

APPLICATION OF SEQUENTIAL EXTRACTION METHODS TO DETERMINE
THE SPECIATION OF CR-CONTAMINATED SOILS FROM THE NEW JERSEY
MEADOWLANDS

By

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ABSTRACT OF THE DISSERTATION

Application of sequential extraction methods to determine the speciation of Cr-contaminated soils from the New Jersey Meadowlands

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Three sequential extraction methods (SE) were implemented to determine the speciation of Cr in soil samples taken from a Chromite Ore Processing Residue (COPR) dump site located in the New Jersey Meadowlands. The results from the SE methods indicated that Cr was primarily associated with the oxidizable and reducible soil fractions, and that a significant amount of Cr remained un-extracted and was present in the residual soil fraction. The quantitative analysis of the SE data proved to be difficult due to strong differences in the estimates of associated Cr to soil fractions. This is due to the limitations associated with the sequential extraction schemes such as re-adsorption of metals between steps. To avoid the issues in analysis due to the limitations seen in the SE data; it is proposed that a secondary method, such as X-ray Absorption Spectroscopy (XAS), is to be used in conjunction with the SE methods.

Here, results from XAS analyses were proven to provide proper constraint to the SE data. The results from the XAS method qualitatively supported the sequential extraction scheme results, but demonstrated that comparisons between the SE and XAS data resulted in poor correlations meaning that direct comparisons is unreliable. Since application of XAS along with sequential extraction schemes is not feasible in many

situations, it is suggested to so the suggestion is to design optimized sequential extraction scheme.

Preface

Acknowledgements/Dedication

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I would like to dedicate this to my late father Thomas A. Cirmo.

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1. Introduction:

Chromium (Cr) can be either very harmful to humans or it can be an important element for human digestion, depending on its oxidation state (Stern et al., 2010; Burke et al., 1991; Geelhoed et al., 2003; and Higgins et al., 1998). Hexavalent chromium is the more dangerous form due to its mobility and toxicity, whereas trivalent Cr is mostly found in a solid stable form with relatively low solubility and toxicity (Geelhoed et al., 2003). As a result, at sites where chromium contamination is a concern, it is important to determine the Cr species present in the soil and water as a first step towards assessing the risk posed by the contaminants and the need for site remediation.

There are several well noted locations in the U.S. and abroad where Cr contamination has been, and continues to be, a major concern including; Jersey City, NJ (Burke et al., 1991; Chrysochouu et al., 2009; Geelhoed et al., 2002; Geelhoed et al., 2003; and Tinjum et al., 2008), Baltimore, MD (Burke et al., 1991; Chrysochouu et al., 2009; and Tinjum et al., 2008), and Glasgow, Scotland (Chrysochouu et al., 2009; Geelhoed et al., 2002; Geelhoed et al., 2003; Hursthouse et al., 2001; and Thomas et al., 2001). At all of these locations, chromium was introduced into the environment through deposition of the waste resulting from local chromite ore processing plants, commonly referred to as chromite ore processing residue, or COPR. In Northern New Jersey, health concerns associated with Cr contamination first became a major issue in 1988 in the Jersey City, NJ area after the local paper (Jersey City Reporter) reported that chromium exposure was part of the reason why a local man had died. This man happened to be working at a truck loading facility that was built on a COPR waste site (Burke et al., 1991). Growing concerns regarding the impact of Cr on human health and natural

ecosystems, both in the US and abroad, have prompted numerous studies dealing with the dispersion of Cr in the soil, air, and groundwater (Stern et al., 2010) in order to obtain an improved understanding of the stability, mobility and fate of Cr(VI) released into the natural environment.

The vast majority of environmental Cr contamination in Hudson County, New Jersey can be linked to chromite ore processing residue (Burke et al., 1991; Geelhoed et al., 2003; Geelhoed et al., 2002; Chrysochoou et al., 2009; and Tinjum et al., 2008). Between 1905 and 1976 several chromite ore processing plants that produced chromium products were established in Hudson County (Chrysochoou et al., 2009; Higgins et al., 1998, NJDEP website visited Oct 2012). Two factories were found in Jersey City, NJ; PPG industries, Inc. and the predecessors of AlliedSignal, Inc. and one plant in Kearny, the predecessors and subsidiaries of Occidental Chemical Co., Maxus Energy Corp and Chemical Landing Holding, Inc. (NJDEP website visited Oct 2012, Burke et al., 1991). These plants would extract chromium from chromite ore by mixing the ore with lime and soda ash, and then heating the mixture at high temperatures in order to oxidize the chromium to chromate (CrO_4^{2-}), which is water soluble and therefore readily extractable from the treated material (Burke et al., 1991; Geelhoed et al., 2002; and Geelhoed et al., 2003). Chromite ore processing residue (COPR) is the remaining waste product from this extraction procedure. Due to the materials' sand-like properties it was widely used as fill material at residential and commercial construction sites until 1976 (Chrysochoou et al., 2009; Burke et al., 1991; Geelhoed et al., 2002; and Geelhoed et al., 2003). This fill material contained approximately 2 to 7 wt% of Cr, of which up to 35% is present as Cr(VI) (Tinjum et al., 2008). As a result, these COPR sites have become a major

environmental concern throughout Northern New Jersey as Cr(VI) is leaching into the surround soils, surface and groundwaters. Over 130 such sites have been identified in the Jersey City area (Burke et al., 1991 and Tinjum et al., 2008).

Chromium is found in a variety of chemical forms in the COPR material. Calcium chromate ($\text{Ca}(\text{CrO}_4)$), hydrogarnet ($\text{Ca}_3(\text{Al,Fe})_2(\text{H}_4\text{O}_4,\text{CrO}_4)_3$) and chromium hydrocalumite ($\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{CrO}_4 \cdot 6\text{H}_2\text{O}$) have been identified as major Cr(VI) bearing chemical components of COPR (Burke et al., 1991; Chrysochoou et al., 2009; Geelhoed et al., 2002; and Geelhoed et al., 2003), whereas trivalent chromium is commonly found in brownmillerite ($\text{Ca}_2(\text{Al,Fe,Cr})_2\text{O}_5$) and residual chromite (Geelhoed et al., 2002 and Geelhoed et al., 2003).

The release of Cr from COPR deposits is the result of weathering of Cr-containing minerals and salts formed during the high temperature roasting process. The extent and rate of weathering are controlled by the stability and solubility of the Cr(VI) compounds present, as well as the geochemical conditions at the sites where the material was deposited. Compounds such as calcium chromate and chromium hydrocalumite have generally slow dissolution rates and therefore continue to release Cr(VI) into the environment many years after the material has started weathering (Burke et al., 1991 and Geelhoed et al., 2002). Natural organic matter at COPR sites is beneficial in the sense that organic material is capable of reducing Cr(VI) to Cr(III) naturally and thus can slow the leaching of Cr(VI) into the surrounding environment. Other naturally occurring reductants capable of converting Cr(VI) to Cr(III) include leaf litter (James 1994) and bacteria (Lee et al., 2006). However, at locations where Cr(VI) remains in the soluble and mobile hexavalent form, leaching to the surface and ground waters may allow the

contaminant to spread to a broad area (Burke et al., 1991; Geelhoed et al., 2002; and Geelhoed et al., 2003). The fate and mobility of Cr(VI) following release thus depend to a large extent on the geochemical and hydrological conditions controlling the reduction and transport of Cr(VI). Understanding these processes may aid decisions on the urgency and best strategy of site remediation, and aid improvement of remediation techniques.

The most common strategy for slowing the release of Cr(VI) from COPR deposits into the surrounding environment is to promote reduction of Cr(VI) to the stable Cr(III) form. There are two general ways to promote reduction of Cr(VI): introduction of chemicals capable of reducing Cr(VI) (Tinjum et al., 2008); and introduction of microbes capable of Cr(VI) reduction (Higgins et al., 1998). Based on laboratory studies several chemical reductants have been proven to be capable of reducing Cr(VI) to Cr (III) including; ferrous Iron (Fe^{2+}) (Higgins et al., 1998; Sedlak and Chan, 1997; Tokunaga et al., 2003; Eary and Rai, 1988; and Buerge and Hug 1997), zero valent magnesium (Lee, G, Park., J., and Harvey, O.R., 2013), organic acids (Wittbrodt and Palmer, 1996) and hydrogen sulfide (Pettine et al., 1994). However, these chemicals work most effectively in the pH range of 6.5-9.5 (Tinjum et al., 2008). This poses a problem, since COPR is highly alkaline with a pH near 12, and the material has a high pH buffer capacity (Geelhoed et al., 2003), so that remediation by chemical reduction requires large inputs of acidity to adjust the pH to the optimal value for the chemicals to be effective (Tinjum et al., 2008).

The introduction of organic materials are also being considered especially after a study that indicated that the layer of organic material in some New Jersey Meadowlands sites was preventing the Cr(VI) from migrating to other areas (Higgins et al., 1998). It is

suggested that manure, organic matter (Higgins et al., 1998) would possibly aid in remediation. The introduction of bacteria to these sites is another source of study and has been shown to reduce Cr(VI) in anaerobic conditions (Lee et al., 2006).

The research presented in this thesis focused on characterization of the Cr speciation at a COPR site in the New Jersey Meadowlands, denoted as site 51 in the survey of Burke et al. (1991). The site is located in Kearny Marsh approximately 2.6 miles east of the town of Kearny, New Jersey (Figure A), off of the Belleville Turnpike. The site is bound by the New Jersey Turnpike to the north, the Hackensack River to the east, and a train line for the New Jersey Transit Rail system to the south. The site is a brackish marsh that is mostly submerged except for a dike that separates two containment ponds. Since the termination of dumping COPR material in 1972 by the passing of the Clean Water Act (EPA website visited Apr 2013) the material has broken down due to weathering and now supports life. Plants (phragmites) are now growing along the dike and swans were seen swimming in the containment ponds during collection. The samples taken for this investigation were collected from the transition zone between the dike and the waters of the pond. We selected this site because of the higher concentrations of chromium (15,000 to 20,000 ppm) compared to other sites in Hudson County (Burke et al., 1991). The location was also a factor, this particular site has not been developed which allowed easy access to the site in order to take samples.

The purpose of this investigation is to determine the speciation of the chromium in these soils using sequential extraction techniques; schemes used are described in the materials and methods section. These methods provide quantitative information on the chemical forms (e.g. organically bound, iron-oxide bound) in which the element of

interest (Cr) exists in the soil. This is accomplished by applying a series of extractants, each aimed at extracting a specific species of the element of interest. Using a multi-step sequential extraction method versus a single step extraction will provide much more detailed information about the metal, such as mobilization (Tessier et al., 1979). The results from these methods will then be compared to the XAS data presented in the Elzinga and Cirmo (2010) paper for further qualitative analysis. Though a multi-step extraction scheme theoretically can provide very detailed information on the metals found in the soil samples, limitations have been reported in previous studies.

The 1999 study by Ostergren et al. EXAFS data indicated that the first step of a two part sequential extraction scheme did not extract Pb from selected tailings as expected. Instead, readsorption of the Pb in the samples occurred after adding MgCl_2 . Similar results were found by Bunzl et al. (1999) which investigated the use of sequential extraction methods on slag soils contaminated with Ag, Cu, Ni, Pb and Zn. It was found that significant amounts of metals were readsorbed to the soils after certain extraction steps such as those targeting the reducible and the oxidizable fractions. A study performed on Pb contaminated soils from Germany also investigated the issues caused by sequential extraction methods (Calmano et al., 2001). It was found that readsorption to clay materials occurred by adding Na-Acetate in the second step as well as the 4th step where the moderately reducible soil fraction was targeted. Another mechanism that was found in this investigation was that some re-precipitation of Pb occurred (Calmano et al., 2001). Another study used XAS in conjunction with a sequential extraction method to determine the speciation of arsenic and chromium in soils at a decommissioned wood treatment plant (Hopp et al., 2008). The results found that the sequential method step

utilizing dithionite extracted a significant amount of Cr from the samples but still did not extract the full amount expected from those samples. The use of XAS helped confirm that the Cr was associated with the Fe-oxides (Hopp et al., 2008).

Although spectroscopic results identified limitations to the sequential extraction schemes limitations were also found with the implementation of spectroscopy methods to soil samples. It was explained by Doelsch et al. (2006) that these methods can provide poor information on minor soil fractions. Preparing the samples in a specific way can overcome this limitation. This particular study utilized multiple techniques such as a sequential extraction method, EXAFS, and Density Fractionation to determine the speciation of chromium in soil samples. Although the use of these three methods provided insight on the speciation of Cr (found as Chromite, associated with HCO and Fe-Cr- oxyhydroxides) there were also contradictions between the EXAFS and the sequential extraction method. The sequential extractions indicated that some Cr was associated with the organic soil fraction, where the EXAFS was unable to identify the carbon associations. This issue was explained to be a potential problem early in the Doelsch et al., 2006 paper because this particular method has difficulty differentiating between “light” and “heavy” elements.

2. Methods

2.1 Sample Collection and Treatment

The samples in this investigation were collected from the Kearny Marsh Site along the containment pond barrier which separates two containment ponds (Figure 1). The first sampling took place on July 2, 2008. The samples were collected using a spade

shovel where the top 0-20 cm of the soil was kept for analysis. These samples were stored in zip-top bags and transported to the Rutgers-Newark Campus where they were dried at 90°C for 24 hours, and then sieved to 1 mm. The sieved samples were then stored in zip top bags at room temperature.

2.2 Sample Characterization

2.2.1 *pH Measurements*

All samples were measured for pH with a pH probe and meter, following the method described in the Methods of Soil Analysis Part 3: Chemical Methods, which employs a 1:1 sample to water ratio. Approximately 5 grams of each of the initial 15 samples were weighed out and 5 mL of DI H₂O was added. The samples were mixed rigorously and let sit for 10 minutes. Some samples were placed in the centrifuge and spun for approximately 5-10 minutes so that the soil would not interfere with the pH meter during the measurement.

2.2.2 *Organic Matter Content*

The organic content of the samples was determined using the Loss on Ignition Method (LOI) as described by Nelson and Sommers (1996). This method is a modified version of the method developed by Ben-Dor and Banin (1989).

Before starting the procedure the porcelain crucibles were heated in a furnace for 2 hours at 400°C. They were removed from the furnace and let cool for approximately 5 minutes in a fume hood and then were weighed (± 0.0001 g). Then dried soil sample was added to the crucible, between 1 and 3 grams of sample (± 0.0004 g). Next the samples

were heated at 105°C for 24 hours. After 24 hours the samples were cooled in a vacuum. The samples were weighed; the weight of the sample (± 0.0001 g) was determined by subtracting the crucible weight (from the first steps). The samples were then put back into the furnace for another 16 hours at 400°C. Afterwards the samples were cooled again in a vacuum and weighed a second time (± 0.0001 g).

The LOI content was calculated using the following equation:

$$\text{LOI \%} = \frac{\text{Weight}_{105} - \text{Weight}_{400}}{\text{Weight}_{105}} \times 100$$

2.2.3 Total Cr and Fe Contents

A microwave-assisted extraction using concentrated HNO_3 was performed at the Meadowlands Environmental Research Institute (MERI) to determine total contents of Cr and Fe in the samples. Several sample sets were analyzed over the course of the summer of 2008. Each set included 5 soil samples, which are analyzed in duplicate, and a Cr soil standard. The duplicates and standards showed that the method was consistent throughout the course of these extractions.

The method involved addition of 0.2 g of sample to 7 mL of concentrated HNO_3 (90%); the resulting suspension was allowed to react (open to air) for about an hour before starting the pressurized heating step to allow time for readily oxidizable organic material to be digested. The samples were then placed in the microwave and heated and pressurized for approximately 40 minutes. The samples were cooled in a fume hood for

one hour. After cooling the samples were placed on a hot plate to reduce the acid volume to ≤ 10 mL by evaporation. The sediment samples were then transferred to a 10 mL volumetric flask, brought to volume by addition of DI H₂O, and transferred to a 15 mL centrifuge tube. The samples were analyzed for dissolved Fe and Cr using Atomic Absorption Spectrometry (AAS). The Fe and Cr contents of the original solids were calculated based on the dissolved Fe and Cr concentrations and the amount of solid used in the extraction. These concentrations were considered to be the total Cr and Fe concentrations present in the samples. The values were used in evaluating the results of the four other analytical extraction methods performed in the Geochemistry Laboratory at Rutgers-Newark, as described below.

2.3 Sequential Extractions

Sequential extraction methods were performed on the soil samples collected from the Kearny Marsh site to provide an estimate of the speciation of the chromium in the samples. Four extraction methods were used: (1) the Community Bureau of Reference (BCR) method (Ure et al., 1993); (2) the method described by Voegelin et al. (2008); (3) the Tessier method (1979); and (4) a combination of the Voegelin method and the Tessier method, which was labeled the Hybrid method for this investigation. A detailed description of each of the four methods is provided in Table 1.

