth of 66 cm revealing Ap, AB, and Bt1 horizons. Location at 39°00’45.71”N, 76°51’14.65”W.

The horizons sampled from the Russett soil profile were sandy with the Ap and AB horizons having 58 and 53% sand, respectively and having a sandy loam texture (Table B-1). The Bt1 horizon had less sand and was a loam in texture. The pH for the three horizons ranged from 5.0 - 6.0, and were aerobic with Eh values from 507 - 577 mV relative to standard hydrogen electrode (SHE). The Ap horizon reduced 2.0 mg/L Cr(VI), which was the most reduced in the quick redox assessment for this profile, and the AB horizon oxidized 0.91 mg/L, which was the most for this profile.

Table B-1 Soil characterization data for Russett soil profile. CDB refers to the citrate-dithionite extraction and N/A is not analyzed.

Characteristics	**Soil Horizons**		
	Ap (0-36 cm)	**AB (36-66 cm)**	**Bt1 (>66 cm)**
Texture (% sand, silt, clay)	Sandy loam (58, 37, 5)	Sandy loam (53, 38, 9)	Loam (40, 42, 18)
Field pH	5.0	6.0	4.5 – 5.0
Lab Eh (mV)	577	507	540
Organic Carbon by LECO (g/kg soil)	25 ± 0.1	6.3 ± 0.03	1.4 ± 0.01
Cr Oxidized (mg/L)	0.38 ± 0.03	0.91 ± 0.04	0.0 ± 0.02
Cr Reduced (mg/L)	2.0 ± 0.12	0.64 ± 0.02	0.84 ± 0.03
CDB Fe (g/kg)	4.1 ± 0.32	N/A	N/A
CDB Mn (g/kg)	0.25 ± 0.02	N/A	N/A

Downer Soil

A soil profile from a delineation of the Ingleside mapping unit was dug to 61cm, allowing for sampling from the A, Ap, and BA horizons (Figure B-2). The profile was similar to the Downer soil series (coarse-loamy, siliceous, semiactive, mesic Typic Hapludult).

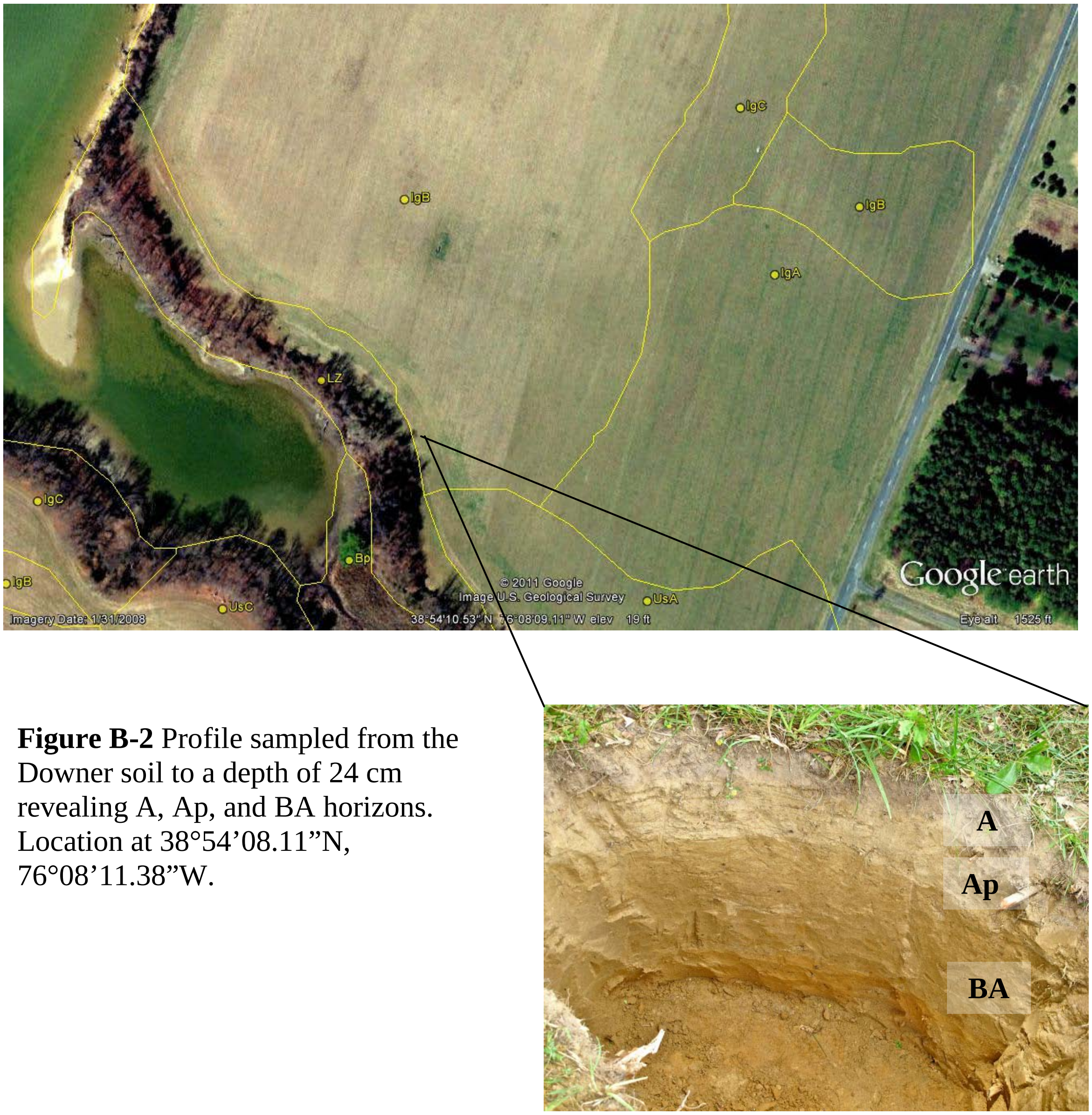


Figure B-2 Profile sampled from the Downer soil to a depth of 24 cm revealing A, Ap, and BA horizons. Location at 38°54’08.11”N, 76°08’11.38”W.

The horizons sampled from the Downer soil profile were relatively sandy with the A and Ap horizons having 75 and 66% sand, respectively (Table B-2). The BA horizon had slightly less sand at 30%. The pH for the three horizons ranged from 5.5 - 6.0, and were aerobic with Eh values from 437 - 500 mV relative to standard hydrogen electrode (SHE). The A horizon reduced 1.0 mg/L Cr(VI) and the Ap horizon reduced 1.1 mg/L Cr(VI), and although the A horizon didn't oxidize any Cr(III), the Ap horizon oxidized 2.4 mg/L which was similar to the BA horizon which oxidized 2.6 mg/L.

Table B-2 Soil characterization data for the Downer soil profile. CDB refers to the citrate-dithionite extraction and N/A is not analyzed.

Characteristics	**Soil Horizons**		
	A (0-8 cm)	**Ap (8-18 cm)**	**BA (18-61 cm)**
Texture (% sand, silt, clay)	Loamy sand (75, 21, 4)	Sandy loam (66, 28, 6)	Silt loam (30, 52, 18)
Field pH	5.5	6.0	5.5
Lab Eh (mV)	490	437	500
Organic Carbon by LECO (g/kg soil)	3.1 ± 0. 1	2.5 ± 0.1	1.0 ± 0.1
Cr Oxidized (mg/L)	0.0	2.4 ± 0.03	2.6 ± 0.10
Cr Reduced (mg/L)	1.0 ± 0.05	1.1 ± 0.07	0.85 ± 0.0
CDB Fe (g/kg)	1.5 ± 0.4	N/A	N/A
CDB Mn (g/kg)	0.05 ± 0.0	N/A	N/A

Jackland Soil

A soil profile from a delineation of the Jackland mapping unit was dug to 78 cm, allowing for sampling from the Ap, Bt, and BC horizons (Figure B-3). The profile was similar to the Jackland series (fine, smectic, mesic Aquic Hapludalf).

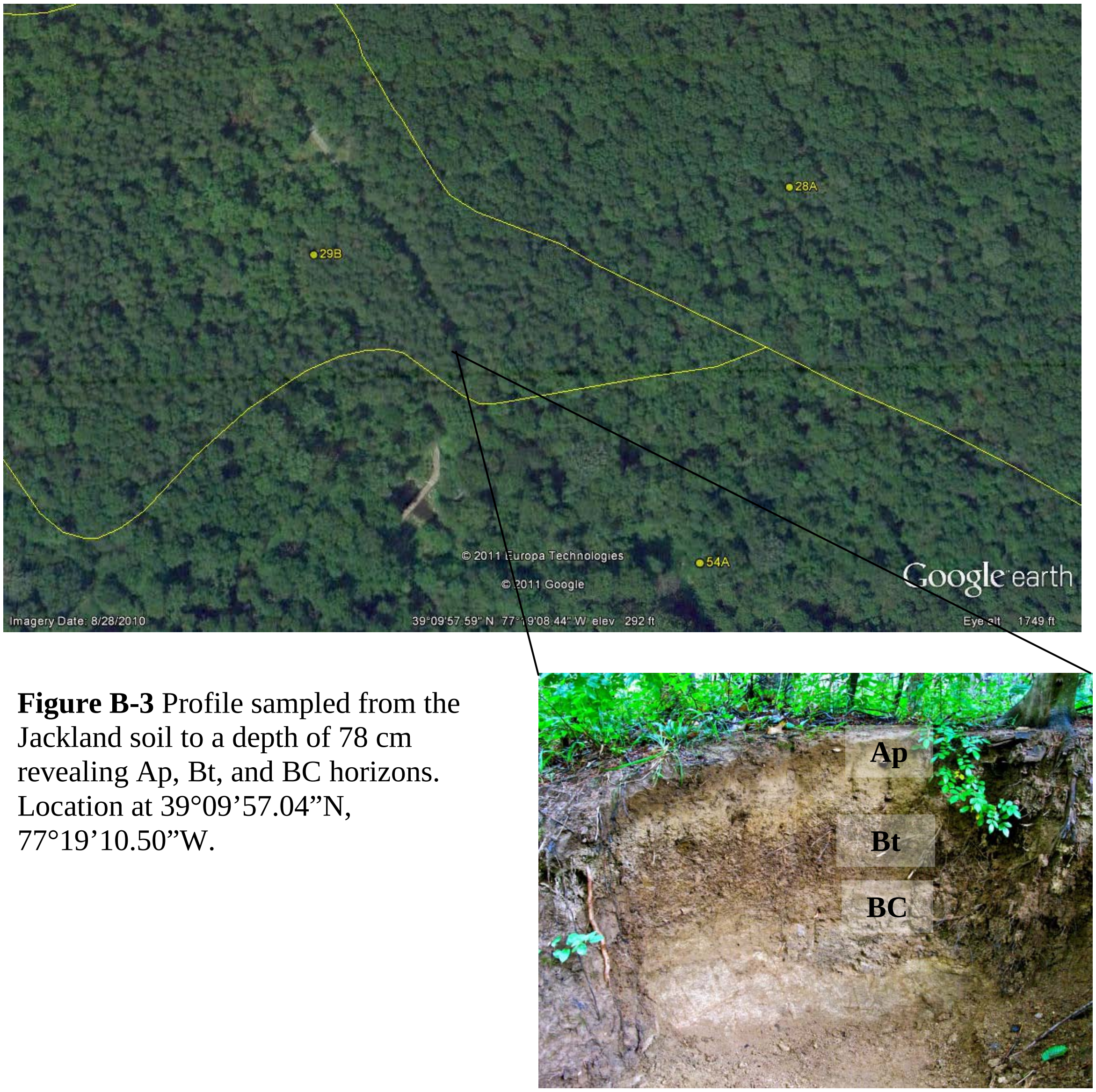


Figure B-3 Profile sampled from the Jackland soil to a depth of 78 cm revealing Ap, Bt, and BC horizons. Location at 39°09’57.04”N, 77°19’10.50”W.

