THE DISTRIBUTION OF CHROMIUM SPECIES AS A FUNCTION OF PARTICLE SIZE FOR CHROMIUM WASTE LADEN SOILS

FINAL REPORT

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1. BACKGROUND

Fill laden with Chromate Production Waste Material (COPR) was deposited in Hudson County over the course of nearly a century and as a result, the various sites of deposition contain chromium at various concentrations with valence states of trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}). Chromium in the form of Cr^{3+} is an essential element for life and has a low toxicity, while Cr^{6+} has a range of toxic effects including carcinogenicity. Further, it is known that different levels of chromium in each valence state can be present in soil or fill. For many elements found in soil, it has been observed that the mass of a particular element can be distributed toward either larger or smaller particle sizes. Thus, the distribution of mass may not be uniform as a function of particle size. One study completed by Kitsa et al (1992) examined the distribution of total chromium and chromium species concentrations versus size, but this study addressed COPR at only one site, Liberty State Park. Another study conducted by Falerios, et al. (1992) only investigated the difference in concentrations between total and hexavalent chromium in indoor and outdoor environments associated with contaminated soil chromite ore processing sites, but did not examine the concentrations of Cr^{6+} as a function of particle size in soil. Given the fact that the mobility and variability of chromium species can be quite large and further, that chromium contaminated soil can have different physical and chemical characteristics based upon environmental conditions such as moisture, pH value, etc., it is important to determine the distribution of both Cr^{3+} and Cr^{6+} in soil as a function of particle size. The information obtained is critical for assessing potential exposure to chromium species through different pathways as well as developing effective management plan for the waste sites.

2. OBJECTIVES

With the continuing concern about the presence of COPR at various sites in Hudson County, and the potential for human exposure, the objectives of this study were 1) to determine the concentrations of Cr^{6+} and Cr^{3+} and characterize the distribution of Cr^{6+} and Cr^{3+} as a function of particle size for a number of COPR waste laden soils that still exist in Hudson County, 2) to provide the NJ Department of Environmental Protection (NJDEP) with data that can then be applied for use in a variety of risk assessments for inhalation, dermal and ingestion exposure to chromium species, and to determine whether any generalizations can be drawn that bear on risk assessment and risk management activities.

3. METHODS

To achieve the above objectives, NJDEP identified 11 un-remediated and/or partially/interim remediated COPR sites in Hudson County to collect soil samples under this project for chromium species analyses as a function of particle size of the soil. Included are Nicholas Truck, Garfield Ave., Liberty Park, Colony Diner, IMTT (3 sites), and Honeywell (4 sites) (Table 1). The samples were collected by NJDEP personnel from each site. The samples were then separated into a specific number of particle size fractions and analyzed for chromium species to determine the concentration of chromium species in different particle size. The Cr^{3+} and Cr^{6+} concentrations measured in each size were also divided by those measured in the unsized soil sample to determine the ratio of each species in each soil particle size. The specific descriptions of soil sample collection, sizing and analyses are presented below.

3.1 Sample Collection

The primary goal of this project was to determine the relationship between particle size and Cr^{6+} concentration of the COPR that could potentially pose a risk of exposure - mostly, but not exclusively, by inhalation. The material that most directly relates to such exposures is the material at or close to the surface. Hence, the original objective of taking samples at a 1 inch depth. However, all of the remaining sites are under at least interim remediation controls, and many of the sites were a combination of different waste sites because the sites of COPR production that presumably represent the range of material that was moved from these sites to other waste sites around Hudson County, material at greater depth at the current time could be available for exposure in the future. Thus, samples were collected from 1-6 inches at each site. In addition one sample from 6-12 inches and one from 10 feet was collected at Honeywell site to examine the distribution of Cr^{6+} concentration in depth.

3.2 Size Segregation by Sieving and Elutriation

The approach employed for obtaining size segregated sub-samples involved the following two steps.

First, the soils were separated into size fractions using dry molecular sieving down to 250 µm, 75 µm and 38 µm and smaller size in diameter, respectively. As was the case in our previous work (Kitsa et al., 1992), we dried the sample before sieving, and then separated the soil by particle size. The sieves employed were made of brass to prevent contamination of the samples by chromium that was present in stainless steel sieves. All sub-samples were then stored at 4°C prior to extraction and analysis for Cr^{6+} and Cr^{3+}.