2.3.1 Community Bureau of Reference (BCR)

This sequential extraction method was developed by the Community Bureau of Reference (BCR). It was designed to extract heavy metals such as Cr from sediments,

soils and sewage by using the most effective steps seen in other methods (Filgueiras et al. 2002). The method minimizes metal re-adsorption between the extraction steps, and is also noted to limit effects of the solid-to-solution ratio (Filgueiras et al. 2002). The BCR method focuses on three soil metal fractions: (i) acid soluble metal; (ii) metal associated with reducible soil components (i.e. with Mn-oxides and Fe-oxides); and (iii) metal associated with oxidizable soil components (i.e. with organic matter). The technical details of extraction are provided in Table 1, and a description of the extraction procedure is provided below.

To extract acid-soluble Cr, 1.0 g of each sample was weighed out, and placed into a 50 mL centrifuge tube, and 40 mL of 0.11 mol l⁻¹ HOAc was added. The samples were reacted at room temperature for 16 hours; the samples were then centrifuged (20 minutes at 6000 rpm) and the extractant was collected and stored at 4°C in a 50 mL tube. The soil sample was washed before the second step with 8 mL DI H₂O, centrifuged once again and the wash was discarded.

For the second step, which involves extraction of Cr associated with the reducible soil fraction, 40 mL of 0.1 mol l⁻¹ NH₂OH•HCl (pH = 2) was added to the previously washed samples and left to react for 16 hours at room temperature. The extractant from this step was centrifuged, collected and stored, as described above. The samples were washed with 8 mL DI H₂O and centrifuged and the wash was discarded.

The third and final step for this method aimed to extract Cr associated with oxidizable soil components. This step involved three parts. First, 10 mL of H₂O₂ (30% w/v) was added to each sample. The samples were placed in the oven at 25°C and were allowed to react and evaporate. Another 10 mL of H₂O₂ 30% w/v was added to the

samples then was put into the oven at 85°C for one hour until the H₂O₂ was evaporated. Lastly, 50 mL of 1.0 mol l⁻¹ NH₄OAc was added to the samples and were allowed to react at room temperature for 16 hours. The extractant was collected and stored then the samples were washed and centrifuged one last time, the wash was discarded.

After the extraction scheme was completed, the extractant solutions were filtered and stored in 15 mL centrifuge tubes in the laboratory refrigerator at 4°C. Approximately 10 µL of concentrated HCl was added to each solution, and the samples were taken to the MERI laboratory for analysis of dissolved Cr by flame AA.

The solids remaining from the sequential extraction were dried in the oven overnight at 35°C. The dried soils were collected and transferred to small 5 mL tubes and then stored in the laboratory refrigerator at 4°C. A representative group of samples were taken back to MERI and analyzed using microwave-assisted digestion to determine the content of residual Cr left after the extraction method.

2.3.2 Voegelin Method

The second extraction method used for analysis of the soil samples was based on the scheme described in the paper by Voegelin et al. (2008), and is therefore referred to as the Voegelin method. The original method uses six sequential steps, but for this investigation the first two steps were combined into one, so that only 5 steps were applied. This modified version of the Voegelin method focuses on the following soil Cr fractions: (i) readily mobile Cr; (ii) Mn-oxide bound Cr; (iii) organically bound Cr; (iv) Cr associated with weakly-crystalline Fe-oxides; and (v) Cr associated with crystalline Fe-

oxides. The technical details of extraction are provided in Table 1, and the procedures are described below.

Samples were first weighed to 1.00 g and stored in a centrifuge tube. After each step, the samples were centrifuged at 6000 rpm for 20-25 minutes and the extractant was removed and stored in a 15 mL centrifuge tube at 4°C. This remains the same for the washing stages, the samples were centrifuged and the wash was collected and stored with the initial extractant removed from the samples.

The first step, targeting the Cr associated with CaCO₃-bound and weak metal-organic complex fraction, 25 mL of 1.0 mol l⁻¹ NH₄-Acetate (pH = 6) was added to each sample. The samples were left to react at room temperature for 24 hours on a shaker table. The samples were centrifuged to collect the extractant. Then the samples were washed with 12.5 mL 1.0 mol l⁻¹ NH₄NO₃ for 10 minutes and centrifuged to collect the wash.

To extract Fe-oxide and Mn-oxide bound Cr, 12.5 mL of 0.1 M NH₂OH-HCl in addition to 12.5 mL 1.0 mol l⁻¹ NH₄-Acetate (pH = 6) were added to the samples and then the samples were left on a shaker table for 30 minutes. The extractant was then collected after the samples were centrifuged as described above. The samples were then washed twice with 12.5 mL 1.0 mol l⁻¹ NH₄-Acetate (pH = 6) for 10 minutes and centrifuged to collect the wash

The third step, which targeted the organically bound Cr, 25 mL of 0.025 mol l⁻¹ NH₄-EDTA (pH = 4.6) was added and left to react on a shaker table at room temperature for 90 minutes. The samples were then centrifuged and the extractant was collected and

stored. Prior to the fourth step the samples were washed with 12.5 mL 1.0 mol l⁻¹ NH₄-Acetate (pH = 4.6) for 10 minutes then centrifuged to collect the wash.

Step four aimed to target the Cr associated with the weakly crystalline iron oxides. In this step 25 mL of 0.2 M NH₄-Oxalate (pH = 3.25) was added, then the samples were wrapped in aluminum foil, to keep the soils in the dark, and placed on the shaker table for 2 hours. As described above, the samples were centrifuged and the extractant was collected and stored. The samples were then washed once with 12.5 mL of the 0.2 M NH₄-Oxalate (pH = 3.25) solution for 10 minutes in the dark (aluminum foil wrap) and then centrifuged in order to collect the wash

To extract the Cr associated with the crystalline iron oxides, 12.5 mL 0.1 M Ascorbic acid and 12.5 mL of 0.2 M NH₄-Oxalate (pH = 3.25) were added and the samples were placed in a water bath for 2 hours at 96°C. The final extractants were centrifuged collected and stored. The samples were washed with 12.5 mL 0.2 M NH₄-Oxalate (pH = 3.25) for 10 minutes in the dark (aluminum foil wrap) and centrifuged again to collect the wash.

Upon completion of the extraction method, the collected extractant solutions and washes were filtered and stored in new 50 mL centrifuge tubes. These were stored in the laboratory refrigerator at 4°C. Approximately 10 µL of concentrated HCl was added to each solution in preparation for AAS analysis at MERI.

The solids left from the sequential extraction were oven-dried overnight at 35°C. The dried materials were placed in 15 mL tubes and stored in the laboratory refrigerator at 4°C. A select group was analyzed using microwave-assisted digestion at MERI to determine the residual Cr content after extraction.

2.3.3 Tessier Method

The sequential extraction method described by Tessier et al. (1979) was the third extraction method used on the samples. This method distinguishes four different Cr forms: (i) exchangeable Cr; (ii) acid soluble Cr; (iii) Cr associated with reducible soil components; and (iv) Cr associated with oxidizable soil components. The technical details of extraction are provided in Table 1, and a description of the procedures involved is provided below.

One gram of each sample was weighed in preparation for the extraction. After each of the four steps, the samples were centrifuged at 6000 rpm for 20-25 minutes and the extractant was transferred to a 50 mL centrifuge tube and stored in the refrigerator at 4°C. After each step the samples were washed and centrifuged following the same parameters for extractant collection. The washes were discarded after each step.

The first extraction step of the Tessier method (T.1) targets the exchangeable Cr fraction. 8 mL of 1.0 mol l⁻¹ MgCl₂ (pH = 7) was added to each of the soil samples then the samples were placed on a shaker table for one hour at room temperature. The samples were then centrifuged as described above in order to collect the extractants. Prior to step 2 the samples were washed with 8 mL DI H₂O and centrifuged.

The second step (T.2) targeted the acid soluble fraction of the soil. Here 25 mL 1.0 mol l⁻¹ NaOAc (pH = 5) was added to the samples. The samples were then placed on a shaker table and left to react at room temperature for 5 hours. The samples were then centrifuged to collect the extractant, as described above. Next, 8 mL of DI H₂O was used

to wash the samples. The samples were centrifuged again so that the wash could be removed.

The third step (T.3) aimed to extract the Cr associated with the reducible soil fraction. This step involved the addition of 20 mL 0.04 mol l^{-1} $\text{NH}_2\text{OH HCl}$ in HOAc 25% w/w to the samples. The samples were then placed in a water bath for 6 hours at 96°C . After the samples cooled for a short time they were run through the centrifuge and the extractant was collected. Then the samples were washed with 8 mL of DI H_2O and centrifuged.

The final step (T.4) which targeted the oxidizable soil fraction was composed of three parts. First, 3 mL of 0.02 mol l^{-1} HNO_3 and 5 mL of H_2O_2 30% w/v was added to the samples. The samples were placed in a water bath for two hours at 85°C . The samples were then taken out and 3 mL H_2O_2 30% w/v was added. The samples were then returned to the water bath and left to react at 85°C for 3 hours. Some of the samples analyzed for this study contained a high percentage of organic material and when introduced to the high temperatures of the water bath, for the first two parts of the final step, a strong reaction occurred causing some sample loss. It was found that if the samples were set aside for 5-15 minutes prior to the water bath it helped reduce the risk of sample loss. The samples were taken out once again and 5 mL 3.2 mol l^{-1} NH_4OAc was added to the samples. Then the samples were placed on a shaker table and left to react for 30 minutes at room temperature. The samples were centrifuged to collect the extractants and then the samples were washed with 8 mL of DI H_2O and centrifuged a final time.

The extractant solutions were processed in the same fashion as described in the previous scheme descriptions. The remaining solutions were filtered using cellulose

acetate filters, and acidified with 10 μ L of concentrated HCl and stored in the laboratory refrigerator at 4°C. The solutes were analyzed for dissolved Cr using FAAS at MERI.

The solids remaining after sequential extraction were stored in 50 mL centrifuge tubes at room temperature. These soils were later dried in the oven overnight at 35°C. The dried samples were then transferred to smaller centrifuge tubes (5 mL) these were stored in the laboratory refrigerator at 4°C. A representative sample from each triplicate was taken back to the laboratory at MERI and analyzed for residual Cr content using microwave-assisted digestion.

2.3.4 Hybrid Method

The final extraction method combined steps from previous sequential methods. The method used steps 1, 2, and 4 from Tessier et al. (1979) and steps 4 and 5 from Voegelin et al. (2008), as described below and in Table 1. This method was designed to extract the Cr and Fe content from 5 fractions; the exchangeable (H.1), acid soluble (H.2), weakly crystalline Fe-Oxides (H.3), crystalline Fe-Oxides (H.4), and the oxidizable fraction (H.5). We decided to utilize Tessier step 1 for H.1 because it was specifically designed to target the exchangeable soil fraction. The preliminary results of Tessier step 2 and BCR step 1 were not significantly different; therefore, we selected the second step from the Tessier method for H.2 since it was designed to follow Tessier step 1. Voegelin steps 4 and 5 were selected for H.3 and H.4, respectively, because they specifically target Fe-oxides. Lastly, for targeting the oxidizable soil fraction (H.5), we selected Tessier step 4 because we believed these solutions would be more appropriate for our samples.

One gram of each sample was weighed in preparation for the extraction. After each of the five steps, the samples were centrifuged at 6000 rpm for 20-25 minutes and the extractant was transferred to a 50 mL centrifuge tube and stored in the refrigerator at 4°C. After each step, the samples were washed and centrifuged following the same parameters for extractant collection. The washes were discarded after each step.

The first step (H.1) follows the Tessier methods first step by targeting the Cr associated with the exchangeable soil fraction. This is performed by adding 8 mL 1.0 M MgCl_2 (pH = 7) to each 1 gram of soil sample and was left to react for 1 hour on a shaker table at room temperature (25°C). The sample was then centrifuged and the extractant was collected as described above. After the extractant was removed the samples were washed with 8 mL of DI H_2O and centrifuged.

The second step (H.2) targeted the acid soluble Cr by adding 25 mL 1.0 M NaOAc (pH = 5) to each sample. The samples were then set on the shaker table and left to react for 5 hours at 25°C. Next the samples were centrifuged and the extractant was collected. The samples were then washed with 8 mL DI H_2O and centrifuged as described above.

The next step (H.3) follows the Voegelin step by targeting the Cr associated with weakly bound crystalline iron oxides. 25 mL of 0.2 M NH_4 -Oxalate (pH = 3.25) was added to each sample and the samples were then transferred to a shaker table for 2 hours at room temperature. The extractant was collected the samples were centrifuged. The samples were then washed by adding 12.5 mL NH_4 -Oxalate (pH = 3.25) and reacted in the dark for 10 minutes (aluminum foil wrap), the samples were centrifuged and this

wash was collected. The samples were then washed once again with 8 mL DI H₂O, centrifuged and this wash was discarded.

To extract the Cr associated with the crystalline iron oxides, 12.5 mL of 0.1 M Ascorbic Acid and 12.5 mL 0.2 M NH₄-Oxalate were added and then the samples were placed in a water bath (91.5°C) for two hours. The samples were then centrifuged and the extractant was collected. Next the samples were washed with 12.5 mL of 0.2 M NH₄-Oxalate for 10 min in the dark. Once again the samples were centrifuged, as described previously, and the wash was collected. The sample was then washed again with 8 mL of DI H₂O, centrifuged and this was discarded.

The fifth and final step (H.5) aimed to extract the Cr associated with the oxidizable soil fraction. This was performed by adding 3 mL 0.02 HNO₃ and 5 mL of H₂O₂ 30% w/v to each sample and then the samples were placed in the water bath for 2 hours at 85°C. An additional 3 mL of H₂O₂ was added to the samples and then were placed back in the water bath for another three hours at 85°C. Next 5 mL of 3.2 M NH₄OAc was added and the samples were placed on the shaker table for 30 minutes and left to react at room temperature. The extractant solution was collected after running the samples through the centrifuge. The extractant solution was removed and the samples were washed with 8 mL of DI H₂O, centrifuged and the wash was discarded.

Once again at the completion of the extractions on the 5 triplicate samples the extractant solutions were filtered using cellulose acetate filters and stored in 15 mL centrifuge tubes. The samples were acidified using concentrated HCl (~10 µL). These were then taken to MERI for analysis.

The solids remaining from the extraction method were stored at room temperature in 50 mL centrifuge tubes. The samples were later dried overnight in an oven at 35°C, after drying the samples were transferred from the 50 mL centrifuge tubes to smaller 5 mL centrifuge tubes. These dried samples were then stored in the laboratory refrigerator at 4°C. One soil sample from each triplicate was selected and taken to MERI for the final analysis using the previously described microwave-assisted digestion method. This analysis measured the residual Cr and Fe content in the soils remaining from the extraction method.

3. Results

3.1 Soil Properties

The properties of the marsh soils (the soil Cr and Fe concentrations, organic matter contents, and pH values) measured for this study are summarized in Table 2. The pH of the soils ranged from slightly acidic to near-neutral composition with pH values of 4.5 - 6.71. Total contents of chromium ranged from 427 to 858 (mg/kg), and the total iron concentrations ranged from 15822 to 22022 (mg/kg), both determined by the microwave-assisted digestion. It is important to compare the measured soil Cr contents to standards set by the New Jersey Department of Environmental Protection (NJDEP website visited Feb 2012). The NJDEP has several soil standards for Cr (VI) in non-residential sites within the state. This includes the accidental ingestion criteria of 6100 ppm, and the inhalation pathway criteria of 20 ppm. There is no regulated criterion for trivalent Cr in non-residential sites, though there is a standard for residential sites at 120,000 ppm

(NJDEP website visited Feb 2012). The total soil Cr contents exceed the Cr (VI) inhalation pathway criterion of 20 ppm for non-residential sites, but are below the Cr (VI) accidental ingestion criterion and the Cr (III) standards for residential sites.

The soil organic matter contents, determined from the LOI method, ranged from 11.2 to 24.7 wt% (Table 3). These high organic contents are explained by the characteristics of the sampling site, which is located in Kearny Marsh. This is a wetland area with a high water table, and with extensive growth of tall grasses and reeds, which are expected to be the main contributor to the organic material found in the soils. The extensive accumulation of organic matter in these wetland soils reflects the wet conditions at the site inhibiting organic matter decomposition. Figure 1 compares the iron and chromium soil contents, showing a correlation between these elements with a R^2 value of 0.56, suggesting that a significant amount of the chromium is associated with iron-based soil minerals. However, the correlation is not particularly strong, indicating that soil factors other than soil Fe influence the Cr retention in these soils as well. The results from the sequential extraction schemes discussed below provide further constraints on the factors controlling retention of soil Cr.