The horizons sampled from the Jackland soil profile were higher in silt and clay than the other profiles with 8.9, 33, and 13% clay in the Ap, Bt, and BC horizons, respectively (Table B-3). The pH for the three horizons ranged from 6.0 – 6.5, and were aerobic with Eh values from 449 - 470 mV relative to standard hydrogen electrode (SHE). The Ap horizon reduced the most Cr(VI) at 1.0 mg/L; however, the Ap and Bt horizons oxidized 2.4 and 2.6 mg/L Cr(III), respectively, which is indicative of the higher concentrations of Mn(III,IV)(hdyr)oxides present relative to the other soils.

Table B-3 Soil characterization data for the Jackland soil profile. CDB refers to the citrate-dithionite extraction and N/A is not analyzed.

Characteristics	**Soil Horizons**		
	Ap (0-20 cm)	**Bt (20-45 cm)**	**BC (45-78 cm)**
Texture (% sand, silt, clay)	Silt loam (35, 57, 8)	Clay loam (30, 37, 33)	Sandy loam (69, 19, 12)
Field pH	6.0	6.0-6.5	5.5-6.5
Lab Eh (mV)	470	460	449
Organic Carbon by LECO (g/kg)	9.0 ± 0.1	4.0 ± 0.1	1.3 ± 0.0
Cr Oxidized (mg/L)	2.4 ± 0.03	2.6 ± 0.10	0.79 ± 0.02
Cr Reduced (mg/L)	1.1 ± 0.07	0.85 ± 0.05	0.49 ± 0.08
CBD Fe (g/kg)	6.3 ± 0.26	N/A	N/A
CBD Mn (g/kg)	1.0 ± 0.03	N/A	N/A

Collington Soil

A soil profile from a delineation of the Annapolis mapping unit was dug to 90 cm, allowing for sampling from the A, Ap, and Bt horizons (Figure B-4). The profile was similar to the Collington series (fine-loamy, mixed, active, mesic Typic Hapludult).

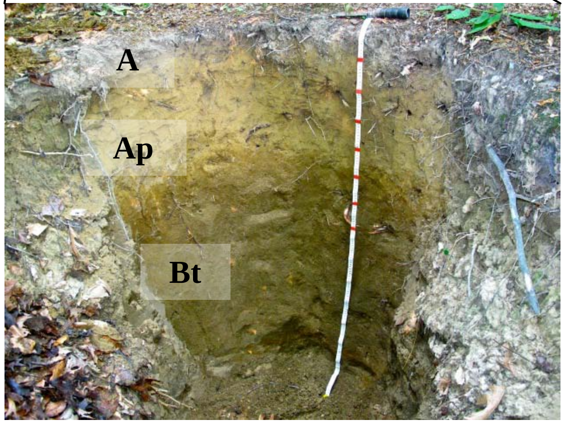


Figure B-4 Profile sampled from the Collington soil to a depth of 90 cm revealing A, Ap, and Bt horizons. Location at 38°51’23.51”N, 76°46’53.74”W.

The horizons sampled from the Collington soil were relatively high in sand with 83, 76, and 71% sand in the A, Ap, and Bt horizons, respectively (Table B-4). The pH for the three horizons ranged from 4.0 - 4.5. These horizons had the highest Eh values ranging from 597 - 607 mV relative to standard hydrogen electrode (SHE). The A horizon reduced the most Cr(VI) from this profile at 3.9 mg/L; and none of the horizons oxidized any Cr(III), which is indicative of very low concentrations of Mn(III,IV)(hdyr)oxides present relative to the other soils.

Table B-4 Soil characterization data for the Collington soil profile. CDB refers to the citrate-dithionite extraction and N/A is not analyzed.

Characteristics	**Soil Horizons**		
	A (0-10 cm)	**Ap (10-24 cm)**	**Bt (24-90 cm)**
Texture (% sand, silt, clay)	Loamy sand (83, 14, 3)	Loamy sand (76, 20, 4)	Sandy clay loam (71, 5, 24)
Field pH	4.0	4.0-4.5	4.0
Lab Eh (mV)	606	597	607
Organic Carbon by LECO (g/kg)	37 ± 0.02	2.5 ± 0.01	1.7 ± 0.01
Cr Oxidized (mg/L)	0.0	0.0	0.0
Cr Reduced (mg/L)	3.9 ± 0.12	0.88 ± 0.01	1.3 ± 0.04
CBD Fe (g/kg)	3.0 ± 0.41	N/A	N/A
CBD Mn (g/kg)	0.01 ± 0.0	N/A	N/A

Atsion Soil

A soil profile from a delineation of the Askecksy mapping unit was dug to 114 cm, allowing for sampling from the O/A, E, Bh, Bs, and C horizons (Figure B-5). The profile was similar to the Atsion series (sandy, siliceous, mesic, Aeric Alaquod).

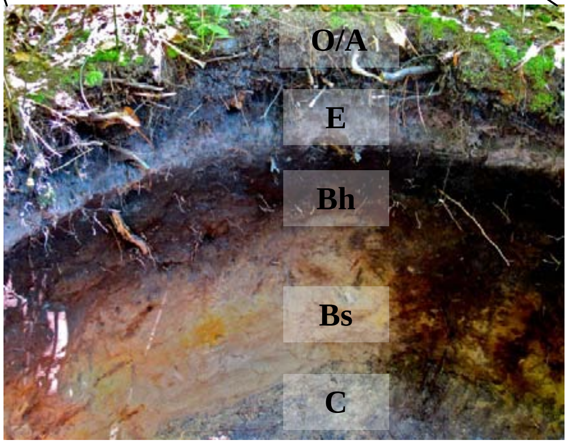


Figure B-5 Profile sampled from the Atsion soil to a depth of 84 cm revealing O/A, E, Bh, Bs, and C horizons. Location at 38°12’52.11”N, 75° 31’20.05”W.

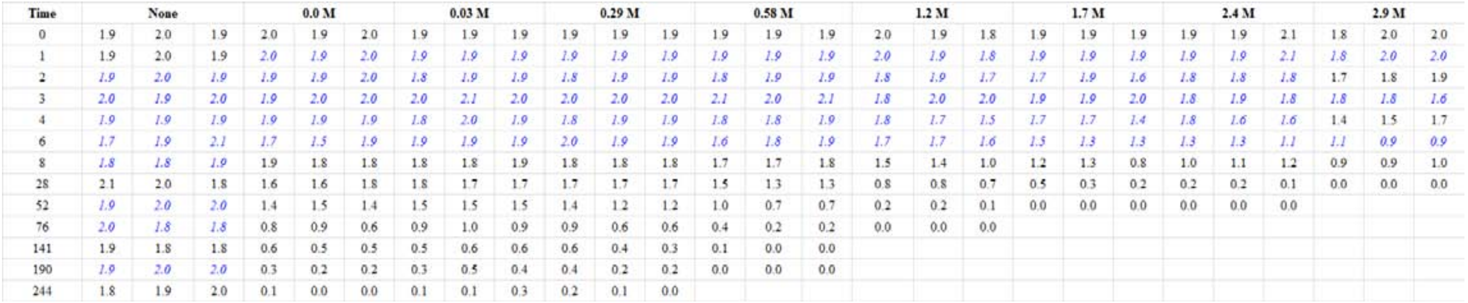
The horizons sampled from the Atsion soil had the highest amount of sand of all the soils with 94, 88, 89, and 95% sand in the E, Bh, Bs, and C horizons, respectively (Table B-5). The pH for the profile ranged from 3.5 - 5.0, and the Eh values ranged from 477 - 530 mV relative to standard hydrogen electrode (SHE). The O/A horizon reduced the most Cr(VI) than any of the other soil horizons sampled in the five soils at 5.2 mg/L; and none of the horizons oxidized any Cr(III), which is indicative of very low concentrations of Mn(III,IV)(hdyr)oxides present relative to the other soils.

Table B-5 Soil characterization data for the Atsion soil profile. CDB refers to the citrate-dithionite extraction and N/A is not analyzed.

Characteristics	**Soil Horizons**				
	O/A (0-30 cm)	**E (30-69 cm)**	**Bh (69-89 cm)**	**Bs (89 -114 cm)**	**C (>114 cm)**
Texture (% sand, silt, clay)	N/A	Sand (94, 5.9, 0.1)	Sand (88, 10, 2)	Sand (89, 8, 3)	Sand (95, 3, 2)
Field pH	4.0	3.5-4.0	4.5-5.0	4.5	5.0
Lab Eh (mV)	530	524	477	484	488
Organic Carbon by LECO (g/kg)	117 ± 8.0	20 ± 0.4	44 ± 2.1	29 ± 1.1	1.9 ± 0.02
Cr Oxidized (mg/L)	0.0	0.0	0.0	0.0	0.0
Cr Reduced (mg/L)	5.2 ± 0.0	2.3 ± 0.13	2.2 ± 0.16	1.4 ± 0.02	0.45 ± 0.02
CBD Fe (g/kg)	N/A	0.09 ± 0.0	N/A	N/A	N/A
CBD Mn (g/kg)	N/A	0.002 ± 0.0	N/A	N/A	N/A

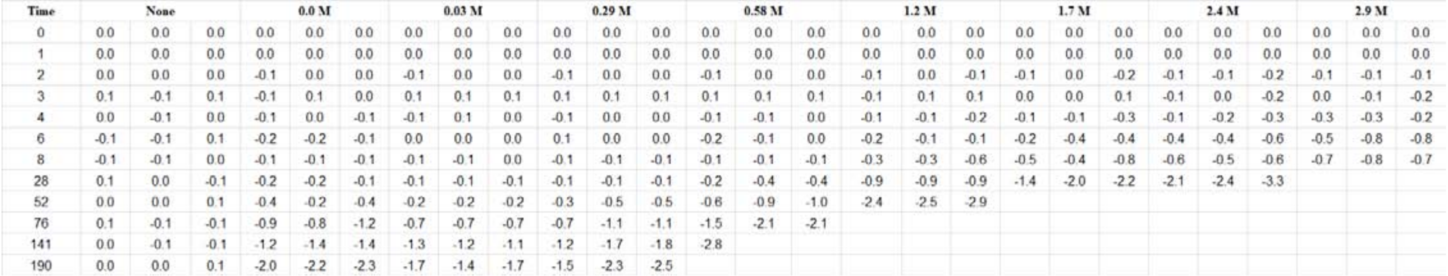
APPENDIX C

Table C-1 Data Set for Figure 2-1A. Time in hours and data in mM soluble Cr(VI) for increasing concentration isopropyl alcohol.