The second step in the process was to take a portion of each <38 µm soil sample and sub-divide it down to <10 µm and <2.5 µm size sub-samples. These new sub-samples provided us with the ability to determine the Cr^{6+} and Cr^{3+} mass distribution within the thoracic ($PM_{10-2.5}$) and the fine ($PM_{2.5}$) aerodynamic particle size ranges, which were most critical particle size fractions for assessing inhalation exposures and risks. An aerodynamic particle size separator, i.e. the elutriator system (Figure 2) that was built to separate dust particles from the World Trade Center Disaster site (Lioy et al 2003, McGee et al 2003) was used for sizing by Dr. Lung Chi Chen at NYU. Briefly, the soil dusts were mechanically separated using a sieve with a mesh size of 30 µm. The fraction of particles below 30 µm was further separated, aerodynamically, into three size fractions (30-10 µm, 10-2.5 µm, and < 2.5 µm). Particles were re-suspended by a jet of filtered air into a resuspension chamber, passing through an inlet (Wedding Inlet, 10 µm cut size, Anderson Instrument) to collect particles between 30 and 10 µm before entering a cyclone with a sharp cut size of 2.5 µm (BGI, Inc). Particles between 10 – 2.5 µm were collected by the cyclone while particles smaller than 2.5 µm ($PM_{2.5}$), which penetrated through the cyclone, were collected on Teflon filters. Particles collected in the Wedding Inlet as well as the BGI cyclone were swept into glass jars weighed before and after collection in an electro-microbalance. 47-mm size Teflon filters were used to collect $PM_{2.5}$ and were equilibrated, before and after sample collections, at NYU's weighing laboratory (described below) at constant temperature and humidity for 24 hours using an electro-microbalance. The sample ID is reported in Table 1.

3.3 Sample Analysis

The samples were analyzed for Cr^{6+}, Cr^{3+} and total chromium. Samples included for analysis were: 1) the bulk composited soil, 2) the sub-samples obtained by sieving (<250 µm, 75 µm and 38 µm fractions), and 3) the sub-samples obtained by aerodynamic size separation (38 to 10 µm, 2.5 to 10 µm and, ≤2.5 µm).

For Cr^{6+} and Cr^{3+} analysis, the sample was placed in the vessel and digested using microwave assisted extraction with 0.28M Na_3CO_3/0.5M NaOH solution heating at 90-95°C for 60 minutes (EPA 3060a) to dissolve the Cr^{6+} and stabilize it against reduction to Cr^{3+}. Minimal reduction of Cr^{6+} or oxidation of native Cr^{3+} occurred under the alkaline conditions. The detailed procedures can be found in the EPA 3060a. The accuracy of the extraction and detection procedure of Cr^{6+} was monitored by the measurement of certified soils. The vessels were left to cool to room temperature and the solutions were then filtered using a 0.2 μm PTFE filter and stored at 4°C until analysis. The filtrates were acidified to pH of approximately 6 with drop-wise nitric acid (Optima, ultra high purity trace, VWR) just before analysis. Soluble Cr^{6+} was separated from Cr^{3+} using an ion chromatographic (IC) technique. The IC conditions were as followed:

- Column: CG5A Guard Column (Dionex)
- 100 μL injection loop
- 1.25 mL/min flow rate
- Isocratic 40% dI Water, 60% 1 M Nitric Acid
- 4 minute runtime

Measurement was performed by a Fisons VG PlasmaQuad 3 inductively coupled plasma mass spectrometry (ICPMS).The ICPMS was run in Transient Time Resolved Analysis Mode (TRA) with a dwell time of 300 ms per m/z. The instrument was tuned with a 10 ng/mL indium solution (Multi-element Tune A, Thermo Electron, Cheshire, England) before use.

For analysis of total chromium**,** soil samples were microwave digested using 10 mL 100% HNO_3 at 180 °C for 15 min followed by detection by ICPMS. One of two SRMs, either Montana soil (NIST 2710) or Buffalo River Sediment (NIST 8704), were extracted concurrently to make the recovery correction for soil samples. The ICPMS was run in continuous mode and total concentrations of chromium were determined. The calibration curve was generated for all elements using a multi-element calibration standard. After the calibration curve is generated, a 10 ng/mL standard (NIST AB, Calibrant A and B, 1811-001, 1811-005, High Purity Standards, Charleston, SC) was analyzed. If the NIST AB concentration was > 20% for chromium, the calibration curve was regenerated before sample analysis. After each sample was analyzed, a 2% nitric acid rinse solution was used to clean the probe. Ten to twelve samples were analyzed before a blank and the NIST AB were run again.