3.2 Mass Balance of Extraction Schemes

The mass balance of the chromium sequential extraction was used to determine the efficiency of the extraction methods, as well as to evaluate the effectiveness of the analytical methods used for measuring soil chromium. The mass balance is a comparison between the total chromium extracted in each sequential extraction scheme (including residual Cr) versus the total Cr content determined from digestion of the original soil

material (listed in Table 2). The comparison is done by summing the Cr contents measured in the individual steps of each extraction method including the residual concentration, yielding total extracted Cr, which can then be compared to total soil Cr content determined by whole soil digestion. The comparison between these two total Cr measurements is presented in Figure 2. To facilitate comparison, the data was plotted along with the 1:1 line, which represents the ideal relationship (i.e. perfect match) between the two chromium concentrations; the two gray lines define $\pm 20\%$ deviation from the 1:1 line.

There are notable differences between the mass balances of the various extraction schemes. For the BCR, Voegelin, and Tessier methods, the two Cr soil content values are mostly found within the 20-25% error boundary, indicating reasonable agreement between the two soil Cr measurements (Figure 2). The results of the hybrid method, however, did not fall within the 20% error boundary, but instead shows deviations that are much larger than for the other extraction schemes, with an approximate average of 45% deviation between total Cr extracted in the sequential extraction scheme versus total soil Cr measured during acid digestion (Figure 2). This large mass balance discrepancy suggests that the extraction data for this method are unreliable. The reasons for the poor mass balance obtained for this method are not entirely clear. A contributing factor may have been loss of sample during the extraction procedure, particularly the step targeting the organic fraction, which produced extensive CO₂ gas. The samples reacted strongly when introduced to the high temperatures of the water bath, and this resulted in some suspension loss in various samples. Another possible factor may have been the lack of matrix matching between the extraction samples and the aqueous Cr reference solutes

used for calibration of the AA. Contrary to the other schemes, the hybrid method employs organic extractants in nearly all extraction steps (Table 1), whereas the aqueous Cr standards for AA calibration were made up in dilute nitric acid. The presence of organics in the extractant solutes of the hybrid method may have made the instrument particularly sensitive to differences in the compositions of the background electrolyte of the AA standards. Due to the poor consistency of the data obtained, the results from the hybrid method are not further considered.

3.3 Extraction Results

The overall Cr extraction results obtained for the BCR (Tables 4a and 4b), Voegelin (Tables 5a and 5b), and Tessier (Tables 6a and 6b) methods are presented in Figures 3-5 respectively, which show the amount of Cr extracted in each step for each sample. The Cr contents reported in these figures have been converted to percent of total soil Cr, in order to provide a starting point for comparison of the results obtained for the various methods. To accomplish this, we used the total Cr content measured from microwave-assisted digestion of the whole soils (reported in Table 2) to normalize the Cr values determined in the extraction methods.

The sequential extraction results show similarities as well as differences between the three methods. Generally all three of the methods extracted significant amounts of Cr from the reducible soil components, with a range of 14.3% to 70.9% Cr extracted in targeting these soil components. All three methods also showed very low acid soluble and exchangeable soil Cr contents, with a range of 2.6 to 3.4%. The oxidizable (organic) soil fraction had high Cr content according to both the BCR and Tessier methods, with an

average 20.7 and 31.0 % Cr extracted by these methods, respectively. In contrast, the Voegelin method did not extract much Cr from the organic soil fraction, at an average of 1.97 % of total Cr, but this method did extract a majority of the Cr from the reducible fraction with an average of 37.72% Cr extracted.

Although the estimates of Cr speciation vary between the schemes, the results from the three extraction methods are consistent in that they indicate substantial association of soil Cr with reducible soil components. For the Tessier and the Voegelin schemes, the reducible fraction was the highest yielding fraction, whereas in the BCR scheme it was second to the organically complexed Cr fraction (Figures 3 through 5). Readily mobile Cr represented by the acid soluble and exchangeable Cr fractions was estimated to be a minor component in all three schemes, whereas organically bound Cr was identified as a major Cr species in the BCR and Tessier schemes, but not in the Voegelin scheme. More detailed comparisons between the extraction results are discussed below.

3.3.1 Comparison of extraction between schemes

Since these three sequential extraction schemes are composed of steps that target the same or similar soil Cr fractions, direct comparisons can be made between the speciation estimates. In Table 7, a summary of comparisons is presented. These comparisons provide the information to better determine the use and limitations of sequential extractions measure Cr speciation of these soils, and to assess the uncertainties associated with the application of these extractions. Therefore, soil Cr values determined for comparable Cr species in the extraction methods were compared to each other. Table 7

presents the comparable steps of the three methods. There are three soil Cr fractions that were directly comparable between the extraction schemes; acid soluble/exchangeable Cr fraction, Cr associated with oxidizable soil components, and Cr associated with reducible soil components. In cases where multiple extraction steps in a method targeted a fraction the values obtained for the individual steps were added together and then plotted for comparison with the results of the other methods. A comparison was also performed on the values obtained for the residual soil Cr fractions. Comparisons were performed for both the absolute Cr soil content values (in ppm) as well as for the relative values (% Cr extracted). The percentages were calculated based on the total Cr soil concentrations determined from the microwave-assisted digestion performed at MERI (Table 2).

3.3.2 Comparison of soil fraction estimates

The comparisons of the extraction results are presented in Figures 7-10, with Figure 7a/b comparing the acid soluble and exchangeable Cr fractions, Figure 8a/b comparing Cr associated with reducible soil components (i.e. Fe-oxide and Mn-oxide bound Cr), Figure 9a/b comparing the estimates of Cr associated with oxidizable soil components (i.e. soil organic matter), and Figure 10a/b comparing residual Cr. Similarities between the methods were judged on two criteria; first, the similarity in the actual numbers (absolute estimates), and second, similarity in trends across the soil dataset (i.e. relative differences between soils). Although we found that the absolute estimates differed notably between the schemes in all cases, reasonable correlations between the extraction results were observed for several Cr fractions, as discussed in more detail below.

3.3.2.1 Acid Soluble and Exchangeable-weakly bound Cr

Acid soluble and weakly bound Cr fractions measured in the soils were strongly correlated for the three extraction schemes, as shown in Figure 7. All three comparisons had R^2 value > 0.9 , with the correlation of the Voegelin and BCR showing the strongest correlation in terms of both the Cr % extracted (Fig. 7a) and the absolute Cr content in ppm (Fig. 7b) with R^2 values of 0.99 and 1.00 respectively. The Tessier versus Voegelin comparisons showed similarly strong correlations with R^2 values of 0.96 (Cr %) and 0.97 (Cr in ppm), whereas comparison of the Tessier versus BCR results yielded R^2 values 0.94 (Cr %) and 0.95 (Cr in ppm). These strong correlations suggest that all three methods are targeting the same soil Cr fraction, i.e., they appear to be selective. However, substantial deviation of the estimates from the 1:1 lines (the dashed line seen in graph 7) indicates that these methods, though selective, are not equally efficient in extracting this soil Cr fraction.

3.3.2.2 Mn- and Fe-oxide bound soil Cr:

The comparison plots for the steps targeting Cr associated with reducible soil components are presented in Figure 8. Compared to the weakly bound soil Cr fraction, correlations between the results obtained in the three schemes for this Cr fraction are much weaker. The results of the Tessier and BCR methods were the most strongly correlated, yielding R^2 values of 0.82 (Cr %, Fig. 8a) and 0.86 (Cr in ppm, Fig. 8b). The relationship between the results of the Voegelin and BCR methods was weak, with R^2 values of 0.01 for Cr % and 0.49 for Cr in ppm. Similarly poor correlations were found for the results of the

Voegelin and Tessier extraction methods with R^2 values of 0.10 (Cr %) and 0.45 (Cr in ppm).

The strong correlation of the Tessier and BCR results suggests these methods target similar soil Cr fractions in this extraction step. This is perhaps not surprising given the fact that both methods use the same extractant (hydroxylamine hydrochloride) for dissolving soil Mn- and Fe-oxides, whereas the Voegelin method employs three different solutions to extract this soil Cr fraction (Table 1). Despite the correlation of the Tessier and BCR extraction results, however, the actual estimates of soil Cr for this fraction are notably different for the two schemes, as evidenced by the deviation of the estimates obtained from the 1:1 line (Figure 8), which indicates that the methods are not equally efficient in extracting soil Cr in this step. The Tessier method used an acetate base for the hydroxylamine solution and also allowed a shorter reaction time at a higher temperature compared to the BCR method. These differences in extraction conditions are likely to have impacted the amount of Cr extracted.

3.3.2.3 Cr bound to oxidizable soil components

Comparison of the estimates of soil Cr associated with the organic soil fraction in these soils is presented in Figures 9a and 9b. The results show that the correlation between the Tessier and BCR results is weak, with $R^2 = 0.58$ (Cr %) and $R^2 = 0.34$ (Cr in ppm). The weakest correlation was found between the results of the Voegelin and Tessier extraction schemes, yielding R^2 values of 0.01 (%Cr) and 0.05 (Cr in ppm) (Figure 9b). The results of the Voegelin and BCR methods expressed in concentration (Cr in ppm) showed the strongest similarity for this fraction, with an R^2 value of 0.83 (Fig. 9b). Somewhat

surprisingly, the correlation of soil Cr expressed as a percentage showed a much lower R^2 value of 0.48 for these two methods (Fig. 9a). The explanation to this difference probably lies in the conversion from absolute values to percentages, and the small number of samples analyzed. In this dataset there are samples that have very different absolute concentrations of Cr extracted in this step, but when converted to % Cr the resulting percentages are almost identical. For sample 1A, an average of 515.83 ppm of Cr was extracted in this extraction step for the BCR scheme, which corresponds to 60.14% of total Cr extracted for the sample. For sample 2A, an average of 277.55 ppm of Cr was extracted in this step, which is a very different concentration than for sample 1A; however, this amount of Cr represents 59.76 % of total Cr in this sample, which is very similar to the % Cr of sample 1A. As a result, when the samples are plotted based on % Cr values, the difference between the samples as to the amount of Cr extracted is lost. This demonstrates the importance of analyzing a large number of samples, producing large datasets where effects like these are much less pronounced so that more robust statistical results are obtained.

It can be concluded that the Voegelin and the BCR methods extracted similar Cr fractions in this extraction step, based on the high R^2 value in the ppm comparison plot. However, the strong deviation from the 1:1 line indicates that the two methods are not equally efficient, with the BCR scheme extracting larger amounts than the Voegelin scheme. The low R^2 values of the comparisons of the Tessier vs. BCR results and the Tessier vs. Voegelin results indicate that the Tessier extraction scheme targeted different or additional Cr species than the Cr fractions extracted by the BCR and Voegelin schemes. Further studies are needed to resolve the difference selectivity and efficiency of

the three schemes, and to assess the most appropriate method for extracting organically bound Cr in these soils.

3.3.2.4 Residual chromium

A final comparison that can be made is that of the results of residual chromium, i.e. the Cr soil fraction left un-extracted over the course of each extraction scheme (Table 8). Like the relationships above the comparisons are made in terms of both % Cr (Figure 10a) and absolute Cr content (ppm; Figure 10b). All comparisons yielded very poor correlations among the methods, with R^2 values of 0.41 and lower (Figure 10). The main reason for these poor correlations is that, unlike the soil Cr fractions discussed in the previous sections, residual Cr is not actively extracted but instead represents the difference between total initial soil Cr content and total extracted Cr. As a result, the residuals are entirely dependent on the Cr values determined from the individual extraction steps, and are subject to the accumulated uncertainties and incompatibilities of the Cr estimates of the various extractions, which are substantial, as discussed in the sections above. The lack of correlation seen for the residual Cr fraction is thus not surprising in view of the variability in the individual extraction steps discussed in sections 3.3.2.1-3.3.2.3.

3.3.3 Correlation of extraction data to soil properties

It is useful to determine whether Cr speciation as determined from the sequential extraction schemes can be correlated to soil properties. In this section we will discuss the correlations between the estimated soil Cr fractions and relevant measured soil properties, including organic matter content, iron content, and soil pH values.

A first correlation of potential interest is that between the acid soluble Cr fraction and soil pH value. It is useful to make this comparison, because acid soluble Cr represents an estimate of the amount Cr adsorbed at mineral surfaces, and soil pH plays a major role in the determining the favorability of adsorption of cations to particle surfaces, with higher pH values promoting adsorption (Eby Textbook, pg 342). It is therefore reasonable to expect a correlation between soil pH and the amount of acid soluble Cr. Figure 11a displays the correlation of soil pH values to the acid-soluble Cr concentrations (in ppm) for the three extraction methods. Correlation analysis reveals R^2 values of 0.47, 0.56 and 0.57 found for the Tessier, Voegelin and BCR methods, respectively. The control of soil pH on the level of readily available Cr is thus relatively weak, suggesting that soil pH is not the sole factor determining the amount of adsorbed Cr in these samples. The overall trend evident from the correlation analysis in Figure 11a shows that higher Cr concentrations are extracted at lower pH values, which is inconsistent with what would be expected from this comparison. Chromium (III) is a cation, and therefore Cr (III) adsorption increases with pH. As a result, a positive correlation would be expected between pH and acid-extractable Cr, which represents adsorbed Cr species. The unexpected pH relationship could be explained by the negative relationships seen in the comparison between pH and Fe content of the native soils (Figure 11c). This negative correlation likely represents a mechanism influencing the adsorption of the Cr to the soil surfaces causing the relationship between pH and Cr associated with the acid soluble fraction. Figure 11b, shows the relationship between the pH and the organic material percentage, determined from the LOI method. This relationship shows a very weak

positive correlation, this could also represent another mechanism influencing the adsorption of Cr.

A second comparison of interest is that between the amounts of Cr associated with soil organic matter estimated in the sequential extraction schemes and the soil organic matter content as measured with the LOI method (Table 3 and section 2.2.2.a). The comparisons are presented in Figure 11d for the three extraction schemes, and resulted in generally weak relationships between the estimated amount of Cr associated with soil organic matter and the soil organic matter content, with R^2 value of 0.00, 0.35 and 0.53 found for the BCR, Tessier and Voegelin results, respectively. These generally weak correlations may be due to poor selectivity of the reagents used to extract organically bound Cr, or indicate that organic matter is not a particularly important sink of Cr in these soils. The results from the Tessier and Voegelin extraction schemes suggest that organic matter may be involved in soil Cr retention, but is not the only factor that needs to be considered to explain Cr partitioning in these soils. The distinct differences in correlation quality between the extraction schemes underscores the poor correlations of the extraction results obtained for this soil Cr fraction, as discussed in section 4.3.2.3, making comparisons between the results difficult.

A final comparison of interest is between the estimates of Cr associated with reducible soil compounds (nominally Fe- and Mn-oxides), and total soil Fe contents as measured during initial soil characterization (Table 2). The correlations are presented in Figure 11e. The results of the Voegelin exhibited the strongest relationship, with an R^2 value of 0.99, suggesting that this method was selective in dissolving soil Fe-oxides phases from the soils during extraction of Fe-bound Cr. The two other schemes exhibited

much weaker correlations with R^2 values of 0.35 and 0.39 for the BCR and Tessier methods, respectively. The results for the Voegelin data suggest an important role of Fe in Cr retention in these soils, whereas the relative weak correlations between Fe-bound Cr and soil Fe content observed for the Tessier and BCR schemes most likely reflects poor selectivity of the chemical reagents used for extracting Fe-bound Cr in these two methods.

3.3.4 Correlation of extraction data to spectroscopic measurements

The Meadowlands soils investigated here were also analyzed using synchrotron-based X-ray techniques performed at the national Synchrotron Light Source at Brookhaven national Laboratory in Upton, New York. This work was presented in the paper of Elzinga and Cirimo (2010), and utilized two methods to characterize Cr speciation in the soils: (i) X-ray fluorescence mapping combined with micro-focused X-ray absorption spectroscopy (XAS) to determine the spatial distribution and heterogeneity of Cr speciation in the soil matrix, as well as (ii) bulk XAS spectroscopy to characterize the average Cr speciation in each sample. The spectroscopic data verified that hexavalent Cr was no longer present in these soils. The XRF maps and micro-focused XAS results demonstrated the presence of μm -size chromite (FeCr_2O_4) particles in the soil matrix. These particles are from the original chromite ore used by the manufacturing facilities, and represent Cr species that have resisted weathering since deposition of the COPR at the Meadowlands site. Besides chromite, the bulk XAS data indicated the additional presence of Cr (III) associated with organic matter (Cr-SOM) and Cr(III) incorporated into Fe(III)-oxide minerals (Represented by $\text{Cr}_{0.1}\text{Fe}_{0.9}(\text{OH})_3$). Moreover, linear

combination fits applied to the bulk XAS data allowed quantitative estimates of the relative proportions of chromite, Cr-SOM, and $\text{Cr}_{0.1}\text{Fe}_{0.9}(\text{OH})_3$ in five of the soil samples investigated here as well. These results are summarized in Table 9.