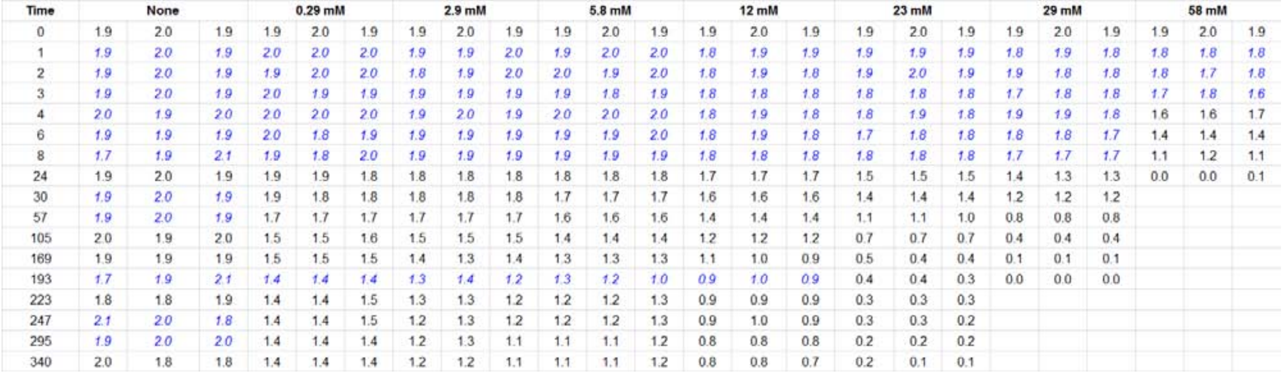
Time	None			0.0 M			0.03 M			0.29 M			0.58 M			1.2 M			1.7 M			2.4 M			2.9 M		
0	1.9	2.0	1.9	2.0	1.9	2.0	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	2.0	1.9	1.8	1.9	1.9	1.9	1.9	1.9	2.1	1.8	2.0	2.0
1	1.9	2.0	1.9	2.0	1.9	2.0	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	2.0	1.9	1.8	1.9	1.9	1.9	1.9	1.9	2.1	1.8	2.0	2.0
2	1.9	2.0	1.9	1.9	1.9	2.0	1.8	1.9	1.9	1.8	1.9	1.9	1.8	1.9	1.9	1.8	1.9	1.7	1.7	1.9	1.6	1.8	1.8	1.8	1.7	1.8	1.9
3	2.0	1.9	2.0	1.9	2.0	2.0	2.0	2.1	2.0	2.0	2.0	2.0	2.1	2.0	2.1	1.8	2.0	2.0	1.9	1.9	2.0	1.8	1.9	1.8	1.8	1.8	1.6
4	1.9	1.9	1.9	1.9	1.9	1.9	1.8	2.0	1.9	1.8	1.9	1.9	1.8	1.8	1.9	1.8	1.7	1.5	1.7	1.7	1.4	1.8	1.6	1.6	1.4	1.5	1.7
6	1.7	1.9	2.1	1.7	1.5	1.9	1.9	1.9	1.9	2.0	1.9	1.9	1.6	1.8	1.9	1.7	1.7	1.6	1.5	1.3	1.3	1.3	1.3	1.1	1.1	0.9	0.9
8	1.8	1.8	1.9	1.9	1.8	1.8	1.8	1.8	1.9	1.8	1.8	1.8	1.7	1.7	1.8	1.5	1.4	1.0	1.2	1.3	0.8	1.0	1.1	1.2	0.9	0.9	1.0
28	2.1	2.0	1.8	1.6	1.6	1.8	1.8	1.7	1.7	1.7	1.7	1.7	1.5	1.3	1.3	0.8	0.8	0.7	0.5	0.3	0.2	0.2	0.2	0.1	0.0	0.0	0.0
52	1.9	2.0	2.0	1.4	1.5	1.4	1.5	1.5	1.5	1.4	1.2	1.2	1.0	0.7	0.7	0.2	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0			
76	2.0	1.8	1.8	0.8	0.9	0.6	0.9	1.0	0.9	0.9	0.6	0.6	0.4	0.2	0.2	0.0	0.0	0.0									
141	1.9	1.8	1.8	0.6	0.5	0.5	0.5	0.6	0.6	0.6	0.4	0.3	0.1	0.0	0.0												
190	1.9	2.0	2.0	0.3	0.2	0.2	0.3	0.5	0.4	0.4	0.2	0.2	0.0	0.0	0.0												
244	1.8	1.9	2.0	0.1	0.0	0.0	0.1	0.1	0.3	0.2	0.1	0.0															

Table C-2 Data Set for Figure 2-1B. Time in hours and data are ln C/Co for soluble Cr(VI) for increasing concentration isopropyl alcohol..



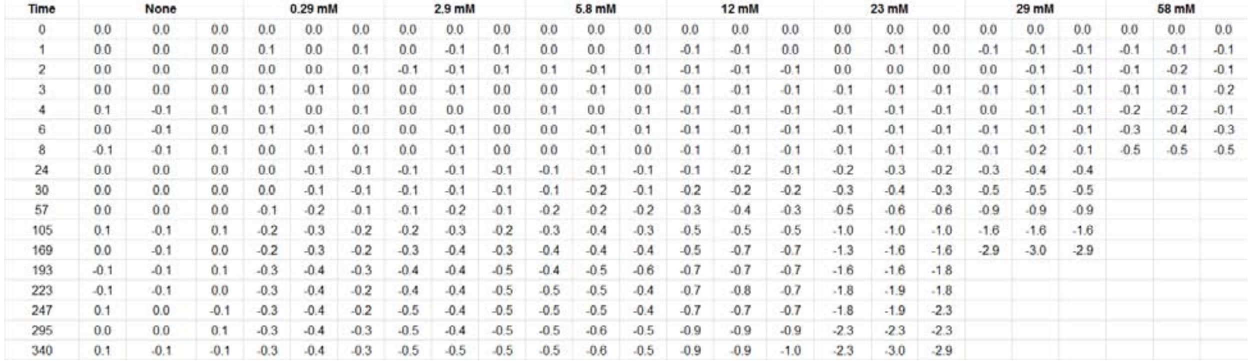
Time	None			0.0 M			0.03 M			0.29 M			0.58 M			1.2 M			1.7 M			2.4 M			2.9 M		
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	-0.1	0.0	0.0	-0.1	0.0	0.0	-0.1	0.0	0.0	-0.1	0.0	0.0	-0.1	0.0	-0.1	-0.1	0.0	-0.2	-0.1	-0.1	-0.2	-0.1	-0.1	-0.1
3	0.1	-0.1	0.1	-0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	-0.1	0.1	0.1	0.0	0.0	0.1	-0.1	0.0	-0.2	0.0	-0.1	-0.2
4	0.0	-0.1	0.0	-0.1	0.0	-0.1	-0.1	0.1	0.0	-0.1	0.0	0.0	-0.1	-0.1	0.0	-0.1	-0.1	-0.2	-0.1	-0.1	-0.3	-0.1	-0.2	-0.3	-0.3	-0.3	-0.2
6	-0.1	-0.1	0.1	-0.2	-0.2	-0.1	0.0	0.0	0.0	0.1	0.0	0.0	-0.2	-0.1	0.0	-0.2	-0.1	-0.1	-0.2	-0.4	-0.4	-0.4	-0.4	-0.6	-0.5	-0.8	-0.8
8	-0.1	-0.1	0.0	-0.1	-0.1	-0.1	-0.1	-0.1	0.0	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.3	-0.3	-0.6	-0.5	-0.4	-0.8	-0.6	-0.5	-0.6	-0.7	-0.8	-0.7
28	0.1	0.0	-0.1	-0.2	-0.2	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.2	-0.4	-0.4	-0.9	-0.9	-0.9	-1.4	-2.0	-2.2	-2.1	-2.4	-3.3			
52	0.0	0.0	0.1	-0.4	-0.2	-0.4	-0.2	-0.2	-0.2	-0.3	-0.5	-0.5	-0.6	-0.9	-1.0	-2.4	-2.5	-2.9									
76	0.1	-0.1	-0.1	-0.9	-0.8	-1.2	-0.7	-0.7	-0.7	-0.7	-1.1	-1.1	-1.5	-2.1	-2.1												
141	0.0	-0.1	-0.1	-1.2	-1.4	-1.4	-1.3	-1.2	-1.1	-1.2	-1.7	-1.8	-2.8														
190	0.0	0.0	0.1	-2.0	-2.2	-2.3	-1.7	-1.4	-1.7	-1.5	-2.3	-2.5															

Table C-3 Data Set for Figure 2-2A. Time in hours and data in mM soluble Cr(VI) for increasing concentration tartaric acid.