3.4 Method Precision

Given the concern of inhomogeneity of soil samples, 30 soil samples (42% of total Cr^{+6} samples) with a mass of 0.05-0.08g were analyzed along with 20 triplicates and 10 duplicates to evaluate the precision of the measurement of hexavalent chromium. The method precision was calculated as the absolute percent difference (%diff, which equals to the absolute difference of the two measured values divided by their average) between duplicate samples and Coefficient of Variation (%CV, which equals the standard deviation divided by the mean) for triplicates.

A good precision was obtained for all samples analyzed (Table 2). The average %CV (or %diff for duplicate samples) was 20%. The large variability was found in two unseived soil samples, one from Liberty Park (72%) and one from Nicholas Trucking Site (44%). The variability was probably attributed to inhomogeniety of the unseived soil samples. A large difference (76%) was also found in one 2.5-10 μm soil fraction collected from the Nicholas Trucking site. The large difference between the duplicate was unclear. Excluding those 3 outliers, the average %CV (or %diff for duplicate samples) was 15%. These results suggested that current analytical method is suitable for the measurement of hexavalent chromium in soil samples.

For the measurement of total chromium, 24 soil samples (42% of total chromium measurements) along with 17 triplicates and 7 duplicates, were analyzed to examine the method precision. A good precision was obtained for all samples analyzed (Table 3). The average %CV was 10%. The large variability was found in the Liberty Park unseived soil sample and the 75 μm particle size, with %CV of 36% and 25%, respectively. Excluding these 2 outliers, the average %CV was 8%, proving that our analytical method is suitable for total chromium measurement in soil samples.

3.5 Method Accuracy

Two Cr^{6+} certified soil samples were used to examine the method accuracy for Cr^{6+} detection. One (SQC012) was purchased from R.T. Corporation (Laramie, WY) and another one (SRM 2701) was provided by Dr. Brian Buckley at EOHSI. The method accuracy was evaluated by calculating relative error, which is the absolute difference of the two measured values divided by the certified value. Table 4 shows the comparison results with the certified value. The concentration of Cr^{6+} in SQC012 was detected as 68-106 mg/kg, which was in the acceptance range of 64.0 to 170 mg/kg that provided by the company. The relative error of Cr^{6+} concentration in SQC012 and SRM 2701 sample were 25% and 2%, respectively, demonstrating that the our analysis method is accurate for the measurement of hexavalent chromium in soil samples. No correction was made for the Cr^{6+} concentrations measured in soils.

3.6 Morphology

Polarized Light Microscopy (PLM) analysis was performed by MVA, Inc. (Atlanta, Georgia) on the 75 µm size fraction of 5 soil samples. The soil mineral types were also determined. For each identified mineral constituent, an estimate were made as to its relative abundance using the ranges: <1%, 1-10%, 10-40%, 40-70%, 70-100% or other ranges agreed upon. A general assessment of the size of the soil particles was also made. Soils were generally characterized as sandy, gravel, silt size etc. Special attention were paid to documenting the type of soil minerals present in the dust, (e.g. Quartz, carbonates, feldspars, mica, vermiculite, bentonite clay, kaolin clay, amphiboles, serpentine, gypsum, talc, basalts and minerals associated with cement). Each sample was documented with photographs in addition to a table of results (See Appendices I-III).