The LC fit results presented in Table 9 can be compared to the sequential extraction results, which estimate equivalent Cr species. The expected similarities are as follows: (1) The LC fit of Cr-SOM in Elzinga and Cirimo (2010) represents Cr associated with the oxidizable soil fraction determined from the extraction schemes; (2) The $\text{Cr}_{0.1}\text{Fe}_{0.9}(\text{OH})_3$ species of the LC fit represents Cr associated with the reducible soil fraction in the extractions; (3) Chromite used in the LC fit represents residual Cr from out investigation. These expected correlations allow us to make these comparisons between the sequential extraction methods and the XAS data of the same samples.

Inspection of the results in Table 9 demonstrates that the linear combination fits qualitatively support the results obtained from the sequential extraction methods, since both methods demonstrated substantial association of soil Cr with SOM and soil Fe. However, quantitative comparisons between the extraction results and the LC fits yielded poor correlations (Figure 12a thru 12c), demonstrating that direct relations between these methods are problematic.

4. Conclusions

We applied three common sequential extraction schemes to determine the speciation of Cr in contaminated wetland soils from the New Jersey Meadowlands. These schemes use a select number of steps, each targeting the removal of metals from a specific soil fraction (Tessier et al., 1979, Filgureias et al., 2002, and Scheinost et al., 2002). Theoretically,

these steps will provide a breakdown of how metals are dispersed throughout the soil. The results from the three sequential extraction schemes agreed in that they all indicated that Cr in the Meadowlands soils investigated here was to a large extent associated with the oxidizable soil fraction (i.e. with organic matter) and with the reducible soil fraction (i.e. with Fe- and Mn-oxides). In addition, substantial amounts of Cr were non-extractable. These results are qualitatively in agreement with the XAS data of Elzinga and Cirno (2010), who demonstrated the importance of organic matter and Fe-oxides in the retention of Cr, and demonstrated the presence of substantial (residual) chromite in these soils.

Quantitative comparisons of the results from the extraction schemes revealed notable differences in the estimates of Cr associated with specific soil fractions. These discrepancies reflect basic limitations in the application of these methods to obtain accurate estimates of Cr speciation in the Meadowlands soils. Most likely these were caused by differences in the degree of efficiency (the extent to which the extractant mobilizes the target fraction; Scheinost et al., 2002; Coetzee, 1993; Gholivand et al., 2008) and selectivity (the extent to which the extractant avoids unintentional mobilization of non-target species; Ostergren et al., 1999 and Scheinost et al., 2002; Davidson et al., 1998; Pagnanelli et al., 2004; Sutherland et al., 2000, Silveira et al., 2006) between the extraction steps. Additional limitations associated with sequential extraction schemes, such as adsorption (Rendell et al., 1980), re-adsorption (Arunachalam et al., 1996; Belzile et al., 1989; Tipping et al., 1985; Rendell et al., 1980; Gomez-Ariza et al., 1999; Rauret, 1998; Raksasataya et al., 1996; Raksasataya et al., 1997; Kheboian and Bauer, 1987; Xiao-Quan and Bin, 1993; Ho and Evans, 2000; Gilmore et al., 2001; Howard and

Vandenbrink, 1999; Howard and Shu, 1995), precipitation of mobilized target metal (Calmano et al., 2001 and Bunzl et al., 1999), or redistribution of target metals (Mester et al., 1998) may have contributed as well.

The results of the extraction schemes qualitatively agree that the Cr speciation in the Meadowlands soils is dominated by Cr associated with Fe/Mn-oxides, organic matter, and chromite. The design of a sequential extraction scheme to provide accurate quantitative estimates of Cr speciation in the soils will require selective and efficient extractants to isolate these three main soil Cr species. Since chromite is part of the soil fraction that remains after extraction of the other species, this design in practice will involve the selection and testing of extractants that effectively and selectively target organically bound and Fe/Mn-oxide associated Cr.

From a soil geochemical perspective, organics and Fe/Mn-oxides are very different compounds, representing strongly reducing and strongly oxidizing soil components, respectively. An extraction scheme can exploit this difference in chemical character to selectively target and extract the Cr species associated with these components. A basic design could involve a first extraction step using a chemical reductant to dissolve the Fe/Mn-oxide fraction, followed by mobilization of the organic fraction through addition of a chemical oxidant. In fact, this is the basic set-up of the Tessier and BCR schemes. Optimizing this basic scheme involves selecting and testing of the following main parameters: (1) the chemical oxidant and reductant; (2) the appropriate extractant concentrations, solid solution ratios, and reaction temperatures for each step. Selections should be made based on the selectivity and efficiency of the extractants and the chemical conditions being tested.

A practical issue that should be considered when developing an optimized extraction method is the high percentage of organic compounds in these wetlands soils. The resulting extensive production of CO₂ gas during oxidation posed a practical challenge for several of our samples, causing substantial sample loss due to fizzing during extraction and microwave-assisted digestion. The extraction step to be used to target the organic soil fraction should be designed to avoid build-up and sudden release of high levels of CO₂. In addition, steps that subject the sample and solute to high temperatures should be carefully considered.

Testing of the extraction scheme performance would ideally involve comparison between the sequential extraction method results and spectroscopic measurements that provide direct information on the Cr speciation; application of synchrotron-based X-ray absorption spectroscopy has proven to be particularly useful for this purpose (Elzinga and Cirno, 2010; Calmano et al., 2001; Bunzl et al., 1999; Scheinost et al., 2002; and Ostergren et al., 1999). The study by Scheinost et al. (2002) describes a particularly useful approach of merging XAS analysis with a sequential extraction scheme to assist interpretation of SEM results. In this method a six step sequential method was used to determine the speciation of Zn in smelter-contaminated soils, which contain multiple metal species. After each sequential step the samples were tested using x-ray absorption fine-structure spectroscopy. The study found that both the XAS and SEM showed limitations in the ability to accurately detect specific soil fractions. This was seen by reviewing the Roberts et al. (2002) study where samples were previously analyzed using XAS, were found to have Zn present in only franklinite and sphalerite. The sequential extraction method was able to extract more species which in turn allowed the XAS to

pick up the third Zn associated fraction, which was the hydroxy-Al interlayered phyllosilicates (Scheinost et al., 2002). Although the SEM was able to aid in the identification of the third Zn species when the XAS could not, there are situations where the SEM could not provide accurate information without the use of the XAS method. For example, SEM was unable to identify Zn sorbed by Fe and Mn-Oxides. XAS was able to detect these situations (Scheinost et al., 2002). Despite the clear utility of X-ray absorption methods in determining metal speciation in soils, a major disadvantage is that the technique is not readily accessible and the measurements are time-consuming; as a result, this method is not suitable for use as a standard method in metal speciation studies. It would be very useful if future research efforts employed XAS to test and optimize sequential extraction schemes for a range of general soil types (e.g. organic rich soils, Fe-oxide dominated soils, etc.). In the absence of such generally tested extraction schemes, XAS is currently best used to test and compare the performance of different schemes to a specific site.

Our testing suggestion is based on the description from the Scheinost et al., 2002 paper. It is suggested that only one very well homogenized sample be used to test the suitability of this proposed method. This limitation of sampling will provide more constraint on the results. Dry and sieve the sample to <2mm and then mill the sample using a mortar and pestle. A portion of this sample should be tested for total concentrations using the microwave-assisted digestion, as previously described. Another portion of the sample should be saved for XAS analysis to provide baseline results. Next, the remaining sample should be divided into 15-1gram subsamples to be tested using the optimized sequential extraction method. All 15 samples will be run through the first step

of the optimized method. Of the 15 samples, the solids for 5 samples should be held for XAS analysis as opposed to the one sample, described in the paper. The extractants collected from each step, are to be analyzed using flame spectrometry. The remaining 10 samples will go through the second step, once again after the step is completed, 5 samples (solids) are to be held for XAS analysis. The remaining 5 samples will be run through the final extraction step. Then these samples will be washed and held for XAS analysis. The use of 5 samples versus the one (as described in the Scheinost et al. paper) should provide excellent duplicate data to constrain the results even further.

The Scheinost et al., 2002 paper used both XANES and EXAFS to test the samples. These results were analyzed using two different combinations of mathematical models; multishell fits with linear combination and principle component analysis with linear combination. The analyzed results were compared to a library of Zn species and minerals to aid in the identification of species (Scheinost et al., 2002). Due to the consistent results seen in this study it is advised that the XAS data for our optimized method use these same analytical techniques.

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Appendix A: Tables

Table 1: The breakdown of steps for each Sequential Extraction Method.

BCR Method*				
Step	Fraction	Solution	Duration	Wash
S.1	Acid Soluble	40 mL 0.11 M HOAc	16 hours (25 deg C)	30 mL DI H ₂ O
S.2	Reducible	40 mL 0.1 M NH ₂ OH-HCl (pH = 2)	16 hours (25 deg C)	30 mL DI H ₂ O
S.3	Oxidizable	10 mL H ₂ O ₂ w/v (evaporation)	1 hour (25 deg C)	30 mL DI H ₂ O
		10 mL H ₂ O ₂ w/v (evaporation)	1 hour (85 deg C)	
		50 mL 1.0 M NH ₄ OAc	16 hours (25 deg C)	
Voegelin Method*				
Step	Fraction	Solution	Duration/Conditions	Wash
V.1	CaCO ₃ -bound, weak metal-organic complexes	25 mL 1.0 M NH ₄ -Acetate (pH = 6)	24 hours (25 deg C)	12.5 mL 1.0 M NH ₄ NO ₃ 10 min
V.2	Mn-Oxides	12.5 mL 1.0 M NH ₂ OH-HCl and 12.5 mL 1.0 M NH ₄ -Acetate (pH = 6)	30 min (25 deg C)	2X 12.5 mL 1.0 M NH ₄ -Acetate (pH=6)
V.3	Organically bound	25 mL 0.025 M NH ₄ -EDTA (pH = 4.6)	90 min (25 deg C)	12.5 mL 1.0 M NH ₄ -Acetate (pH=4.6) 10 min
V.4	Weakly Crystalline Iron Oxides	25 mL 0.2 M NH ₄ -Oxalate (pH = 3.25)	2 hours (25 deg C- Dark)	12.5 mL 0.2 M NH ₄ -Oxalate (pH=3.25) 10 min Dark
V.5	Crystalline Iron Oxides	12.5 mL 0.1 M Ascorbic Acid + 12.5 mL 0.2 NH ₄ -Oxalate(pH = 3.25)	2 hours (96 deg C)	12.5 mL 0.2 M NH ₄ -Oxalate (pH=3.25) 10 min Dark
Tessier Method*				
Step	Fraction	Solution	Duration/Conditions	Wash
T.1	Exchangeable	8 mL 1.0 M MgCl ₂ (pH = 7)	1 hour (25 deg C)	8 mL DI H ₂ O
T.2	Acid Soluble	25 mL 1.0 M NaOAc (pH = 5)	5 hours (25 deg C)	8 mL DI H ₂ O
T.3	Reducible	20 mL 0.04 M NH ₂ OH-HCl in HOAc 25% w/w	6 hours (96 deg C)	8 mL DI H ₂ O
T.4	Oxidizable	3 mL 0.02 M HNO ₃ + 5 mL H ₂ O ₂ 30% w/v	2 hours (85 deg C)	8 mL DI H ₂ O
		3 mL H ₂ O ₂ 30% w/v	3 hours (85 deg C)	
		5 mL 3.2 M NH ₄ OAc	30 min (25 deg C)	
Hybrid Method*				
Step	Fraction	Solution	Duration/Conditions	Wash
H.1	Exchangeable	8 mL 1.0 M MgCl ₂ (pH = 7)	1 hour (25 deg C)	8 mL DI H ₂ O
H.2	Acid Soluble	25 mL 1.0 M NaOAc (pH = 5)	5 hours (25 deg C)	8 mL DI H ₂ O
H.3	Weakly Crystalline Iron Oxides	25 mL 0.2 M NH ₄ -Oxalate (pH = 3.25)	2 hours (25 deg C) Dark	12.5 mL 0.2 M NH ₄ -Oxalate (pH=3.25) 10 min Dark then 8 mL DI H ₂ O
H.4	Crystalline Iron Oxides	12.5 mL 0.1 M Ascorbic Acid + 12.5 mL 0.2 NH ₄ -Oxalate(pH = 3.25)	2 hours (96 deg C)	12.5 mL 0.2 M NH ₄ -Oxalate (pH=3.25) 10 min Dark then 8 mL DI H ₂ O
H.5	Oxidizable	3 mL 0.02 M HNO ₃ + 5 mL H ₂ O ₂ 30% w/v	2 hours (85 deg C)	8 mL DI H ₂ O
		3 mL H ₂ O ₂ 30% w/v	3 hours (85 deg C)	
		5 mL 3.2 M NH ₄ OAc	30 min (25 deg C)	

*1 g of sample was used for each method

Table 2: The chemical characteristics found in the meadowland soils. The Cr and Fe concentrations were determined from the microwave-assisted digestion performed at MERI

Sample #	pH	[Cr] (mg/kg)	[Fe] (mg/kg)	Organic Matter (wt%)
1A	4.67	857.76	21896.85	11.20
1B	5.07	613.44	21012.79	11.30
2A	5.58	464.46	16716.36	18.10
2B	6.71	426.71	15822.22	19.10
3A	6.43	532.00	14046.82	24.70
5A	4.50	547.25	22022.24	20.90
6A	5.96	185.32	13758.42	14.60
6B	5.53	284.67	13027.77	22.10
9	5.64	425.45	22184.29	22.20
10A	x	264.82	14877.55	24.60
10B	5.74	319.04	15578.65	19.10

Table 3: The measurements taken through the LOI method as well as the LOI % determined from the equation discussed in the Organic Content section. The asterisk indicates the weight of the sample after the heating step indicated.

Sample #	wt of Sample (before Heating)	wt of Sample (105° C*)	wt of Sample (400° C)	LOI %
1A	1.6525	1.6602	1.4750	11.2
1B	1.6178	1.6230	1.4390	11.3
2A	1.8767	1.8933	1.5498	18.1
2B	1.3153	1.3120	1.0620	19.1
3A	1.5674	1.5663	1.1809	24.7
4A	1.4712	1.4665	1.1578	21.3
5A	1.4685	1.4552	1.1511	20.9
5B	1.6991	1.6854	1.4588	13.4
6A	2.1044	2.0913	1.7851	14.6
6B	1.7394	1.7272	1.3462	22.1
7	1.4162	1.3965	1.0467	25.0
8	1.7015	1.6983	1.3630	19.7
9	1.2470	1.2339	0.9603	22.2
10A	1.6468	1.6262	1.2260	24.6
10B	1.6313	1.6212	1.3108	19.1

Table 4a: The Analytical results for the BCR sequential extraction method in mg/kg.

Sample	Cr – BCR1: Acid Soluble	Cr-BCR2: Reducible	Cr-BCR3: Oxisable	Cr-BCR: Measured Residual	Total extracted	Total measured [Cr]
1A-1	29.8711	152.1124	507.0360	131.7400	820.7595	857.7620
1A-2	37.0322	189.1496	555.3080	131.7400	913.2298	857.7620
1A-3	35.5773	186.8304	485.1440	131.7400	839.2917	857.7620
1B-1	34.1165	139.3576	383.9148	129.3600	686.7489	613.4400
1B-2	35.6774	134.5244	445.7720	129.3600	745.3338	613.4400
1B-3	34.6332	136.9604	484.1240	129.3600	785.0776	613.4400
2A-1	9.7978	47.4892	273.4352	112.5900	443.3122	464.4600
2A-2	9.5506	42.2576	280.7688	112.5900	445.1670	464.4600
2A-3	10.7376	54.8572	278.4488	112.5900	456.6336	464.4600
2B-1	6.6007	46.8380	219.7408	74.7200	347.8995	426.7100
2B-2	6.4291	41.7436	161.2496	74.7200	284.1423	426.7100
2B-3	6.4431	44.6560	173.6840	74.7200	299.5031	426.7100
5A-1	20.3614	48.0684	493.8280	137.9600	700.2178	547.2500
5A-2	19.5752	40.7356	404.1120	137.9600	602.3828	547.2500
5A-3	21.6456	40.5944	419.5440	137.9600	619.7440	547.2500

Table 4b: The Analytical results for the BCR sequential extraction method in percentage.

Sample	Cr – BCR1: Acid Soluble	Cr-BCR2: Reducible	Cr-BCR3: Oxisable	Cr-BCR: Measured Residual
1A-1	3.4824	17.7336	59.1115	15.3586
1A-2	4.3173	22.0515	64.7392	15.3586
1A-3	4.1477	21.7811	56.5593	15.3586
1B-1	5.5615	22.7174	62.5839	21.0876
1B-2	5.8160	21.9295	72.6676	21.0876
1B-3	5.6457	22.3266	78.9195	21.0876
2A-1	2.1095	10.2246	58.8716	24.2411
2A-2	2.0563	9.0982	60.4506	24.2411
2A-3	2.3119	11.8110	59.9511	24.2411
2B-1	1.5469	10.9765	51.4965	17.5107
2B-2	1.5067	9.7827	37.7890	17.5107
2B-3	1.5099	10.4652	40.7031	17.5107
5A-1	3.7207	8.7836	90.2381	25.2097
5A-2	3.5770	7.4437	73.8441	25.2097
5A-3	3.9553	7.4179	76.6640	25.2097

Table 5a: The Analytical results for the Voegelin sequential extraction method in mg/kg.