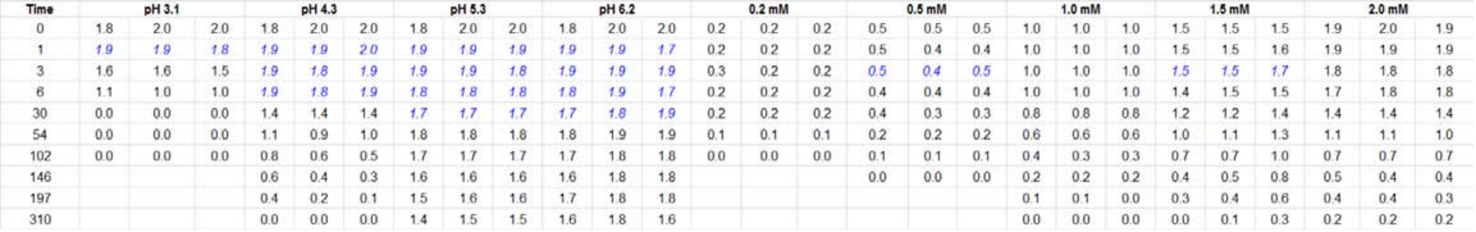
Time	None			0.29 mM			2.9 mM			5.8 mM			12 mM			23 mM			29 mM			58 mM		
0	1.9	2.0	1.9	1.9	2.0	1.9	1.9	2.0	1.9	1.9	2.0	1.9	1.9	2.0	1.9	1.9	2.0	1.9	1.9	2.0	1.9	1.9	2.0	1.9
1	1.9	2.0	1.9	2.0	2.0	2.0	1.9	1.9	2.0	1.9	2.0	2.0	1.8	1.9	1.9	1.9	1.9	1.9	1.8	1.9	1.8	1.8	1.8	1.8
2	1.9	2.0	1.9	1.9	2.0	2.0	1.8	1.9	2.0	2.0	1.9	2.0	1.8	1.9	1.8	1.9	2.0	1.9	1.9	1.8	1.8	1.8	1.7	1.8
3	1.9	2.0	1.9	2.0	1.9	1.9	1.9	1.9	1.9	1.9	1.8	1.9	1.8	1.8	1.8	1.8	1.8	1.8	1.7	1.8	1.8	1.7	1.8	1.6
4	2.0	1.9	2.0	2.0	2.0	2.0	1.9	2.0	1.9	2.0	2.0	2.0	1.8	1.9	1.8	1.8	1.9	1.8	1.9	1.9	1.8	1.6	1.6	1.7
6	1.9	1.9	1.9	2.0	1.8	1.9	1.9	1.9	1.9	1.9	1.9	2.0	1.8	1.9	1.8	1.7	1.8	1.8	1.8	1.8	1.7	1.4	1.4	1.4
8	1.7	1.9	2.1	1.9	1.8	2.0	1.9	1.9	1.9	1.9	1.9	1.9	1.8	1.8	1.8	1.8	1.8	1.8	1.7	1.7	1.7	1.1	1.2	1.1
24	1.9	2.0	1.9	1.9	1.9	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.7	1.7	1.7	1.5	1.5	1.5	1.4	1.3	1.3	0.0	0.0	0.1
30	1.9	2.0	1.9	1.9	1.8	1.8	1.8	1.8	1.8	1.7	1.7	1.7	1.6	1.6	1.6	1.4	1.4	1.4	1.2	1.2	1.2			
57	1.9	2.0	1.9	1.7	1.7	1.7	1.7	1.7	1.7	1.6	1.6	1.6	1.4	1.4	1.4	1.1	1.1	1.0	0.8	0.8	0.8			
105	2.0	1.9	2.0	1.5	1.5	1.6	1.5	1.5	1.5	1.4	1.4	1.4	1.2	1.2	1.2	0.7	0.7	0.7	0.4	0.4	0.4			
169	1.9	1.9	1.9	1.5	1.5	1.5	1.4	1.3	1.4	1.3	1.3	1.3	1.1	1.0	0.9	0.5	0.4	0.4	0.1	0.1	0.1			
193	1.7	1.9	2.1	1.4	1.4	1.4	1.3	1.4	1.2	1.3	1.2	1.0	0.9	1.0	0.9	0.4	0.4	0.3	0.0	0.0	0.0			
223	1.8	1.8	1.9	1.4	1.4	1.5	1.3	1.3	1.2	1.2	1.2	1.3	0.9	0.9	0.9	0.3	0.3	0.3						
247	2.1	2.0	1.8	1.4	1.4	1.5	1.2	1.3	1.2	1.2	1.2	1.3	0.9	1.0	0.9	0.3	0.3	0.2						
295	1.9	2.0	2.0	1.4	1.4	1.4	1.2	1.3	1.1	1.1	1.1	1.2	0.8	0.8	0.8	0.2	0.2	0.2						
340	2.0	1.8	1.8	1.4	1.4	1.4	1.2	1.2	1.1	1.1	1.1	1.2	0.8	0.8	0.7	0.2	0.1	0.1						

Table C-4 Data Set for Figure 2-2B. Time in hours and data are ln C/Co for soluble Cr(VI) for increasing concentration tartaric acid.



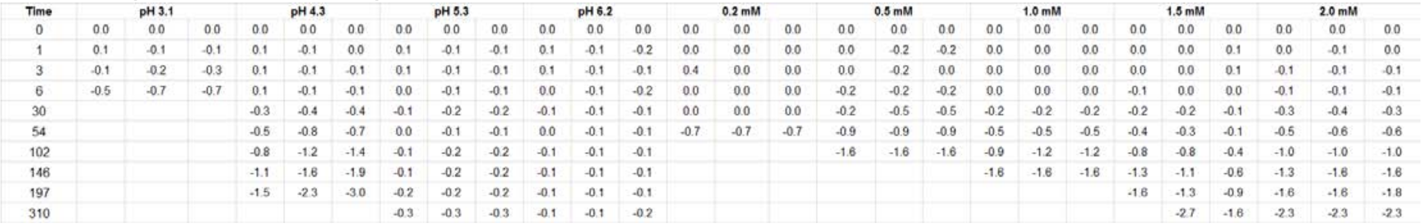
Time	None			0.29 mM			2.9 mM			5.8 mM			12 mM			23 mM			29 mM			58 mM		
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.0	0.0	0.0	0.1	0.0	0.1	0.0	-0.1	0.1	0.0	0.0	0.1	-0.1	-0.1	0.0	0.0	-0.1	0.0	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1
2	0.0	0.0	0.0	0.0	0.0	0.1	-0.1	-0.1	0.1	0.1	-0.1	0.1	-0.1	-0.1	-0.1	0.0	0.0	0.0	0.0	-0.1	-0.1	-0.1	-0.2	-0.1
3	0.0	0.0	0.0	0.1	-0.1	0.0	0.0	-0.1	0.0	0.0	-0.1	0.0	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.2
4	0.1	-0.1	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	0.0	-0.1	-0.1	-0.2	-0.2	-0.1
6	0.0	-0.1	0.0	0.1	-0.1	0.0	0.0	-0.1	0.0	0.0	-0.1	0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.3	-0.4	-0.3
8	-0.1	-0.1	0.1	0.0	-0.1	0.1	0.0	-0.1	0.0	0.0	-0.1	0.0	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.2	-0.1	-0.5	-0.5	-0.5
24	0.0	0.0	0.0	0.0	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.2	-0.1	-0.2	-0.3	-0.2	-0.3	-0.4	-0.4			
30	0.0	0.0	0.0	0.0	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.2	-0.1	-0.2	-0.2	-0.2	-0.3	-0.4	-0.3	-0.5	-0.5	-0.5			
57	0.0	0.0	0.0	-0.1	-0.2	-0.1	-0.1	-0.2	-0.1	-0.2	-0.2	-0.2	-0.3	-0.4	-0.3	-0.5	-0.6	-0.6	-0.9	-0.9	-0.9			
105	0.1	-0.1	0.1	-0.2	-0.3	-0.2	-0.2	-0.3	-0.2	-0.3	-0.4	-0.3	-0.5	-0.5	-0.5	-1.0	-1.0	-1.0	-1.6	-1.6	-1.6			
169	0.0	-0.1	0.0	-0.2	-0.3	-0.2	-0.3	-0.4	-0.3	-0.4	-0.4	-0.4	-0.5	-0.7	-0.7	-1.3	-1.6	-1.6	-2.9	-3.0	-2.9			
193	-0.1	-0.1	0.1	-0.3	-0.4	-0.3	-0.4	-0.4	-0.5	-0.4	-0.5	-0.6	-0.7	-0.7	-0.7	-1.6	-1.6	-1.8						
223	-0.1	-0.1	0.0	-0.3	-0.4	-0.2	-0.4	-0.4	-0.5	-0.5	-0.5	-0.4	-0.7	-0.8	-0.7	-1.8	-1.9	-1.8						
247	0.1	0.0	-0.1	-0.3	-0.4	-0.2	-0.5	-0.4	-0.5	-0.5	-0.5	-0.4	-0.7	-0.7	-0.7	-1.8	-1.9	-2.3						
295	0.0	0.0	0.1	-0.3	-0.4	-0.3	-0.5	-0.4	-0.5	-0.5	-0.6	-0.5	-0.9	-0.9	-0.9	-2.3	-2.3	-2.3						
340	0.1	-0.1	-0.1	-0.3	-0.4	-0.3	-0.5	-0.5	-0.5	-0.5	-0.6	-0.5	-0.9	-0.9	-1.0	-2.3	-3.0	-2.9						

Table C-5 Data Set for Figures 2-3A and 2-4A. Time in hours and data in mM soluble Cr(VI) for increasing pH and increasing initial concentration Cr(VI).



Time	pH 3.1			pH 4.3			pH 5.3			pH 6.2			0.2 mM			0.5 mM			1.0 mM			1.5 mM			2.0 mM		
0	1.8	2.0	2.0	1.8	2.0	2.0	1.8	2.0	2.0	1.8	2.0	2.0	0.2	0.2	0.2	0.5	0.5	0.5	1.0	1.0	1.0	1.5	1.5	1.5	1.9	2.0	1.9
1	*1.9*	*1.9*	*1.8*	*1.9*	*1.9*	*2.0*	*1.9*	*1.9*	*1.9*	*1.9*	*1.9*	*1.7*	0.2	0.2	0.2	0.5	0.4	0.4	1.0	1.0	1.0	1.5	1.5	1.6	1.9	1.9	1.9
3	1.6	1.6	1.5	*1.9*	*1.8*	*1.9*	*1.9*	*1.9*	*1.8*	*1.9*	*1.9*	*1.9*	0.3	0.2	0.2	*0.5*	*0.4*	*0.5*	1.0	1.0	1.0	*1.5*	*1.5*	*1.7*	1.8	1.8	1.8
6	1.1	1.0	1.0	*1.9*	*1.8*	*1.9*	*1.8*	*1.8*	*1.8*	*1.8*	*1.9*	*1.7*	0.2	0.2	0.2	0.4	0.4	0.4	1.0	1.0	1.0	1.4	1.5	1.5	1.7	1.8	1.8
30	0.0	0.0	0.0	1.4	1.4	1.4	*1.7*	*1.7*	*1.7*	*1.7*	*1.8*	*1.9*	0.2	0.2	0.2	0.4	0.3	0.3	0.8	0.8	0.8	1.2	1.2	1.4	1.4	1.4	1.4
54	0.0	0.0	0.0	1.1	0.9	1.0	1.8	1.8	1.8	1.8	1.9	1.9	0.1	0.1	0.1	0.2	0.2	0.2	0.6	0.6	0.6	1.0	1.1	1.3	1.1	1.1	1.0
102	0.0	0.0	0.0	0.8	0.6	0.5	1.7	1.7	1.7	1.7	1.8	1.8	0.0	0.0	0.0	0.1	0.1	0.1	0.4	0.3	0.3	0.7	0.7	1.0	0.7	0.7	0.7
146				0.6	0.4	0.3	1.6	1.6	1.6	1.6	1.8	1.8				0.0	0.0	0.0	0.2	0.2	0.2	0.4	0.5	0.8	0.5	0.4	0.4
197				0.4	0.2	0.1	1.5	1.6	1.6	1.7	1.8	1.8							0.1	0.1	0.0	0.3	0.4	0.6	0.4	0.4	0.3
310				0.0	0.0	0.0	1.4	1.5	1.5	1.6	1.8	1.6							0.0	0.0	0.0	0.0	0.1	0.3	0.2	0.2	0.2

Table C-6 Data Set for Figures 2-3B and 2-4B. Time in hours and data are ln C/Co for soluble Cr(VI) for increasing pH and increasing initial concentration Cr(VI).