4. RESULTS

4.1 Sample Characterization

A total of 11 bulk soil samples were collected from 11 sites in Hudson County. Each sample was size segregated to six size fractions: 250 µm, 75 µm, 38 µm, 30-10 µm, 10-2.5 µm, and < 2.5 µm (Except 2 Honeywell soil samples (Honeywell 1 and Honeywell 10 feet) that were only size segregated to three size fractions: 250 µm, 75 µm, 38 µm because the samples were too hard or too small in quantity for further fraction). Table 1 lists the sample sites and their code in this study. The pH value of the soil sample is one of the main factors that determines the chromium speciation. Therefore, the pH values of the soil samples are also presented in Table 1. The pH values show that the soils at the Colony Diner and Honeywell sites are high alkaline (pH=10-12), the soils at the Nicholas Truck, Garfield and Liberty Park are weak alkaline (pH =7.8-8.0), and the soil at the IMTT site is weak acidic (pH=5). Based on the pH values of the samples and the Eh-pH-diagram (Figure 1, Ball and Nordstrom, 1998), which shows the thermodynamic stability areas of different chromium species in an aqueous solution, for the Eh range of -0.6 to 0.8 v, $Cr(OH)^{2+}$ and $HCrO_4^{-1}$ were expected to be the predominant species in the soil samples collected from the IMTT site, $Cr(OH)_2^{-1}$, $Cr(OH)_3$ and CrO_4^{-1} were expected to be predominant species in the soil samples collected from the Nicholas Truck, Garfield and Liberty Park sites, $Cr(OH)_3$, $Cr(OH)_4^{-1}$ and CrO_4^{-2} were expected to be the predominance species in the soil samples obtained from the Colony Diner and Honeywell sites. The measurement results of Cr^{6+} and Cr^{3+} are presented and discussed in Sections 4.2 and 4.5.

The PLM analysis (see Appendices I-III) showed that Nicholas Truck soil was composed of soil minerals including quartz, mica, carbonate, and zircon, rust/metal flakes, Garfield soil was composed of soil minerals including amphibole, feldspar, mica and quartz grains and Liberty Park soil was composed of soil materials including quartz, mica, carbonate, amphibole, and feldspar, rust/metal flakes. The Colony Diner soil contained carbonate, quartz, feldspar and amphibole. And the Honeywell soil contained quartz grains that are encrusted with yellow crystals and opaque brown particles or aggregates. The particle size distribution in terms of number of particles for each soil samples (in fraction of 75 µm and below) is summarized in Table 5. Similar particle size distribution was observed for the 5 soil samples analyzed, with ~98% particles < 10 µm. The sample collected from the Honeywell site (H3) contains relative more fine particles (89% $PM_{2.5}$) than other sites.

4.2 The concentration and distribution of Cr^{6+} as a function of particle size

The concentration and distribution of Cr^{6+} as a function of particle size at each individual site are presented in Figures 3-13, and the ratio of the Cr^{6+} concentrations measured in each size vs. those measured in the unsized soil sample are presented in Table 6. Among all sites we studied, the Honeywell site was found to be the most contaminated site. The concentrations of Cr^{6+} measured in all samples collected from the 4 Honeywell sites were very high, ranging from 1766-11350 mg/kg (Figures 3-6). The highest concentration was observed at the size of 10-2.5 µm fraction for the samples collected from both 0-6 inches and 6-12 inches, which were 4-8 times higher than the bulk soil samples (Table 6). Samples collected from the Honeywell site at 1 and 10 feet deep, for which analyses were not conducted for particle sizes below 38 µm, had a similar trend, i.e. Cr^{6+}concentrations increased with decrease in particle size, with the highest concentration found in the 38 µm size fraction (Figures 5-6). The percentage of Cr^{6+} in the total Cr in both the 10-2.5 µm and 2.5 µm particle size fractions ranged from 38%-49% (Table 7). The concentrations of Cr^{6+} at the 3 IMTT sites were relatively low, ranging from 1-243 mg/kg, with the highest concentration found at the 2.5 µm size fraction collected from the IMTT 3 site (Figures 7-9). The concentrations of Cr^{6+} collected from the Nicholas Truck, Garfield, Liberty Park were in the range of 28-2602 mg/kg, with Garfield > Nicholas Truck > Liberty Park for the 2.5 µm size fraction (Figures 10-12). These six sites (Nicholas Truck, Garfield, Liberty Park, and 3 sites at IMTT) also exhibit a strong tendency for Cr^{6+} concentrations to increase with decreasing soil particle size, with the highest concentration present at the size of 2.5 µm (Figures 7-12). Correspondingly, the percentage of Cr^{6+} in the total Cr was found to be the highest in the 2.5 µm particle size fraction, ranging from 6%-28% (Table 7). For the Colony Diner site, the distribution of Cr^{6+} and the percentage of Cr^{6+} in the total Cr were found similar in all particle sized fraction (Figure 13). In conclusion, except Colony Diner, all the results showed that Cr^{6+} was more enriched in small size particles either at the particle size of 2.5 µm or 10-2.5 µm size fraction and the percentage of Cr^{6+} in the total Cr was found to be higher toward the 10-2.5 µm and 2.5 µm particle sized fraction.