Sample #	Cr – v1: weakly bound	Cr-v2: Mn oxides	Cr-v3: Organic	Cr-V4: amorphous Fe-oxides	Cr-V5: Crystalline Fe-oxides	Cr-V: Measured Residual	Total extracted	Total measured [Cr]
1A-1	52.0774	24.9304	19.0539	84.4568	182.7484	248.1000	611.3667	857.7620
1A-2	60.6653	27.6663	20.0972	97.1299	221.7116	248.1000	675.3703	857.7620
1A-3	62.0929	23.1411	20.5065	89.6175	215.2909	248.1000	658.7488	857.7620
1B-1	57.9735	23.4828	19.7088	77.6520	189.2535	164.8400	532.9106	613.4400
1B-2	56.3820	23.1602	17.2922	78.8419	152.4161	164.8400	492.9323	613.4400
1B-3	52.9793	24.2367	20.0526	89.7214	178.1865	164.8400	530.0165	613.4400
2A-1	14.7692	6.7084	7.0352	20.7003	117.8779	153.2300	320.3208	464.4600
2A-2	15.2953	6.6406	6.9737	19.0986	111.0341	153.2300	312.2724	464.4600
2A-3	14.5878	6.3395	7.8024	18.1031	122.9415	153.2300	323.0043	464.4600
2B-1	7.5716	3.6477	3.5961	22.0187	81.1043	140.4400	258.3783	426.7100
2B-2	6.9341	3.6158	3.5661	17.9469	60.3026	140.4400	232.8054	426.7100
2B-3	7.8626	3.3622	3.8978	20.1330	77.8103	140.4400	253.5059	426.7100
5A-1	32.2452	10.4452	10.5241	19.9506	267.0956	130.6100	470.8707	547.2500
5A-2	30.4830	9.6023	10.7747	21.0047	263.3329	130.6100	465.8075	547.2500
5A-3	32.3478	9.6980	11.7483	22.4129	276.5434	130.6100	483.3604	547.2500

Table 5b: The Analytical results for the Voegelin sequential extraction method in percentage.

Sample #	Cr – v1: weakly bound	Cr-v2: Mn oxides	Cr-v3: Organic	Cr-V4: amorphous Fe-oxides	Cr-V5: Crystalline Fe-oxides	Cr-V: Measured Residual
1A-1	6.0713	2.9064	2.2213	9.8462	21.3053	28.9241
1A-2	7.0725	3.2254	2.3430	11.3236	25.8477	28.9241
1A-3	7.2389	2.6978	2.3907	10.4478	25.0991	28.9241
1B-1	9.4506	3.8281	3.2128	12.6585	30.8512	26.8714
1B-2	9.1911	3.7755	2.8189	12.8524	24.8461	26.8714
1B-3	8.6364	3.9509	3.2689	14.6259	29.0471	26.8714
2A-1	3.1799	1.4443	1.5147	4.4568	25.3796	32.9910
2A-2	3.2931	1.4297	1.5015	4.1120	23.9061	32.9910
2A-3	3.1408	1.3649	1.6799	3.8977	26.4698	32.9910
2B-1	1.7744	0.8548	0.8428	5.1601	19.0069	32.9123
2B-2	1.6250	0.8474	0.8357	4.2059	14.1320	32.9123
2B-3	1.8426	0.7879	0.9135	4.7182	18.2349	32.9123
5A-1	5.8922	1.9087	1.9231	3.6456	48.8069	23.8666
5A-2	5.5702	1.7546	1.9689	3.8382	48.1193	23.8666
5A-3	5.9110	1.7721	2.1468	4.0956	50.5333	23.8666

Table 6a: The Analytical results for the Tessier sequential extraction method in mg/kg.

Sample #	Cr – T1: Exchangeable	Cr-T2: Acid soluble	Cr-T3: Reducible	Cr-T4: Oxidizable	Cr-T: Measured Residual	Total extracted	Total measured [Cr]
1A-1	2.6554	26.9363	724.1900	188.8608	144.0900	1086.7325	857.7620
1A-2	4.1101	23.6696	703.9800	192.9024	144.0900	1068.7521	857.7620
1A-3	2.7850	21.4104	667.4520	149.9678	144.0900	985.7052	857.7620
1B-1	2.8400	20.8207	766.0040	152.2912	72.7200	1014.6760	613.4400
1B-2	2.9345	18.6983	812.4180	128.4608	72.7200	1035.2316	613.4400
1B-3	3.2259	20.7064	897.9720	164.2080	72.7200	1158.8323	613.4400
2A-1	2.2140	7.7099	252.7480	128.0366	83.7500	474.4586	464.4600
2A-2	2.1620	7.8566	242.0960	142.8749	83.7500	478.7394	464.4600
2A-3	2.0802	7.5475	201.7060	132.1560	83.7500	427.2397	464.4600
2B-1	1.7629	5.3380	168.1034	77.6123	68.0500	320.8666	426.7100
2B-2	1.7883	5.2668	184.6518	78.6419	68.0500	338.3988	426.7100
2B-3	1.8403	5.7034	199.2550	83.2445	68.0500	358.0932	426.7100
5A-1	3.2566	9.2737	246.6560	327.3424	124.0400	710.5687	547.2500
5A-2	3.5655	10.6078	230.2220	353.5280	124.0400	721.9633	547.2500
5A-3	3.4678	10.7296	268.2880	346.9536	124.0400	753.4790	547.2500

Table 6b: The Analytical results for the Tessier sequential extraction method in percentage.

Sample #	Cr – T1: Exchangeable	Cr-T2: Acid soluble	Cr-T3: Reducible	Cr-T4: Oxidizable	Cr-T: Measured Residual
1A-1	0.3096	3.1403	84.4279	22.0179	16.7984
1A-2	0.4792	2.7595	82.0717	22.4890	16.7984
1A-3	0.3247	2.4961	77.8132	17.4836	16.7984
1B-1	0.4630	3.3941	124.8702	24.8258	11.8545
1B-2	0.4784	3.0481	132.4364	20.9411	11.8545
1B-3	0.5259	3.3755	146.3830	26.7684	11.8545
2A-1	0.4767	1.6600	54.4176	27.5668	18.0317
2A-2	0.4655	1.6916	52.1242	30.7615	18.0317
2A-3	0.4479	1.6250	43.4281	28.4537	18.0317
2B-1	0.4131	1.2510	39.3952	18.1885	15.9476
2B-2	0.4191	1.2343	43.2734	18.4298	15.9476
2B-3	0.4313	1.3366	46.6956	19.5084	15.9476
5A-1	0.5951	1.6946	45.0719	59.8159	22.6661
5A-2	0.6515	1.9384	42.0689	64.6008	22.6661
5A-3	0.6337	1.9606	49.0248	63.3995	22.6661

Table 7: This table shows the steps for each sequential extraction method and their associated target soil fraction. These are the steps were used in each of the comparison plots.

Fraction Comparisons			
Soil Fraction	BCR Method	Voegelin Method	Tessier Method
Oxidizable	Step 3	Step 3	Step 4
Acid Soluble/Exchangeable	Step 1	Step 1	Steps 1 and 2
Reducible	Step 2	Steps 2, 4 and 5	Step 3

Table 8: The results of the microwave assisted a digestion performed on the remaining solids from each extraction method to determine the residual amounts for both Cr and Fe.

Sample #	BCR		Voegelin		Tessier	
	Cr-Residual (mg/kg)	Fe-Residual (mg/kg)	Cr-Residual (mg/kg)	Fe-Residual (mg/kg)	Cr-Residual (mg/kg)	Fe-Residual (mg/kg)
1A	130.74	21301.82	248.10	17764.45	144.09	22555.69
1B	129.36	21380.10	164.84	13193.50	72.72	16599.90
2A	112.59	10955.50	153.23	11159.14	83.75	8370.56
2B	74.72	12739.40	140.44	9459.58	68.05	11388.52
5A	137.96	8824.21	130.61	15649.02	124.04	15552.28

Table 9: Linear Combination fit percentages compared to the associated soil fraction and the three sequential extraction methods percentages.

Sample #	Species	LC Percentage	Associated Soil Fraction	Voegelin Total % per fraction	Tessier Total % per fraction	BCR Total % per fraction
1A	Chromite	38%	Residual	53.33%	6.51%	15.38%
	Cr _{0.1} Fe _{0.9} (OH) ₃	28%	Fe-bound	37.56%	81.41%	20.52%
	Cr-DOM	33%	Oxidizable	2.32%	20.66%	60.12%
1B	Chromite	31%	Residual	42.29%	62.62%	0.54%
	Cr _{0.1} Fe _{0.9} (OH) ₃	28%	Fe-bound	45.51%	134.66%	22.34%
	Cr-DOM	41%	Oxidizable	3.10%	24.20%	71.44%
2A	Chromite	45%	Residual	64.37%	18.88%	27.63%
	Cr _{0.1} Fe _{0.9} (OH) ₃	46%	Fe-bound	30.85%	50.04%	10.39%
	Cr-DOM	8%	Oxidizable	1.57%	28.96%	59.82%
2B	Chromite	37%	Residual	74.76%	36.52%	44.78%
	Cr _{0.1} Fe _{0.9} (OH) ₃	63%	Fe-bound	22.63%	43.09%	10.40%
	Cr-DOM	0%	Oxidizable	0.86%	18.70%	43.30%
5A	Chromite	33%	Residual	37.34%	10.54%	8.08%
	Cr _{0.1} Fe _{0.9} (OH) ₃	11%	Fe-bound	54.85%	45.41%	7.89%
	Cr-DOM	56%	Oxidizable	2.01%	62.63%	80.29%

Appendix B: Figures

Figure A: The Kearny Marsh Site including the initial 15 sample locations. Locations are indicated by a yellow star. Some locations where two samples were extracted, i.e. sample 5A and 5B, these were taken at the same location within 2 feet of each other.



Figure 1: A comparison between total Fe and total Cr concentrations. These numbers were determined by the microwave assisted digestion.

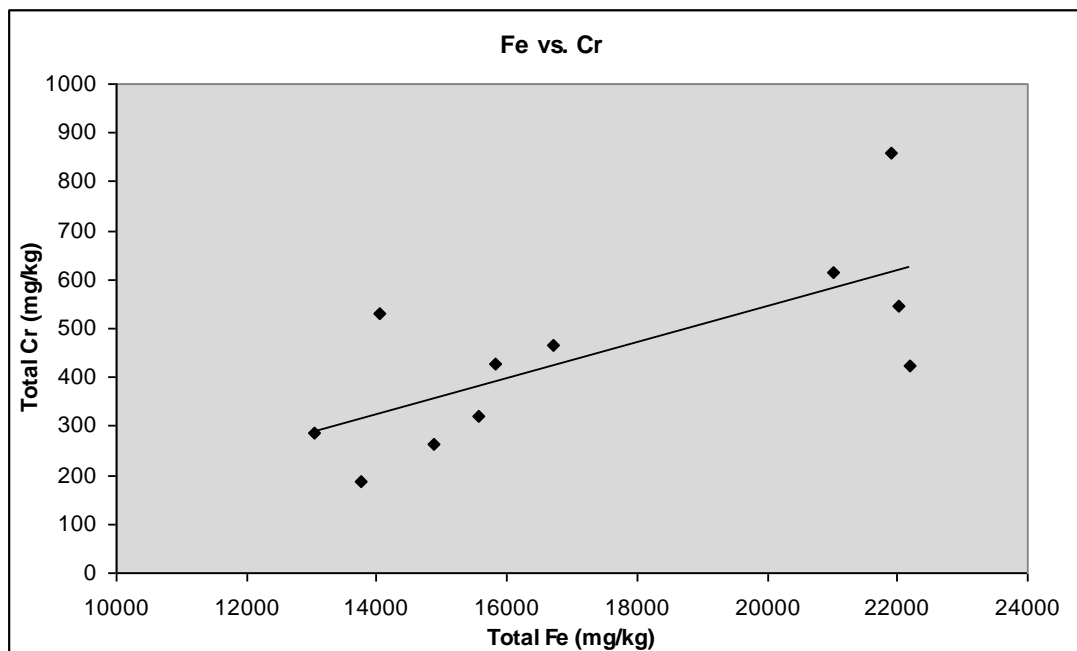


Figure 2: The results of the Cr Mass Balance. This compares the total extracted Cr determined from the sequential methods (x-axis) and the Cr content determined from the microwave-assisted digestion (y-axis).

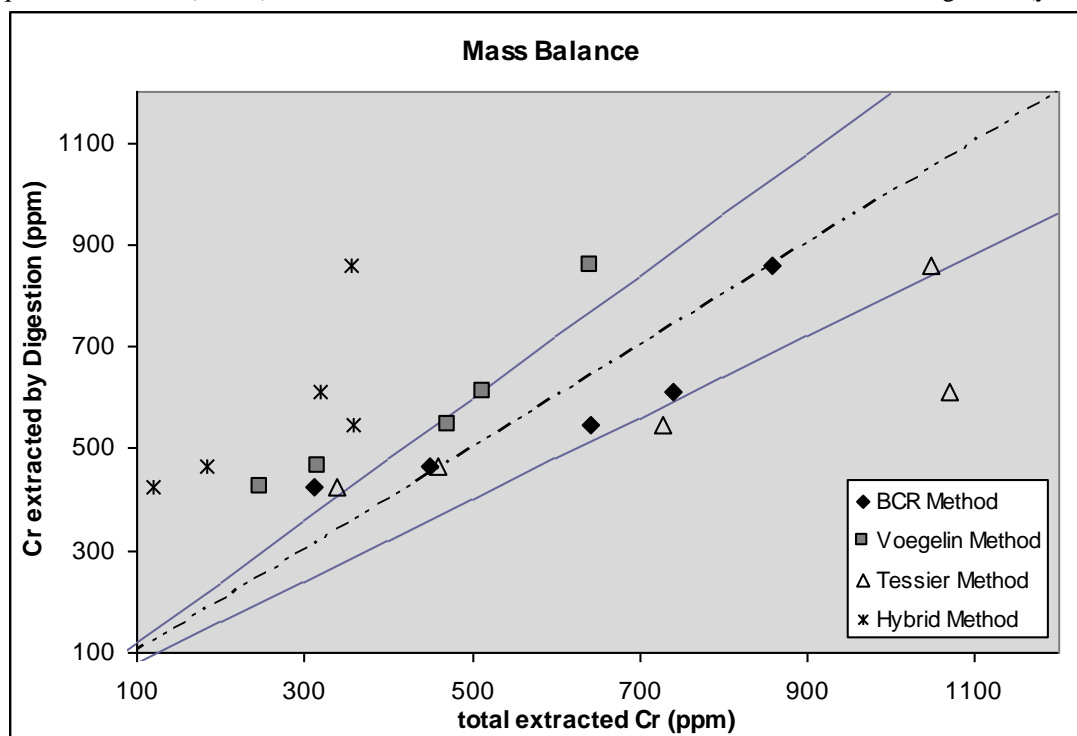


Figure 3: The extraction results of the BCR method. Step 1 targeted the acid soluble fraction, 2 targeted the reducible fraction, and 3 targeted the oxidizable fraction.

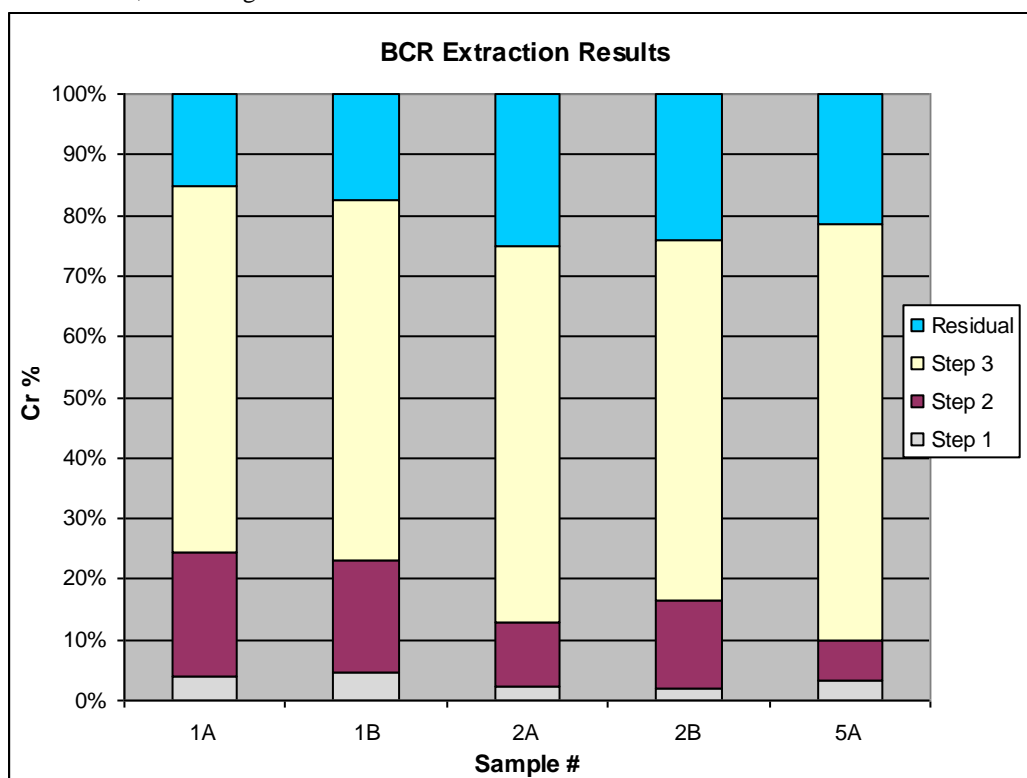


Figure 4: The extraction results of the Voegelin method. Step 1 targeted the acid soluble fraction. Steps 2, 4 and 5 targeted the reducible fraction. Step 3 targeted the oxidizable fraction.