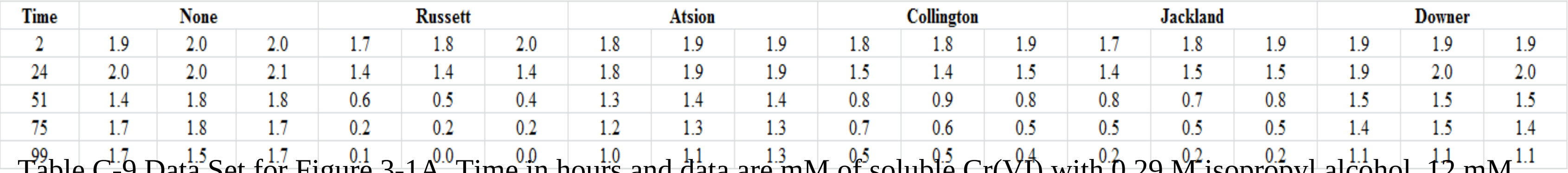
Time	pH 3.1			pH 4.3			pH 5.3			pH 6.2			0.2 mM			0.5 mM			1.0 mM			1.5 mM			2.0 mM		
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.1	-0.1	-0.1	0.1	-0.1	0.0	0.1	-0.1	-0.1	0.1	-0.1	-0.2	0.0	0.0	0.0	0.0	-0.2	-0.2	0.0	0.0	0.0	0.0	0.0	0.1	0.0	-0.1	0.0
3	-0.1	-0.2	-0.3	0.1	-0.1	-0.1	0.1	-0.1	-0.1	0.1	-0.1	-0.1	0.4	0.0	0.0	0.0	-0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.1	-0.1	-0.1	-0.1
6	-0.5	-0.7	-0.7	0.1	-0.1	-0.1	0.0	-0.1	-0.1	0.0	-0.1	-0.2	0.0	0.0	0.0	-0.2	-0.2	-0.2	0.0	0.0	0.0	-0.1	0.0	0.0	-0.1	-0.1	-0.1
30				-0.3	-0.4	-0.4	-0.1	-0.2	-0.2	-0.1	-0.1	-0.1	0.0	0.0	0.0	-0.2	-0.5	-0.5	-0.2	-0.2	-0.2	-0.2	-0.2	-0.1	-0.3	-0.4	-0.3
54				-0.5	-0.8	-0.7	0.0	-0.1	-0.1	0.0	-0.1	-0.1	-0.7	-0.7	-0.7	-0.9	-0.9	-0.9	-0.5	-0.5	-0.5	-0.4	-0.3	-0.1	-0.5	-0.6	-0.6
102				-0.8	-1.2	-1.4	-0.1	-0.2	-0.2	-0.1	-0.1	-0.1				-1.6	-1.6	-1.6	-0.9	-1.2	-1.2	-0.8	-0.8	-0.4	-1.0	-1.0	-1.0
146				-1.1	-1.6	-1.9	-0.1	-0.2	-0.2	-0.1	-0.1	-0.1							-1.6	-1.6	-1.6	-1.3	-1.1	-0.6	-1.3	-1.6	-1.6
197				-1.5	-2.3	-3.0	-0.2	-0.2	-0.2	-0.1	-0.1	-0.1										-1.6	-1.3	-0.9	-1.6	-1.6	-1.8
310							-0.3	-0.3	-0.3	-0.1	-0.1	-0.2											-2.7	-1.6	-2.3	-2.3	-2.3

Table C-7 Data Set for Figure 2-5A. Time in hours and data are pe of solution with increasing concentration isopropyl alcohol.

Time	0.0			0.03 M			0.29 M			0.58 M			1.2 M			1.7 M			2.4 M			2.9 M		
3.0	11.5	11.5	11.6	11.6	11.7	11.7	11.8	11.9	11.9	12.2	12.2	12.2	12.3	12.3	12.4	12.3	12.3	12.4	12.3	12.3	12.3	12.3	12.3	12.3
8.0	12.3	12.4	12.5	12.5	12.6	12.5	12.5	12.7	12.7	12.6	12.6	12.6	12.4	12.3	12.1	12.0	11.9	11.6	11.5	11.5	11.5	11.0	11.0	11.2
28.0	12.4	12.5	12.6	12.6	12.6	12.6	12.5	12.4	12.4	12.4	12.4	12.2	11.3	11.2	11.1	10.7	10.4	10.1	9.9	9.7	9.3	9.0	8.3	8.4
52.0	12.1	12.2	12.3	12.3	12.3	12.3	12.1	12.0	12.0	11.6	11.5	10.0	9.8	9.6	8.4	8.2	8.2	8.1	7.9	7.8	7.9	7.9	8.0	8.1
76.0	11.5	11.2	11.2	11.5	11.6	11.6	11.6	11.2	11.1	10.8	10.3	10.2	8.5	8.1	8.0	8.1	8.1	8.0	7.9	7.8	7.8	7.9	7.9	8.0
141.0	11.2	11.3	10.2	11.1	11.2	11.3	11.3	10.9	10.8	8.6	8.7	8.6	8.5	8.4	8.2	8.2	8.2	8.0	8.0	8.0	7.9	8.1	8.1	8.1
190.0	10.8	10.8	9.7	10.7	10.7	10.9	10.9	10.6	10.3	8.7	8.7	8.9	8.8	8.7	8.5	8.5	8.4	8.4	8.4	8.1	8.1	8.2	8.2	8.2

Table C-8 Data Set for Figure 2-5B. Time in hours and data are pe of solution with increasing concentration tartaric acid.

Time	0.0			0.29 mM			2.9 mM			5.8 mM			12 mM			23 mM			29 mM			58 mM		
0	10.6	10.0	10.6	10.6	10.0	10.6	10.6	10.0	10.6	10.6	10.0	10.6	10.6	10.0	10.6	10.6	10.0	10.6	10.6	10.0	10.6	10.6	10.0	10.6
4	*10.7*	*10.2*	*10.6*	*12.4*	*12.5*	*12.5*	*12.6*	*12.6*	*12.5*	*12.5*	*12.5*	*12.4*	*12.4*	*12.4*	*12.4*	*12.4*	*12.4*	*12.4*	*12.5*	*12.5*	*12.5*	12.3	12.3	12.2
8	*10.7*	*10.2*	*10.6*	11.7	12.0	12.1	12.6	12.6	12.6	12.6	12.6	12.7	12.6	12.6	12.6	12.6	12.6	12.6	12.6	12.6	12.6	11.6	11.5	11.5
24	10.0	9.6	9.9	10.6	10.8	11.0	11.9	12.0	12.0	12.2	12.3	12.3	12.4	12.4	12.4	12.4	12.4	12.4	12.3	12.2	12.2	9.1	9.9	9.9
57	*9.5*	*9.2*	*9.6*	9.1	9.1	9.4	12.3	12.3	12.4	12.6	12.6	12.6	12.6	12.5	12.5	12.4	12.2	12.2	11.9	11.8	11.8	9.8	9.6	9.5
105	*9.3*	*9.1*	*9.4*	8.7	8.8	8.7	11.8	12.1	12.1	12.3	12.3	12.4	12.3	12.2	12.2	11.8	11.7	11.6	11.2	11.0	10.9	9.8	9.6	9.5
169	*9.3*	*9.1*	*9.4*	*8.7*	*8.8*	*8.7*	*11.8*	*12.1*	*12.1*	*12.3*	*12.3*	*12.4*	*12.3*	*12.2*	*12.2*	*11.8*	*11.7*	*11.6*	*11.2*	*11.0*	*10.9*			
193	8.9	8.7	9.0	8.5	8.4	8.4	10.6	10.9	11.2	11.4	11.4	11.4	11.3	11.4	11.4	11.1	10.9	10.8	9.6	9.5	9.2			
223	8.8	8.6	9.0	8.5	8.5	8.4	10.0	10.5	11.0	11.3	11.3	11.3	11.1	11.3	11.3	10.9	10.8	10.7	9.6	9.4	9.2			
247	8.7	8.6	8.9	8.4	8.4	8.4	10.6	11.1	10.8	11.3	11.3	11.4	11.2	11.4	11.3	10.9	10.8	10.7	9.9	9.4	9.3			
340	8.9	8.8	9.0	8.5	8.5	8.4	9.7	10.2	10.5	10.7	10.7	10.7	10.2	10.6	10.5	10.1	9.9	9.8	9.2	8.9	8.8			

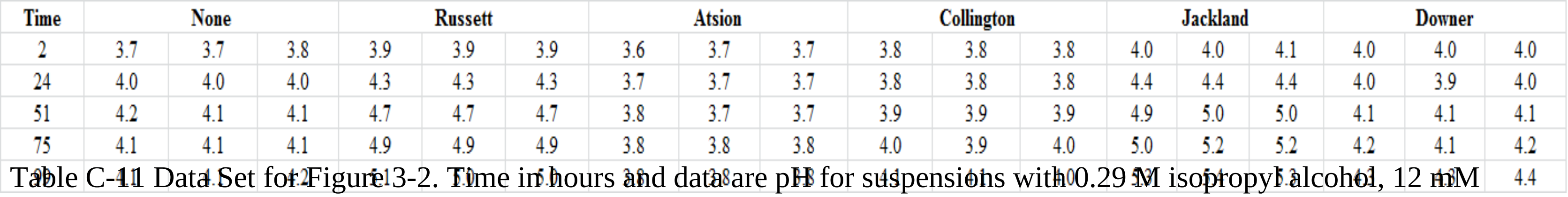


Time	None			Russett			Atsion			Collington			Jackland			Downer		
2	1.9	2.0	2.0	1.7	1.8	2.0	1.8	1.9	1.9	1.8	1.8	1.9	1.7	1.8	1.9	1.9	1.9	1.9
24	2.0	2.0	2.1	1.4	1.4	1.4	1.8	1.9	1.9	1.5	1.4	1.5	1.4	1.5	1.5	1.9	2.0	2.0
51	1.4	1.8	1.8	0.6	0.5	0.4	1.3	1.4	1.4	0.8	0.9	0.8	0.8	0.7	0.8	1.5	1.5	1.5
75	1.7	1.8	1.7	0.2	0.2	0.2	1.2	1.3	1.3	0.7	0.6	0.5	0.5	0.5	0.5	1.4	1.5	1.4
99	1.7	1.5	1.7	0.1	0.0	0.0	1.0	1.1	1.3	0.5	0.5	0.4	0.2	0.2	0.2	1.1	1.1	1.1

Table C-9 Data Set for Figure 3-1A. Time in hours and data are mM of soluble Cr(VI) with 0.29 M isopropyl alcohol, 12 mM tartaric acid, and pH 4 for five Maryland soils.