To examine the general trend of Cr^{6+} distribution in each particle size, the results obtained from all sites were evaluated statistically for the distribution of Cr^{6+} measured. Geometric means (GM) were calculated for the Cr^{6+} concentrations because the Cr^{6+} concentration was not normally distributed. Concentrations of Cr^{6+} detected in each size fraction are listed in Table 8 with GM, geometric standard deviation (GSD), minimum (min) median (median) and maximum (max) concentrations (mg/kg). Geometric means of Cr^{6+} in the unsized soil, 250 µm, 75 µm, 38 µm, 30-10 µm, 10-2.5 µm, and < 2.5 µm fractions were 134±32, 307±18; 384±18; 460±21; 347±11; 691±10 and 1,068±5 mg/kg, respectively. These data demonstrated a trend that more Cr^{6+} was present on the smaller particles.

The Kruskal-Wallis non-parametric multiple comparison test was performed to examine whether there was a significant difference in Cr^{6+} concentration between different particle sizes. Among the 6 sites, including Nicholas Truck, Garfield, Liberty Park, and 3 sites at IMTT, a significant difference of

Cr^{6+} concentration was observed, with the highest Cr^{6+} concentration in the fraction less than 2.5 µm (*p*=0.0394). For the two samples collected from 0-6 inches and 6-12 inches at the Honeywell site, a significant higher Cr^{6+}concentration was observed at the size of 2.5-10 µm (*p*=0.0760).

Interestingly, a strong positive association was observed between the Cr^{6+} concentration measured in the 2.5 µm size fraction and in the unsized soil sample. As shown in Figure 14, a linear relationship was found between the Cr^{6+} concentration in the 2.5 µm size fraction and in the bulk soil sample (R^2=0.7996, n=8), and the relationship remained after excluding the two high values measured at the Honeywell sites, with R^2 of 0.9096 (Figure 15, n=6). These results suggest that the Cr^{6+} concentration in the 2.5 µm fraction, which is the most critical size range for inhalation exposure, can be estimated based on the Cr^{6+} levels found in the bulk soil material for the sites studied. In addition, the Cr^{6+} concentration of the bulk soil sample is representative for comparing the contamination level between sites in the studied area. The relationship observed might be partially due to the high mobility of the Cr^{6+} so that Cr^{6+} is enriched in fine particles and has reached stable size distribution under the specific chemical and physical conditions of the soil at the monitoring sites over a course of years.

4.3 Cr^{6+} concentration and its association with soil depth

The association of the Cr^{6+} concentration and the depth where the soil was collected from the Honeywell site was examined by linear regression analysis. For the depth of 0-6 inches and 6-12 inches, 3 and 9 inches, respectively were used in regression analysis. As shown in Figures 16-19, for the depth of 0-6 inches, 6-12 inches and 10 feet, a linear correlation (r^2>0.9963) was found for the Cr^{6+} concentration and the sampling depth The increasing rate (i.e. the slope of the linear regression line) was 35, 66, 70 and 282 mg/kg per inch for unsized soil sample, samples in 250 µm, 75 µm and 38 µm fractions, respectively (Figures 16-19), and the slope increased as the particle size decreased. Though the data was limited, these results suggested that the concentration of Cr^{6+} in all size fraction increased as the depth in soil increased, and the Cr^{6+} was more enriched in small particles in deeper location at the Honeywell site.

4.4 The concentration and distribution of total chromium as a function of particle size

Total Cr concentration was analyzed for part (56 out of 71) samples that were collected. The concentrations of total Cr at the 3 IMTT sites were relatively low, with a range from 33-1634 mg/kg. The concentrations of total Cr at the Nicholas Truck, Garfield, Liberty Park and Honeywell sites were high, ranging from 7543 to 59695 mg/kg. The ratio of total Cr concentrations measured in each size vs. those measured in the unsized soil sample are presented in Table 9 . The results showed that there was no clear tendency for the total Cr toward a specific size, except at the IMTT sites, where the total chromium seemed to enrich in the 2.5 µm size fraction.