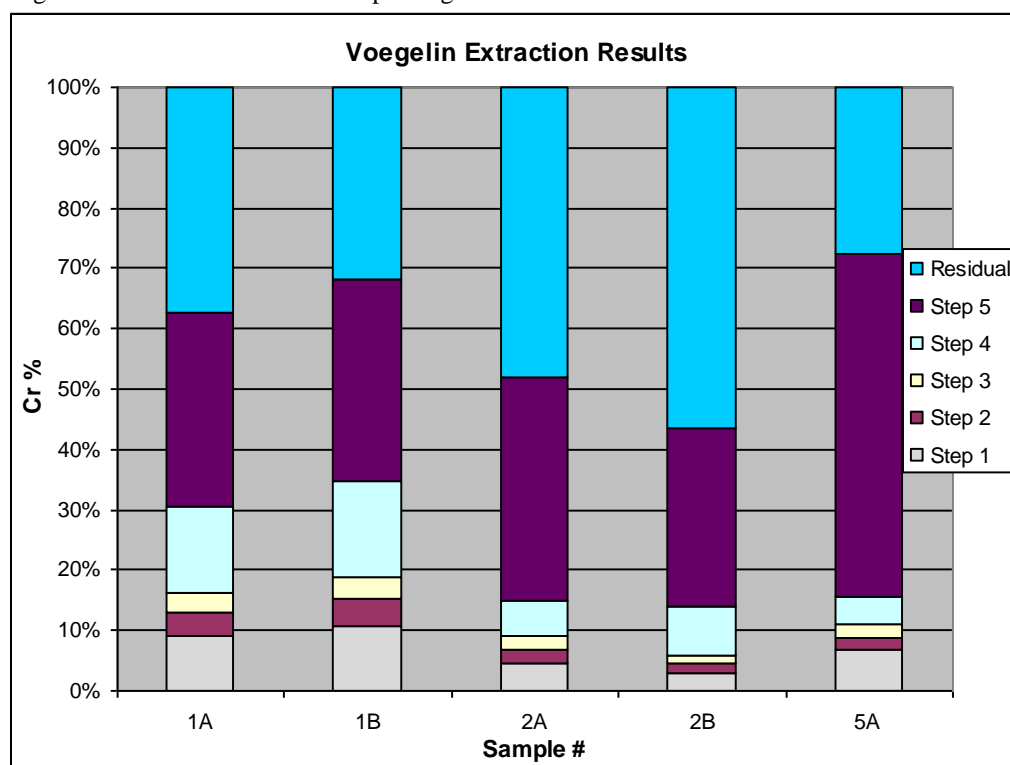


Figure 5: The extraction results of the Tessier method. Steps 1 and 2 targeted the acid soluble fraction. Step 3 targeted the reducible fraction. Step 4 targeted the oxidizable fraction.

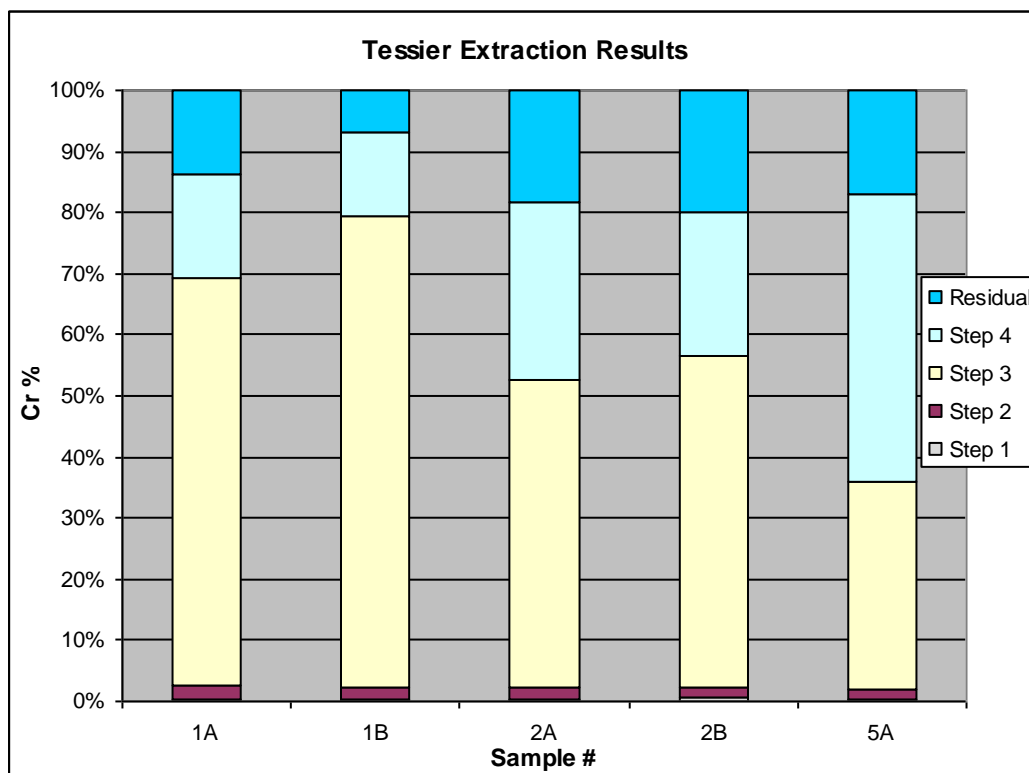


Figure 6: The extraction results of the Hybrid method. Steps 1, 2 and 5 taken from the Tessier method targeted the exchangeable, acid soluble and oxidizable fractions respectively. Steps 3 and 4 taken from the Voegelin method targeted the reducible fraction.

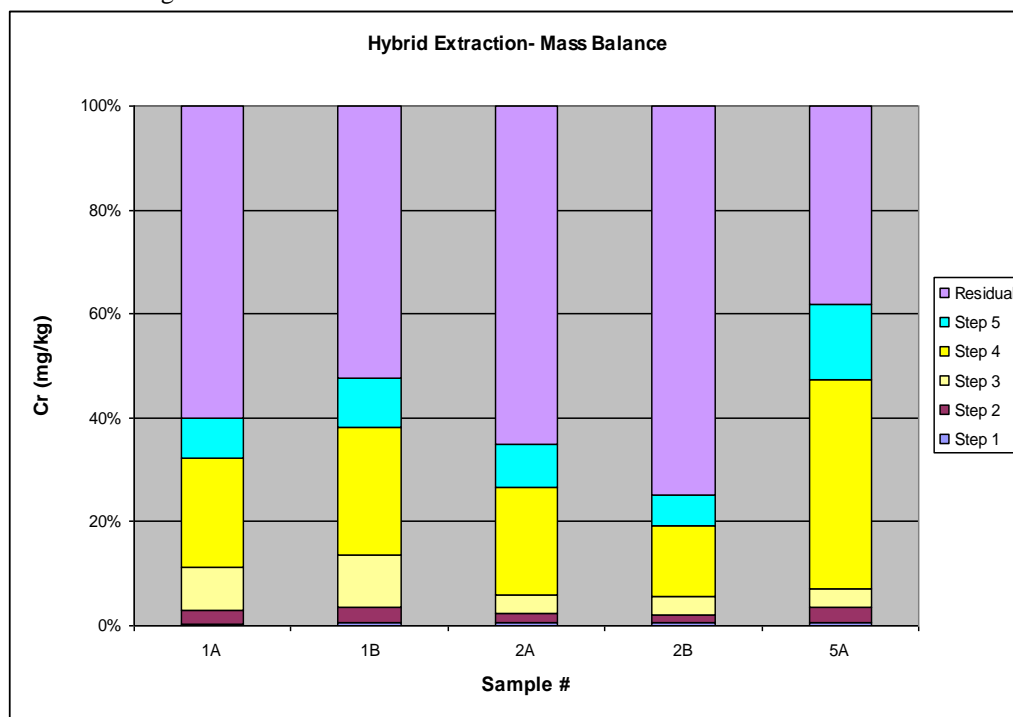


Figure 7a: A comparison of the Cr percent extracted during the acid soluble steps from the three methods. The Cr percentages were taken and plotted against one another. In cases where multiple steps targeted the same fraction the concentrations were added up and that total value was used for that sample.

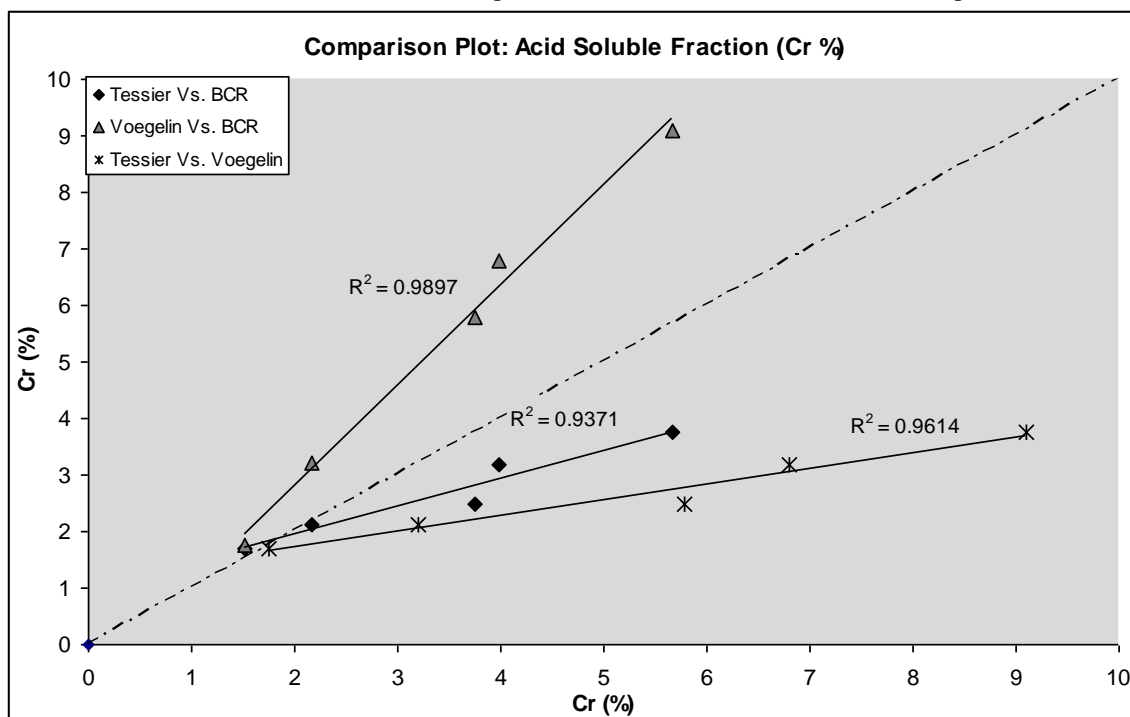


Figure 7b: A comparison of the Cr extracted from the acid soluble fractions of the meadowlands soils in ppm.

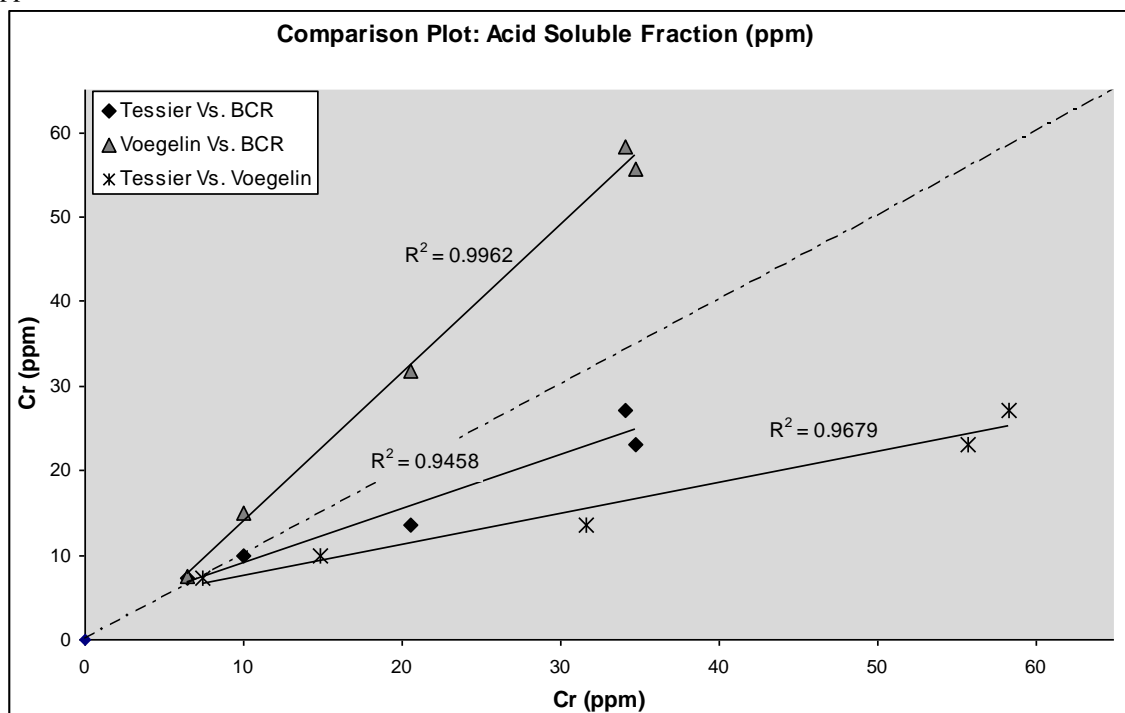


Figure 8a: A comparison of the Cr associated with Mn- and Fe-Oxides. The Cr percentages from each extraction method were plotted against one another.

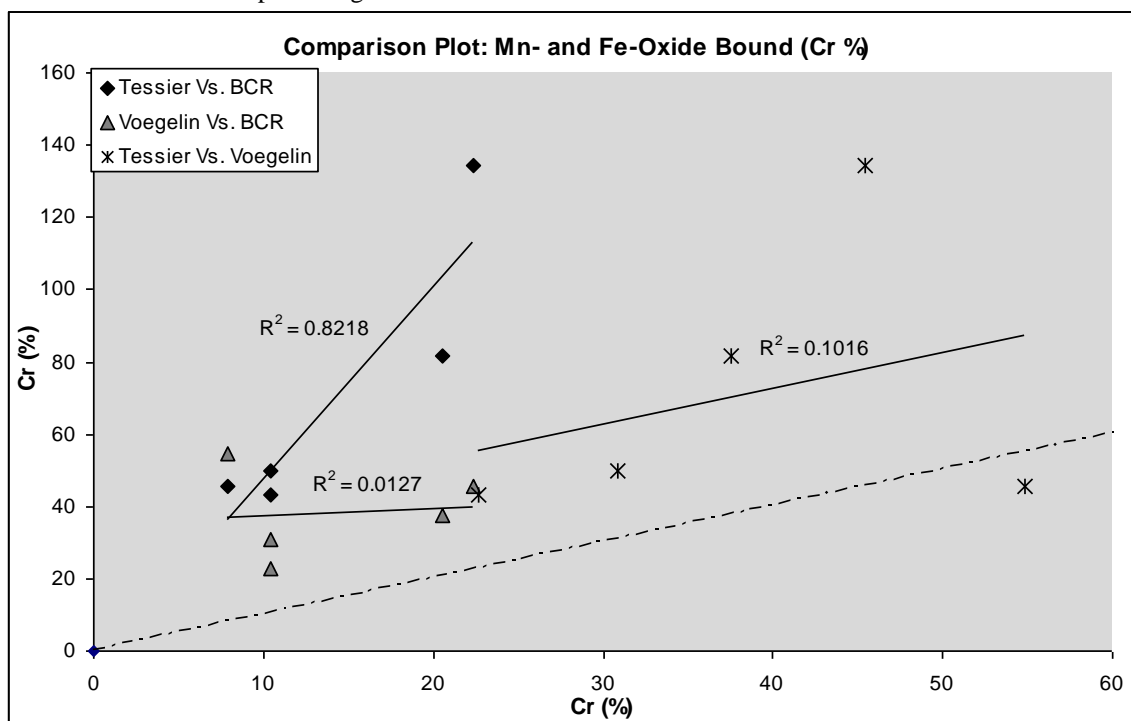


Figure 8b: A comparison of the Mn- and Fe-Oxide bound Cr extracted in the three methods. The Cr concentrations were plotted against one another.