Time	None			Russett			Atsion			Collington			Jackland			Downer		
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
24	0.0	0.0	0.0	-0.2	-0.3	-0.3	0.0	0.0	0.0	-0.2	-0.3	-0.2	-0.2	-0.2	-0.2	0.0	0.0	0.0
51	-0.4	-0.1	-0.1	-1.1	-1.2	-1.5	-0.3	-0.3	-0.3	-0.8	-0.8	-0.8	-0.8	-0.9	-0.9	-0.2	-0.2	-0.2
75	-0.2	-0.1	-0.2	-2.2	-2.3	-2.3	-0.3	-0.3	-0.4	-1.0	-1.2	-1.4	-1.3	-1.3	-1.3	-0.3	-0.3	-0.3
99	-0.2	-0.2	-0.2	-3.2	-3.8	-4.5	-0.6	-0.6	-0.3	-1.2	-1.2	-1.5	-2.0	-2.1	-2.0	-0.5	-0.5	-0.5

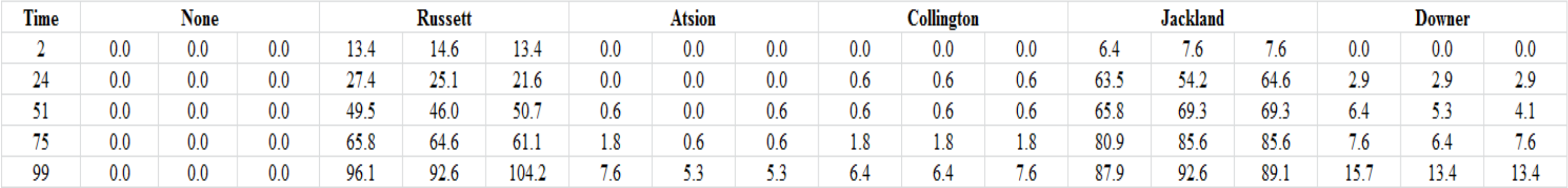
Table C-10 Data Set for Figure 3-1B. Time in hours and data are ln concentration over initial concentration (C/Co) for soluble Cr(VI) with 0.29 M isopropyl alcohol, 12 mM tartaric acid, and pH 4 for five Maryland soils.



Time	None			Russett			Atsion			Collington			Jackland			Downer		
2	3.7	3.7	3.8	3.9	3.9	3.9	3.6	3.7	3.7	3.8	3.8	3.8	4.0	4.0	4.1	4.0	4.0	4.0
24	4.0	4.0	4.0	4.3	4.3	4.3	3.7	3.7	3.7	3.8	3.8	3.8	4.4	4.4	4.4	4.0	3.9	4.0
51	4.2	4.1	4.1	4.7	4.7	4.7	3.8	3.7	3.7	3.9	3.9	3.9	4.9	5.0	5.0	4.1	4.1	4.1
75	4.1	4.1	4.1	4.9	4.9	4.9	3.8	3.8	3.8	4.0	3.9	4.0	5.0	5.2	5.2	4.2	4.1	4.2
99	4.1	4.1	4.2	5.1	5.0	5.0	3.8	3.8	3.8	4.1	4.1	4.0	5.3	5.4	5.3	4.3	4.3	4.4

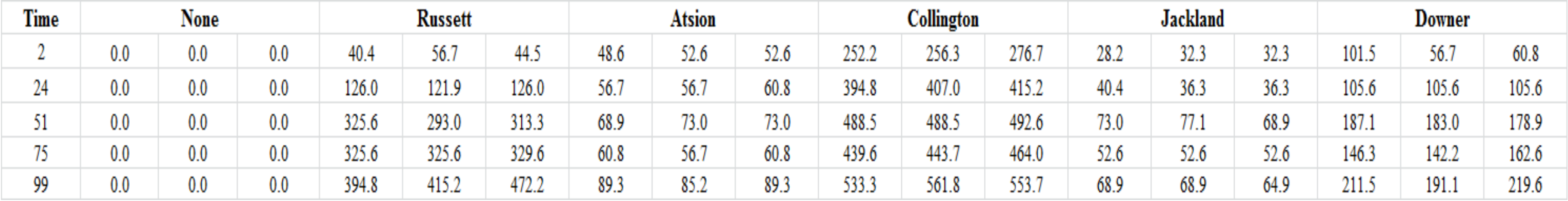
Table C-11 Data Set for Figure 3-2. Time in hours and data are pH for suspensions with 0.29 M isopropyl alcohol, 12 mM tartaric acid, and pH 4 for five Maryland soils.

Table C-12 Data Set for Figure 3-3A. Time in hours and data are µM of soluble Mn with 0.29 M isopropyl alcohol, 12 mM tartaric acid, and pH 4 for five Maryland soils.



Time	None			Russett			Atsion			Collington			Jackland			Downer		
2	0.0	0.0	0.0	13.4	14.6	13.4	0.0	0.0	0.0	0.0	0.0	0.0	6.4	7.6	7.6	0.0	0.0	0.0
24	0.0	0.0	0.0	27.4	25.1	21.6	0.0	0.0	0.0	0.6	0.6	0.6	63.5	54.2	64.6	2.9	2.9	2.9
51	0.0	0.0	0.0	49.5	46.0	50.7	0.6	0.0	0.6	0.6	0.6	0.6	65.8	69.3	69.3	6.4	5.3	4.1
75	0.0	0.0	0.0	65.8	64.6	61.1	1.8	0.6	0.6	1.8	1.8	1.8	80.9	85.6	85.6	7.6	6.4	7.6
99	0.0	0.0	0.0	96.1	92.6	104.2	7.6	5.3	5.3	6.4	6.4	7.6	87.9	92.6	89.1	15.7	13.4	13.4

Table C-13 Data Set for Figure 3-3B. Time in hours and data are µM of soluble Fe with 0.29 M isopropyl alcohol, 12 mM tartaric acid, and pH 4 for five Maryland soils.



Time	None			Russett			Atsion			Collington			Jackland			Downer		
2	0.0	0.0	0.0	40.4	56.7	44.5	48.6	52.6	52.6	252.2	256.3	276.7	28.2	32.3	32.3	101.5	56.7	60.8
24	0.0	0.0	0.0	126.0	121.9	126.0	56.7	56.7	60.8	394.8	407.0	415.2	40.4	36.3	36.3	105.6	105.6	105.6
51	0.0	0.0	0.0	325.6	293.0	313.3	68.9	73.0	73.0	488.5	488.5	492.6	73.0	77.1	68.9	187.1	183.0	178.9
75	0.0	0.0	0.0	325.6	325.6	329.6	60.8	56.7	60.8	439.6	443.7	464.0	52.6	52.6	52.6	146.3	142.2	162.6
99	0.0	0.0	0.0	394.8	415.2	472.2	89.3	85.2	89.3	533.3	561.8	553.7	68.9	68.9	64.9	211.5	191.1	219.6

Table C-14 Data Set for Figure 3-4. Soluble Cr(VI) after 24h shaking in presence of Mn-oxide coated sand with 12 mM tartaric acid and pH 4. Initial Cr(III) concentration at 2 mM, and done in separate experiment.

Mn oxide-sand (mg)	**0**	**0**	**0**	**10**	**10**	**10**	**50**	**50**	**50**	**100**	**100**	**100**
Soluble Cr(VI) (mM)	2.00	1.91	1.97	1.30	1.41	1.44	1.11	1.15	1.12	0.73	0.81	0.75
From Cr(III) (mM)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.37	0.37
Total Cr (mM)	1.95	2.02	2.14	2.06	2.11	1.92	1.89	1.80	2.18	1.87	1.73	1.70
Soluble Mn (uM)	0.0	0.0	0.0	4.2	7.2	1.8	16.2	13.2	43.3	28.3	43.3	40.3

Table C-15 Data Set for Figure 3-5. Soluble Cr(VI) after 24h shaking in presence of trivalent and divalent metals with 12 mM tartaric acid, 0.29 M isopropyl alcohol, and pH 4.

Time	**None**			**Al3+**			**Cr3+**			**Ca2+**			**Mg2+**			**Mn2+**			**Cu2+**			**Zn2+**		
24	1.8	2.0	2.1	2.0	2.0	2.0	2.0	2.0	2.0	2.1	2.1	2.0	2.0	2.0	2.0	0.4	0.5	0.3	1.7	1.8	1.8	2.0	2.0	2.3
48	1.8	1.7	2.0	2.0	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	2.0	0.0	0.0	0.0	1.6	1.6	1.7	1.9	1.9	2.0
72	1.8	1.9	1.8	1.8	1.8	1.8	1.8	1.7	1.8	1.8	1.9	1.9	1.9	1.9	2.0	0.0	0.0	0.0	1.4	1.5	1.4	1.8	1.9	1.7
96	1.8	1.9	1.6	1.6	1.7	1.8	1.6	1.7	1.8	1.9	1.8	1.9	1.9	1.8	1.8	0.0	0.0	0.0	1.2	1.3	1.3	1.7	1.7	1.8
144	1.5	1.7	1.8	1.7	1.7	1.7	1.6	1.6	1.6	1.7	1.6	1.7	1.8	1.8	1.8	-0.1	-0.1	-0.1	0.7	1.0	1.0	1.6	1.8	1.6

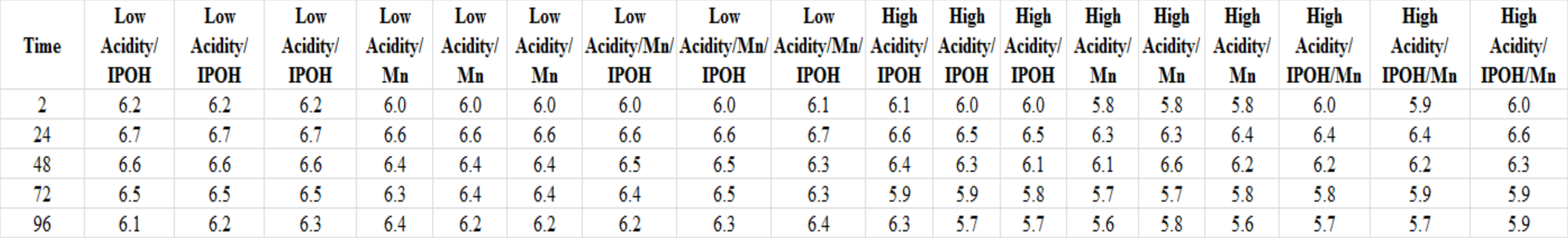
Table C-16 Data Set for Figure 4-1A. Soluble Cr(VI) in mM after 96 h in presence of 1 mM Mn^{2+}, 0.29 M isopropyl alcohol, or both with 12 mM tartaric acid at pH 4 or 5.5.