A general trend of the total Cr distribution in each size fraction for all study sites was examined. As shown in Table 10, the geometric mean concentrations of 4864± 16, 6048±11, 6793±8 and 6029±8 mg/kg were observed for unsized soil sample, 250 µm, 75 µm, and 38 µm size particles. In 30-10 µm and < 2.5 µm soil samples, the geometric mean concentrations of total Cr were 3959±13 and 4963±3 mg/kg, respectively. Non-parametric multiple comparison tests showed that a significant difference was observed at the three IMTT sites, with the highest concentration at the 2.5 µm size portion (*p*=0.0196). However, for other sites, which included Nicholas Truck, Garfield, Liberty Park, Colony Diner and Honeywell, there was no significant difference among different size fractions (*p*=0.1138).

4.5 The concentration and distribution of Cr^{3+} as a function of particle size

The concentrations of Cr^{3+} in the 56 soil sample fractions were obtained by subtracting the Cr^{6+} concentration from the total Cr concentration. The concentrations of Cr^{3+} at the 3 IMTT sites were relatively low, with a range of 31-1541 mg/kg. The concentrations of total Cr^{3+} at the Nicholas Truck, Garfield, Liberty Park and Honeywell sites were high, with a range of 6205-57625 mg/kg. The ratio of the Cr^{3+} concentrations in each particle size was calculated by dividing those measured in the unsized soil sample (Table 11). It showed that there was a tendency for the Cr^{3+} toward the particle size of 2.5 μm for soils at the IMTT sites .

A general trend of Cr^{3+} distribution in each particle size for all study sites was examined and the results are presented in Table 12. The Kruskal-Wallis comparison tests showed a significant difference among the three IMTT sites, with the highest Cr^{3+} concentration at the 2.5 μm portion (p=0.0171). For other sites, including Nicholas Truck, Garfield, Liberty Park, Colony Diner and Honeywell, a significant difference (p=0.0444) among different size fractions was also observed, with the lowest concentration measured in the 2.5 μm particle size fraction.

5. DISCUSSION

The results obtained from this study showed that the Cr^{6+}, Cr^{3+}, and total Cr concentrations and distribution as a function of particle size varied greatly by site. The differences were probably related to the sources, remediation actions, and the physical and chemical properties of the soil at different sites.

For the 3 IMTT sampling sites, the concentrations of Cr^{6+} were found the lowest among all the samples collected, ranging from 1 to 243 mg/kg. We observed a strong tendency of increase in hexavalent chromium concentration with decrease in soil particle size, with the highest concentration found in the size of 2.5 μm fraction. Similar size distribution was observed for Cr^{3+} and total Cr at this site. These results suggested that the adsorption process is probably the determining factor for the size distribution. It is well known that the surface area of small particles is much greater than large particles (Brady et al., 1996). Therefore, chromium species can be adsorbed and enriched in small particle size fraction. In addition, the pH value at this site is weakly acidic. Cr^{3+} can dissolve partially under this pH condition, i.e. Cr^{3+} has some mobility at this condition so that it can distribute in small size fraction.

At the sites of Nicholas Truck, Garfield, and Liberty Park, the concentrations of Cr^{6+} were in a range of 28-2602 mg/kg, which were higher than IMTT but much lower than Honeywell. Also the hexavalent chromium concentrations increased as the particle size decreased. In contrast, the lowest concentration of Cr^{3+} was found for the 2.5 μm particle size, with a concentration range of 6205-13830 mg/kg. There was no significant difference in total chromium concentration among different size fractions. These results suggested that the Cr^{+6} was mobile and able to redistribute onto smaller size soil particles while the Cr^{+3} was generally not mobile and largely remained on its original particles and therefore, the mobility of chromium species may play an important role in the size distribution of Cr^{6+} and Cr^{3+} in the medium level contaminant soils.

The Honeywell site was found to be the most contaminated site for Cr^{6+} among all sites investigated in this study. The Honeywell site is still under remediation. At this site, hexavalent chromium concentrations increased as the soil particle size decreased, with the highest concentration in the particle size of 10-2.5 μm. The lowest concentration of Cr^{3+} was observed at the particle size of 2.5 μm. No significant difference in total chromium among different size fractions was found at this site. The enrichment of Cr^{6+} in the fine particles may be attributed to the high mobility of Cr^{6+}.