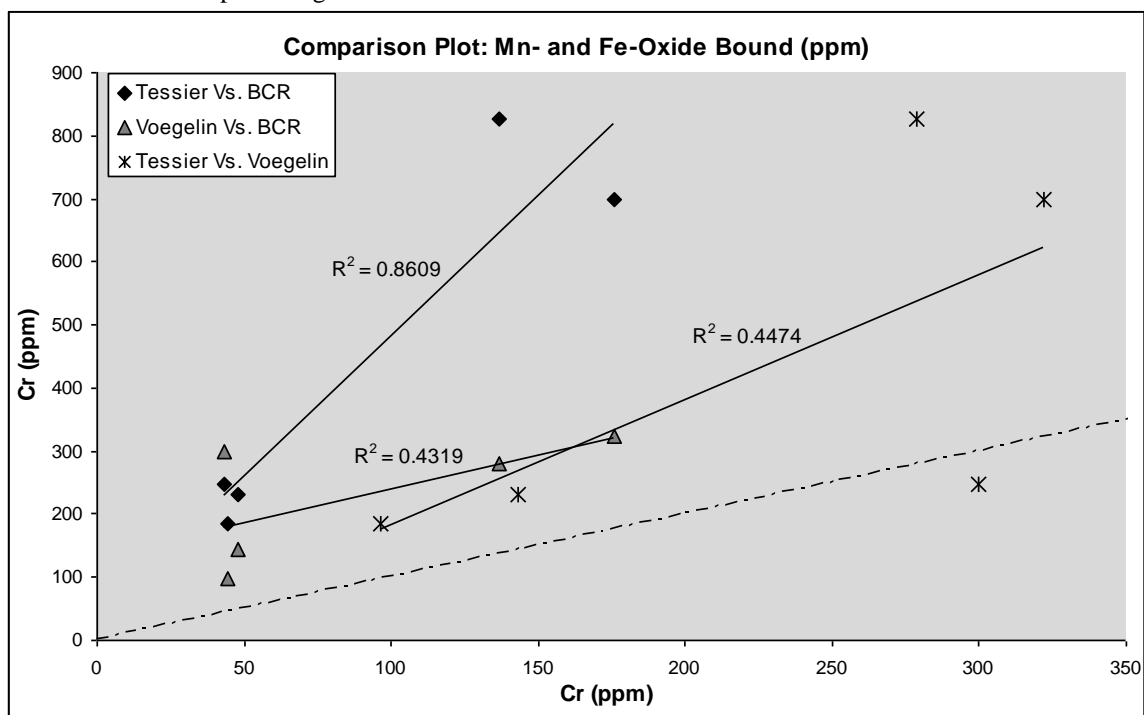


Figure 9a: A comparison of the percent Cr extracted during the steps targeting the oxidizable soil fractions.

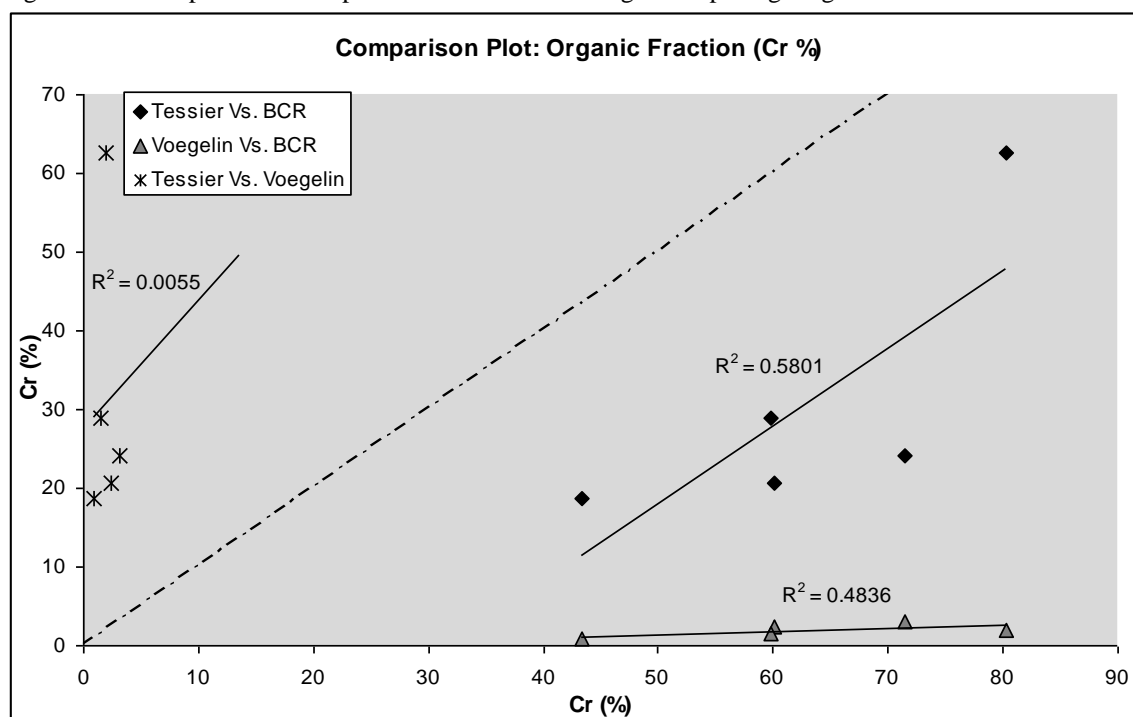


Figure 9b: A comparison of the Cr concentrations (ppm) extracted during the steps targeting the oxidizable fractions.

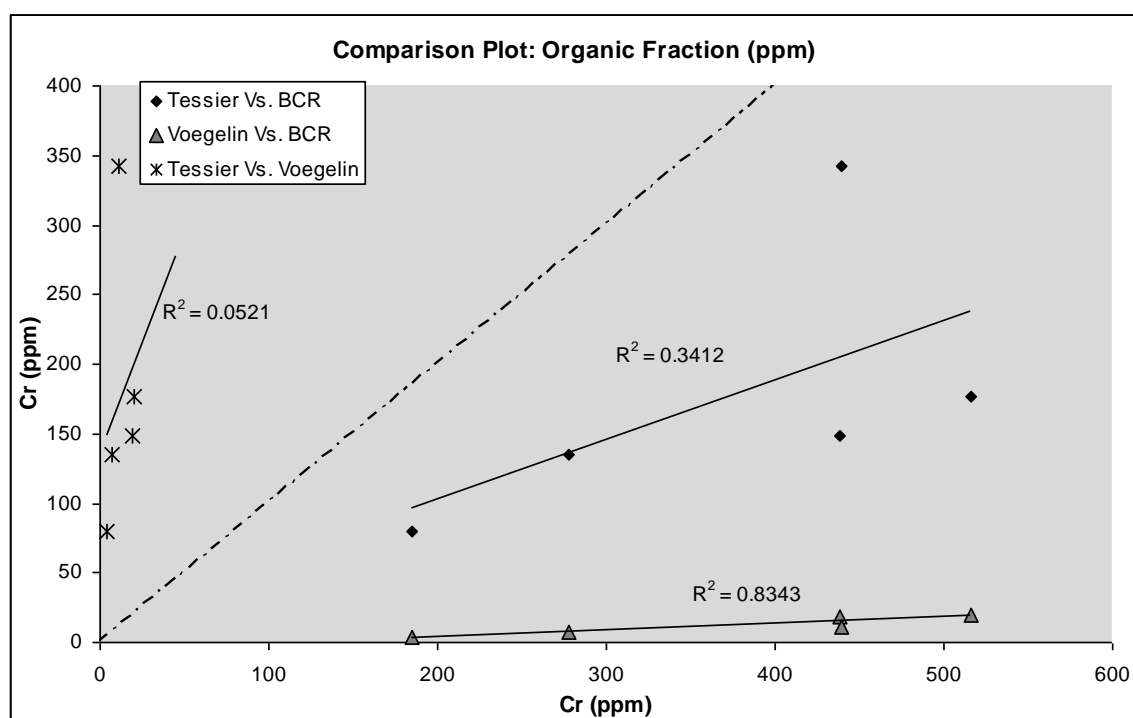


Figure 10a: A comparison of the percent of residual Cr from each extraction method. These are the calculated percentages taken from the extraction amounts compared to the total Cr measured during the microwave assisted digestion.

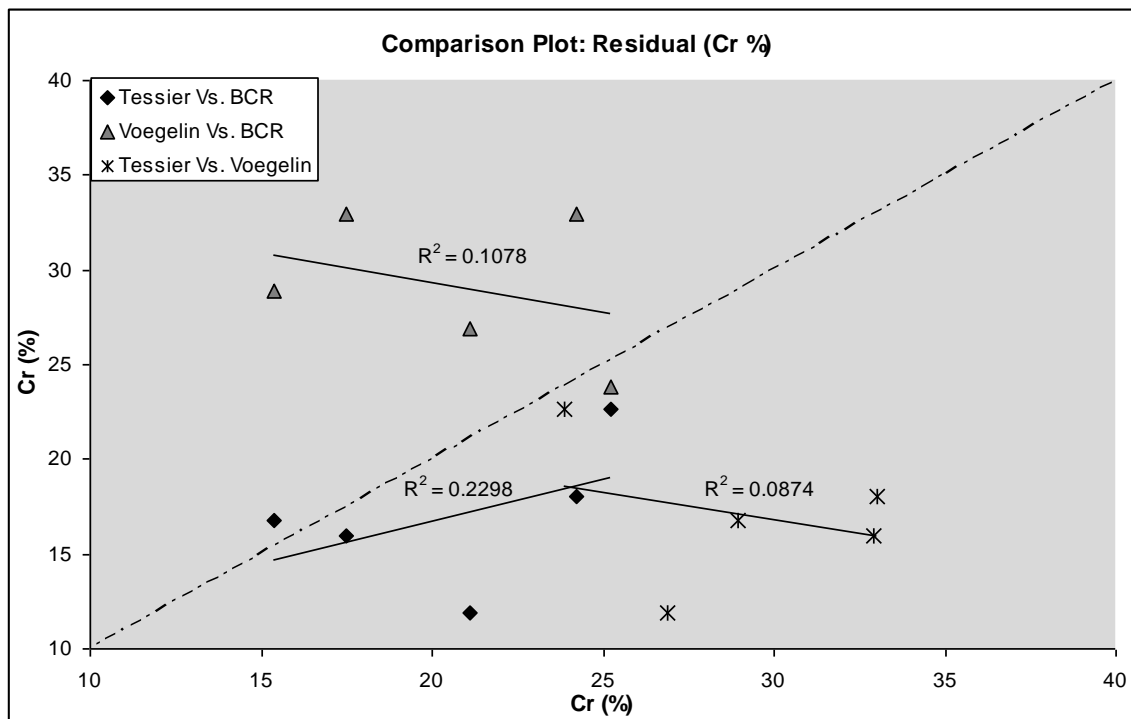


Figure 10b: A comparison of the residual Cr in ppm from each extraction method.

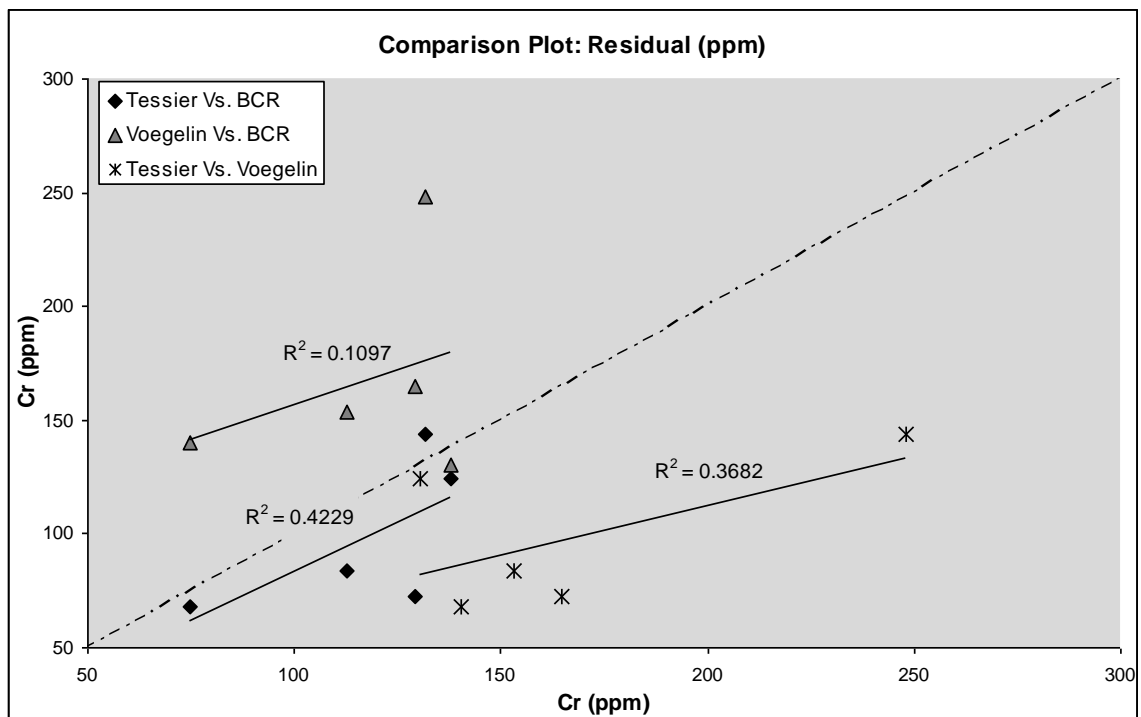


Figure 11a: The comparison between pH and the chromium extracted during the steps targeting the acid soluble soil fraction.

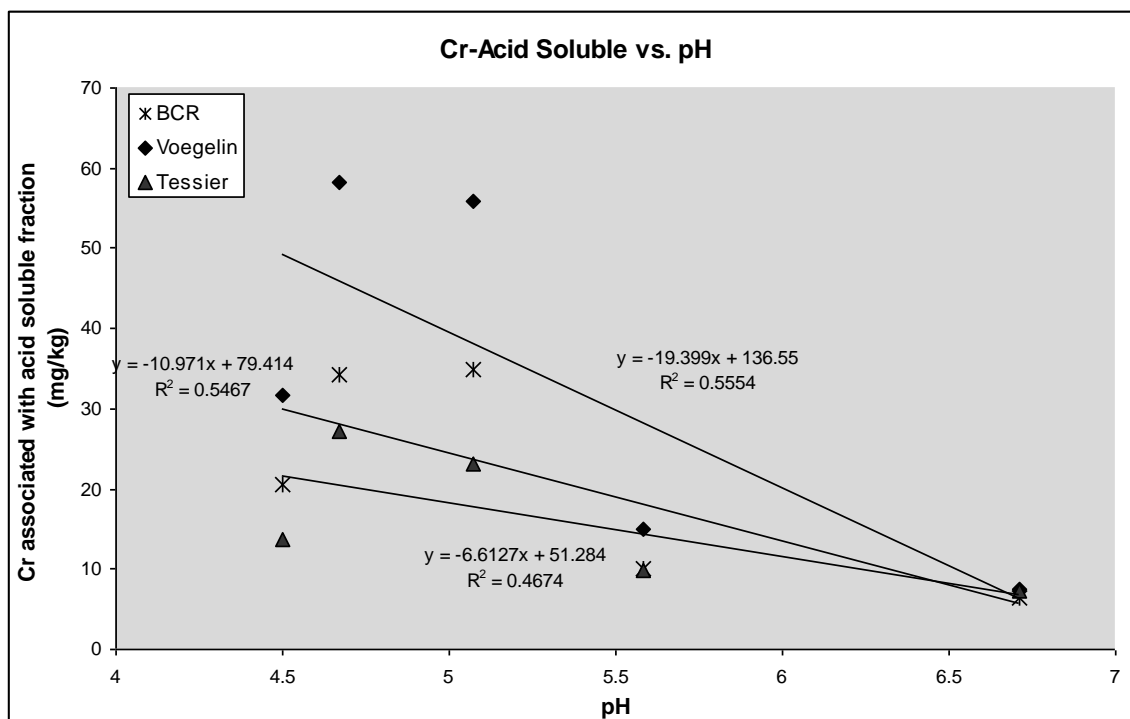


Figure 11b: The comparison between pH and the Organic Matter percentages determined from the LOI method.