Time	pH 4 IPOH	pH 4 IPOH	pH 4 IPOH	pH 4 Mn	pH 4 Mn	pH 4 Mn	pH 4 IPOH/Mn	pH 4 IPOH/Mn	pH 4 IPOH/Mn	pH 5.5 IPOH	pH 5.5 IPOH	pH 5.5 IPOH	pH 5.5 Mn	pH 5.5 Mn	pH 5.5 Mn	pH 5.5 IPOH/Mn	pH 5.5 IPOH/Mn	pH 5.5 IPOH/Mn	pH 4	pH 4	pH 4	pH 5.5	pH 5.5	pH 5.5
2	1.07	1.00	0.99	0.95	0.99	0.95	0.96	0.95	0.96	1.06	0.89	1.00	0.99	0.99	1.01	0.97	0.95	0.98	1.00	0.90	0.93	1.10	1.10	1.00
24	1.11	0.98	0.98	0.17	0.13	0.15	0.12	0.12	0.12	1.00	1.01	1.05	0.88	0.91	0.92	0.90	0.90	0.90	0.80	1.03	1.05	1.00	1.10	1.10
48	0.92	0.90	0.79	0.05	0.04	0.04	0.04	0.04	0.04	1.02	1.03	0.99	0.77	0.75	0.78	0.76	0.75	0.73	0.82	0.67	0.96	1.25	1.07	1.00
72	0.50	0.68	0.63	0.03	0.03	0.03	0.03	0.03	0.03	0.88	0.87	0.85	0.44	0.43	0.50	0.53	0.47	0.47	0.83	0.94	0.77	1.22	1.06	1.00
96	0.46	0.61	0.56	0.02	0.02	0.02	0.02	0.02	0.02	0.90	0.92	0.90	0.40	0.37	0.43	0.41	0.43	0.42	0.76	0.90	0.63	1.19	1.06	1.01

Table C-17 Data Set for Figure 4-1B. Natural log of soluble Cr(VI) concentrations over initial concentration (ln C/Co) for 96 h in presence of 1 mM Mn^{2+}, 0.29 M isopropyl alcohol, or both with 12 mM tartaric acid at pH 4 or 5.5.

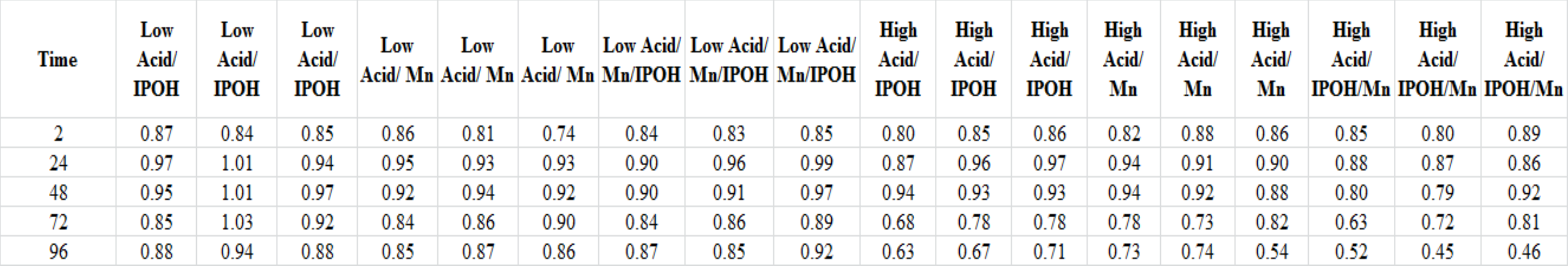
Time	pH 4 IPOH	pH 4 IPOH	pH 4 IPOH	pH 4 Mn	pH 4 Mn	pH 4 Mn	pH 4 IPOH/Mn	pH 4 IPOH/Mn	pH 4 IPOH/Mn	pH 5.5 IPOH	pH 5.5 IPOH	pH 5.5 IPOH	pH 5.5 Mn	pH 5.5 Mn	pH 5.5 Mn	pH 5.5 IPOH/Mn	pH 5.5 IPOH/Mn	pH 5.5 IPOH/Mn
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.04	-0.02	-0.02	-1.73	-2.05	-1.85	-2.12	-2.06	-2.09	-0.06	0.13	0.05	-0.11	-0.09	-0.10	-0.07	-0.06	-0.08
48	-0.14	-0.11	-0.23	-3.04	-3.14	-3.10	-3.14	-3.13	-3.14	-0.03	0.14	0.00	-0.25	-0.27	-0.26	-0.24	-0.24	-0.28
72	-0.76	-0.39	-0.46	-3.38	-3.42	-3.38	-3.38	-3.38	-3.38	-0.18	-0.02	-0.16	-0.81	-0.85	-0.69	-0.60	-0.70	-0.72
96	-0.84	-0.49	-0.57	-3.88	-3.93	-3.88	-3.89	-3.88	-3.89	-0.16	0.03	-0.11	-0.90	-0.97	-0.86	-0.87	-0.79	-0.85

Table C-18 Data Set for Figure 4-2. pH for 96 h in presence of 1 mM Mn^{2+}, 0.29 M isopropyl alcohol, or both with 12 mM tartaric acid at low or high acidity. Low acidity is initial 0.2 M HNO_3 concentration and high acidity is 0.5 M HNO_3. Time is in hours.

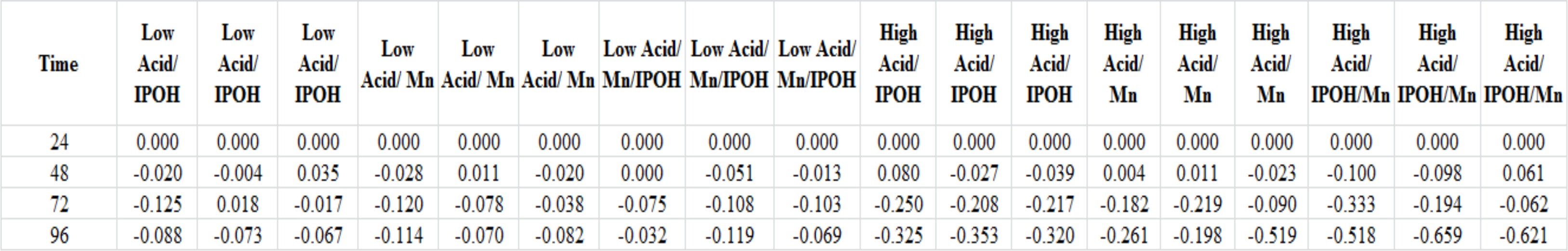


Time	Low Acidity/ IPOH	Low Acidity/ IPOH	Low Acidity/ IPOH	Low Acidity/ Mn	Low Acidity/ Mn	Low Acidity/ Mn	Low Acidity/Mn/ IPOH	Low Acidity/Mn/ IPOH	Low Acidity/Mn/ IPOH	High Acidity/ IPOH	High Acidity/ IPOH	High Acidity/ IPOH	High Acidity/ Mn	High Acidity/ Mn	High Acidity/ Mn	High Acidity/ IPOH/Mn	High Acidity/ IPOH/Mn	High Acidity/ IPOH/Mn
2	6.2	6.2	6.2	6.0	6.0	6.0	6.0	6.0	6.1	6.1	6.0	6.0	5.8	5.8	5.8	6.0	5.9	6.0
24	6.7	6.7	6.7	6.6	6.6	6.6	6.6	6.6	6.7	6.6	6.5	6.5	6.3	6.3	6.4	6.4	6.4	6.6
48	6.6	6.6	6.6	6.4	6.4	6.4	6.5	6.5	6.3	6.4	6.3	6.1	6.1	6.6	6.2	6.2	6.2	6.3
72	6.5	6.5	6.5	6.3	6.4	6.4	6.4	6.5	6.3	5.9	5.9	5.8	5.7	5.7	5.8	5.8	5.9	5.9
96	6.1	6.2	6.3	6.4	6.2	6.2	6.2	6.3	6.4	6.3	5.7	5.7	5.6	5.8	5.6	5.7	5.7	5.9

Table C-19 Data Set for Figure 4-3A. Soluble Cr(VI) in mM for 96 h in presence of 1 mM Mn^{2+}, 0.29 M isopropyl alcohol, or both with 12 mM tartaric acid at low or high acidity. Low acidity is initial 0.2 M HNO_3 concentration and high acidity is 0.5 M HNO_3. Time is in hours.

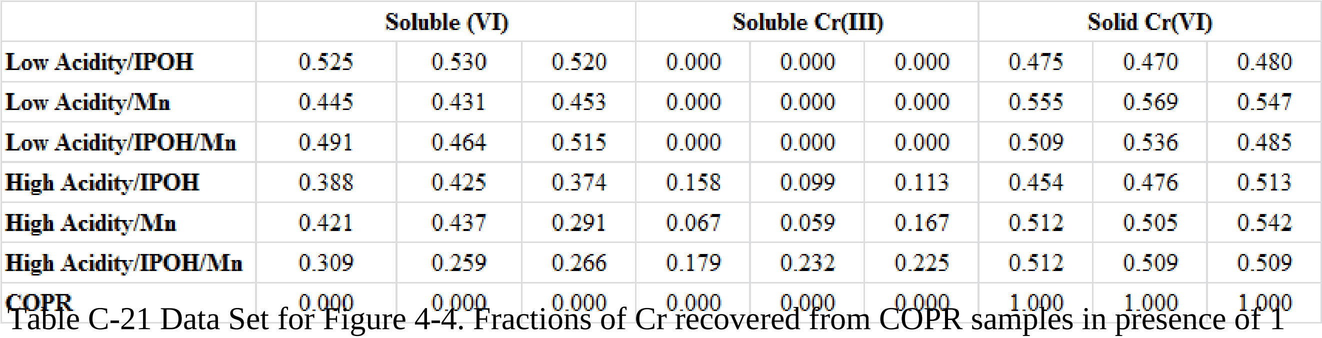


Time	Low Acid/ IPOH	Low Acid/ IPOH	Low Acid/ IPOH	Low Acid/ Mn	Low Acid/ Mn	Low Acid/ Mn	Low Acid/ Mn/IPOH	Low Acid/ Mn/IPOH	Low Acid/ Mn/IPOH	High Acid/ IPOH	High Acid/ IPOH	High Acid/ IPOH	High Acid/ Mn	High Acid/ Mn	High Acid/ Mn	High Acid/ IPOH/Mn	High Acid/ IPOH/Mn	High Acid/ IPOH/Mn
2	0.87	0.84	0.85	0.86	0.81	0.74	0.84	0.83	0.85	0.80	0.85	0.86	0.82	0.88	0.86	0.85	0.80	0.89
24	0.97	1.01	0.94	0.95	0.93	0.93	0.90	0.96	0.99	0.87	0.96	0.97	0.94	0.91	0.90	0.88	0.87	0.86
48	0.95	1.01	0.97	0.92	0.94	0.92	0.90	0.91	0.97	0.94	0.93	0.93	0.94	0.92	0.88	0.80	0.79	0.92
72	0.85	1.03	0.92	0.84	0.86	0.90	0.84	0.86	0.89	0.68	0.78	0.78	0.78	0.73	0.82	0.63	0.72	0.81
96	0.88	0.94	0.88	0.85	0.87	0.86	0.87	0.85	0.92	0.63	0.67	0.71	0.73	0.74	0.54	0.52	0.45	0.46



Time	Low Acid/ IPOH	Low Acid/ IPOH	Low Acid/ IPOH	Low Acid/ Mn	Low Acid/ Mn	Low Acid/ Mn	Low Acid/ Mn/IPOH	Low Acid/ Mn/IPOH	Low Acid/ Mn/IPOH	High Acid/ IPOH	High Acid/ IPOH	High Acid/ IPOH	High Acid/ Mn	High Acid/ Mn	High Acid/ Mn	High Acid/ IPOH/Mn	High Acid/ IPOH/Mn	High Acid/ IPOH/Mn
24	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
48	-0.020	-0.004	0.035	-0.028	0.011	-0.020	0.000	-0.051	-0.013	0.080	-0.027	-0.039	0.004	0.011	-0.023	-0.100	-0.098	0.061
72	-0.125	0.018	-0.017	-0.120	-0.078	-0.038	-0.075	-0.108	-0.103	-0.250	-0.208	-0.217	-0.182	-0.219	-0.090	-0.333	-0.194	-0.062
96	-0.088	-0.073	-0.067	-0.114	-0.070	-0.082	-0.032	-0.119	-0.069	-0.325	-0.353	-0.320	-0.261	-0.198	-0.519	-0.518	-0.659	-0.621

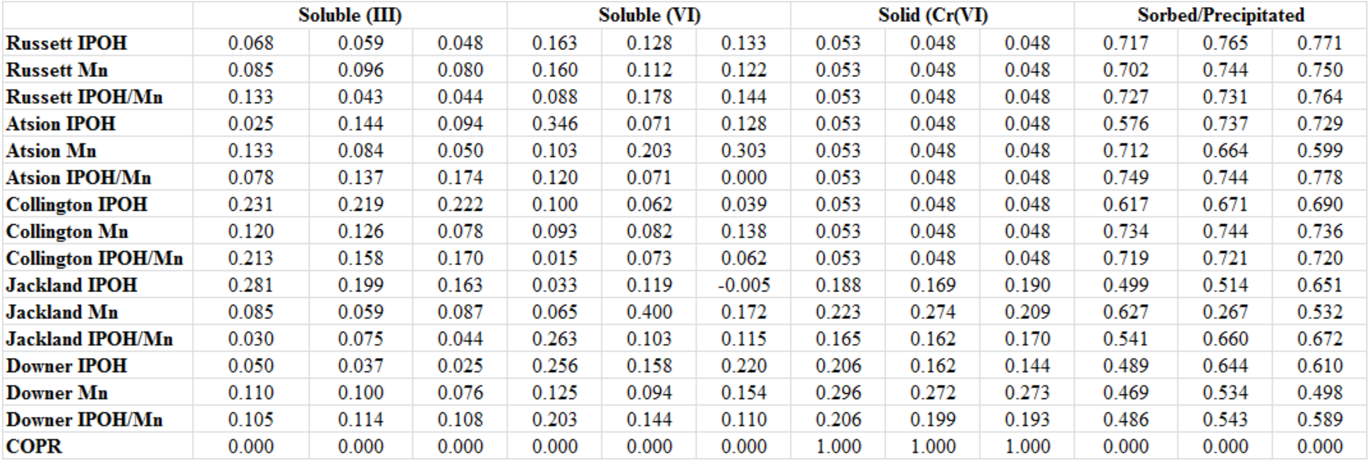
Table C-20 Data Set for Figure 4-3B. Natural log of soluble Cr(VI) concentrations over initial concentration (ln C/Co) starting at 24 h in presence of 1 mM Mn^{2+}, 0.29 M isopropyl alcohol, or both with 12 mM tartaric acid at low or high acidity. Low acidity is initial 0.2 M HNO_3 concentration and high acidity is 0.5 M HNO_3. Time is in hours.



	Soluble (VI)			Soluble Cr(III)			Solid Cr(VI)		
Low Acidity/IPOH	0.525	0.530	0.520	0.000	0.000	0.000	0.475	0.470	0.480
Low Acidity/Mn	0.445	0.431	0.453	0.000	0.000	0.000	0.555	0.569	0.547
Low Acidity/IPOH/Mn	0.491	0.464	0.515	0.000	0.000	0.000	0.509	0.536	0.485
High Acidity/IPOH	0.388	0.425	0.374	0.158	0.099	0.113	0.454	0.476	0.513
High Acidity/Mn	0.421	0.437	0.291	0.067	0.059	0.167	0.512	0.505	0.542
High Acidity/IPOH/Mn	0.309	0.259	0.266	0.179	0.232	0.225	0.512	0.509	0.509
COPR	0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000	1.000

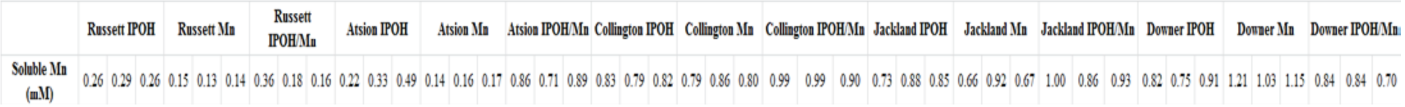
Table C-21 Data Set for Figure 4-4. Fractions of Cr recovered from COPR samples in presence of 1 mM Mn^{2+}, 0.29 M isopropyl alcohol, or both with 12 mM tartaric acid at low or high acidity. Low acidity is initial 0.2 M HNO_3 concentration and high acidity is 0.5 M HNO_3.

Table C-22 Data Set for Figure 4-5. Fraction of Cr remaining after 48 h shaking in presence of five Maryland soils with 1 mM Mn^{2+}, 0.29 M isopropyl alcohol, or both with 12 mM tartaric acid .



	Soluble (III)			Soluble (VI)			Solid (Cr(VI)			Sorbed/Precipitated		
Russett IPOH	0.068	0.059	0.048	0.163	0.128	0.133	0.053	0.048	0.048	0.717	0.765	0.771
Russett Mn	0.085	0.096	0.080	0.160	0.112	0.122	0.053	0.048	0.048	0.702	0.744	0.750
Russett IPOH/Mn	0.133	0.043	0.044	0.088	0.178	0.144	0.053	0.048	0.048	0.727	0.731	0.764
Atsion IPOH	0.025	0.144	0.094	0.346	0.071	0.128	0.053	0.048	0.048	0.576	0.737	0.729
Atsion Mn	0.133	0.084	0.050	0.103	0.203	0.303	0.053	0.048	0.048	0.712	0.664	0.599
Atsion IPOH/Mn	0.078	0.137	0.174	0.120	0.071	0.000	0.053	0.048	0.048	0.749	0.744	0.778
Collington IPOH	0.231	0.219	0.222	0.100	0.062	0.039	0.053	0.048	0.048	0.617	0.671	0.690
Collington Mn	0.120	0.126	0.078	0.093	0.082	0.138	0.053	0.048	0.048	0.734	0.744	0.736
Collington IPOH/Mn	0.213	0.158	0.170	0.015	0.073	0.062	0.053	0.048	0.048	0.719	0.721	0.720
Jackland IPOH	0.281	0.199	0.163	0.033	0.119	-0.005	0.188	0.169	0.190	0.499	0.514	0.651
Jackland Mn	0.085	0.059	0.087	0.065	0.400	0.172	0.223	0.274	0.209	0.627	0.267	0.532
Jackland IPOH/Mn	0.030	0.075	0.044	0.263	0.103	0.115	0.165	0.162	0.170	0.541	0.660	0.672
Downer IPOH	0.050	0.037	0.025	0.256	0.158	0.220	0.206	0.162	0.144	0.489	0.644	0.610
Downer Mn	0.110	0.100	0.076	0.125	0.094	0.154	0.296	0.272	0.273	0.469	0.534	0.498
Downer IPOH/Mn	0.105	0.114	0.108	0.203	0.144	0.110	0.206	0.199	0.193	0.486	0.543	0.589
COPR	0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000	1.000	0.000	0.000	0.000

Table C-23 Data Set for Figure 4-6. Soluble Mn concentrations in mM after 48 h shaking in presence of five Maryland soils with 1 mM Mn^{2+}, 0.29 M isopropyl alcohol, or both with 12 mM tartaric acid.



	Russett IPOH			Russett Mn			Russett IPOH/Mn			Atsion IPOH			Atsion Mn		
Soluble Mn (mM)	0.26	0.29	0.26	0.15	0.13	0.14	0.36	0.18	0.16	0.22	0.33	0.49	0.14	0.16	0.17

	Atsion IPOH/Mn			Collington IPOH			Collington Mn			Collington IPOH/Mn			Jackland IPOH		
Soluble Mn (mM)	0.86	0.71	0.89	0.83	0.79	0.82	0.79	0.86	0.80	0.99	0.99	0.90	0.73	0.88	0.85

	Jackland Mn			Jackland IPOH/Mn			Downer IPOH			Downer Mn			Downer IPOH/Mn		
Soluble Mn (mM)	0.66	0.92	0.67	1.00	0.86	0.93	0.82	0.75	0.91	1.21	1.03	1.15	0.84	0.84	0.70

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