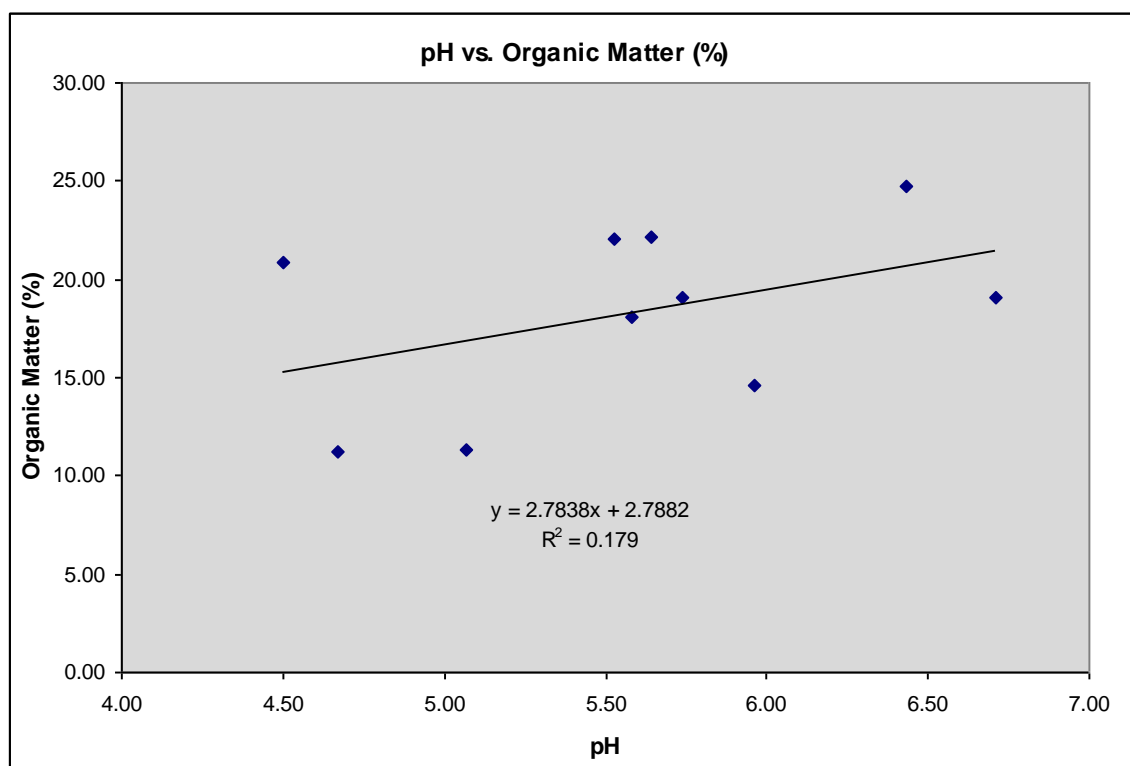


Figure 11c: The comparison between pH and the Fe concentrations derived from the microwave-assisted digestions performed at MERI.

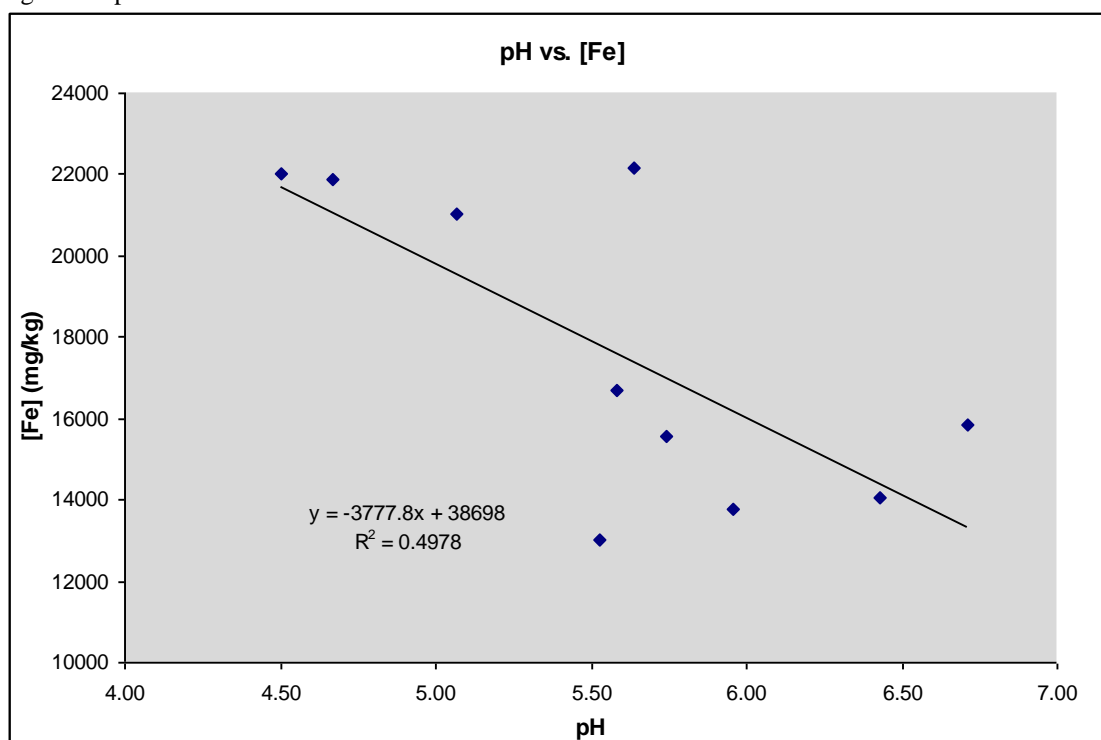


Figure 11d: A comparison between the percent of organic material determined from the LOI method and the percent of Cr extracted during the steps targeting the oxidizable soil fractions.

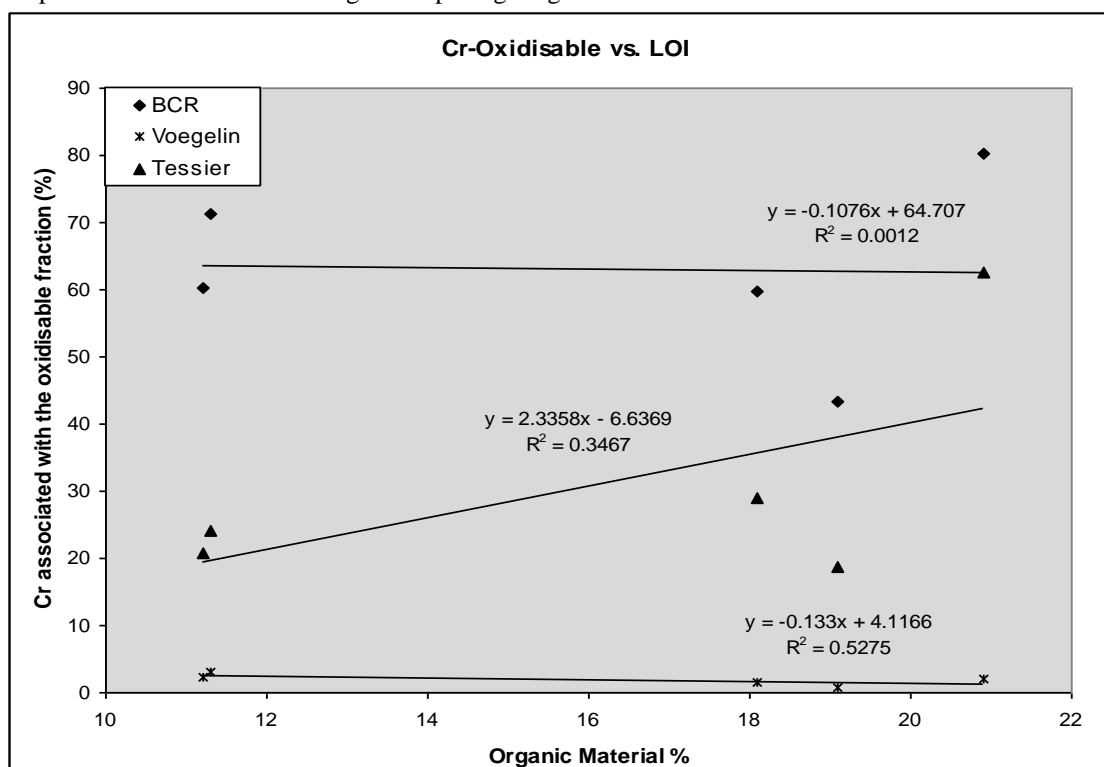


Figure 11e: The comparison between Cr and Fe. The Cr extracted during the steps targeting the reducible soil fraction for each extraction method is plotted against the Fe concentrations determined from the microwave-assisted digestions.

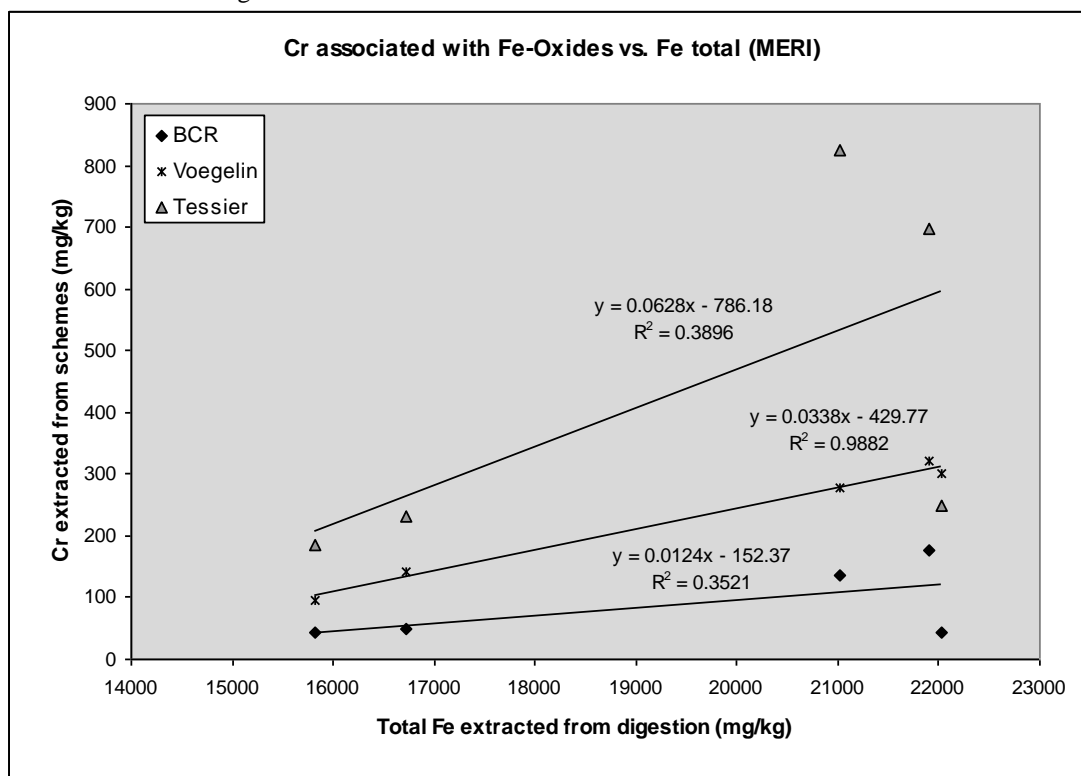


Figure 12a: Comparison between extracted Cr associated with organic material versus the LC fits determined from the XAS method.

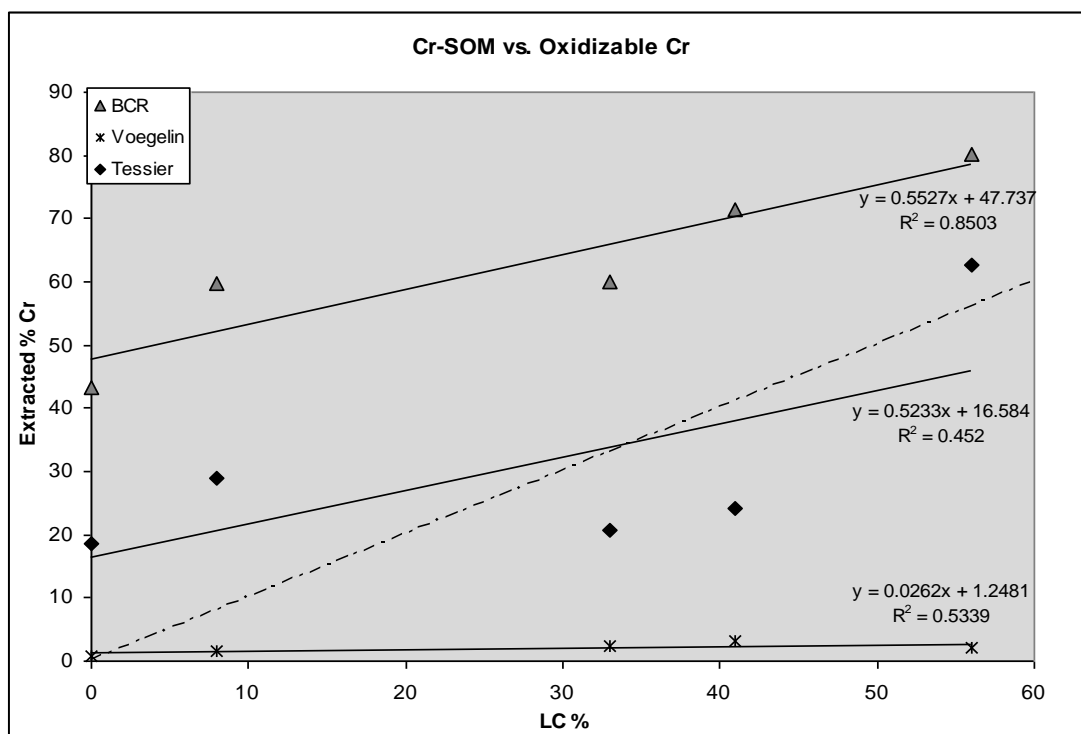


Figure 12b: Comparison between extracted Cr associated with the reducible fraction versus the LC fits of the $\text{Cr}_{0.1}\text{Fe}_{0.9}(\text{OH})_3$ determined from the XAS method.

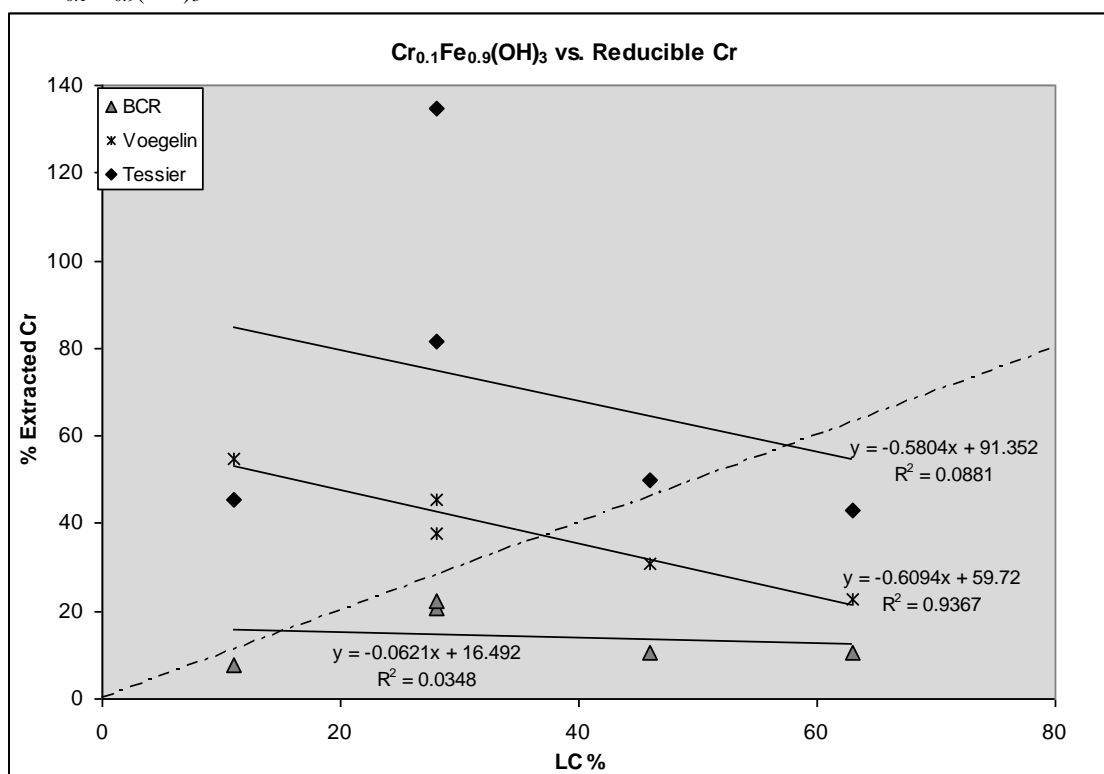


Figure 12c: Comparison between extracted Cr associated with the reducible fraction versus the LC fits of the Chromite determined from the XAS method.