6. CONCLUSIONS

This study collected 11 soil samples from 11 chromium waste sites in Jersey City. The samples were sized to 6 fractions, and each size fraction was analyzed for Cr^{6+}, Cr^{3+}, and total Cr concentrations.

This study showed that the concentrations of chromium species measured in the soil samples collected for the remediated sites (such as IMTT) were significantly lower than other sites. Additionally, the pH values and other physical and chemical characteristics of the soil samples differed greatly between sites (Table 1, Appendices I-III), which may directly affect the distribution of chromium species as a function of particle size. This study showed that the distribution of Cr^{6+} concentration is enriched in small particles with 2.5 μm in diameter at most sites. This may be probably attributable to both the mobility of Cr^{6+} and the large surface area of small particles. The 2.5 μm size particles are the most critical for health concerns in terms of the potential for inhalation exposure.. Thus, the directly measurement of Cr^{6+} concentration by particle size is necessary to conduct accurate assessment of health risks related to exposure to Cr^{6+}. Total Cr concentration is not a good surrogate for assessing exposure to Cr^{6+}.

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TABLES

Table 1. Sample collection sites and their ID code in the study along with soil pH value

Sampling Site	Sample ID Code							Soil pH
	Unsized	250 µm	75 µm	38 µm	30-10 µm	10-2.5 µm	2.5 µm	
IMTT1	A1	A2	A3	A4	A5	A6	A7	5.5
IMTT Fenceline	B1	B2	B3	B4	B5	B6	B7	5.5
IMTT3	C1	C2	C3	C4	C5	C6	C7	5.5
Nicholas Truck	D1	D2	D3	D4	D5	D6	D7	7.8
Garfield	E1	E2	E3	E4	E5	E6	E7	8.0
Liberty Park	F1	F2	F3	F4	F5	F6	F7	8.0
Colony Diner	G1	G2	G3	G4	G5	G6	G7	10
Honeywell 0-6	H1	H2	H3	H4	H5	H6	H7	11
Honeywell 6-12	I1	I2	I3	I4	I5	I6	I7	11
Honeywell 1	J1	J2	J3	J4				12
Honeywell 10 feet	K1	K2	K3	K4				11

The IMTT-1 refers to the sample collected across the street of the IMTT site, and IMTT-Fence refers to the sample collected by the Fenceline of the IMTT, and IMTT-3 refers to the location just besides the IMTT.

No fractions of 30-10 µm, 10-2.5 µm, and < 2.5 µm for Honeywell 1 (cement like sample) and Honeywell 10 feet (with little quantity of sample).

Table 2. Precision for the measurement of Cr^{6+}

	Cr^{6+}(mg/kg)		
Sample ID	**Average**	**SD or Absolute Difference**	**%CV or %diff** (n=3 or 2)*
C3	12	1	10.0%
D1	74	32	43.5%
D2	492	102	20.7%
D3	757	126	16.7%
D4	464	62	13.3%
D5	613	27	6.3%
D6	835	631	75.6%
D7	1337	88	6.6%
E6	437	34	7.8%
F1	28	20	71.7%
F2	99	15	15.4%
F3	108	15	14.0%
F4	135	14	10.6%
F5	192	3	2.0%
F6	346	89	36.5%
F7	964	150	15.6%
G1	6220	996	16.0%
G2	7062	1103	15.6%
G3	3338	997	29.9%
G4	8637	1420	16.4%
G5	6739	2298	34.1%
G6	5642	1140	20.2%
G7	6570	1480	22.5%
H7	4877	640	13.1%
I6	5525	892	16.1%
J1	3582	821	22.9%
J2	4472	225	5.0%
J3	7067	450	6.4%
J4	11040	1046	9.5%
K4	6795	376	5.5%
		All data	20.0%
		Exclude outliers	15.1%

*Outliers marked in red

Table 3. Precision for the measurement of total chromium

Sample ID	Total Cr (mg/kg)		%CV or %diff (n=3 or 2) *
	Average	SD or Absolute Difference	
C7	875	22	2.6%
D1	17292	3925	22.7%
D2	29614	6975	23.6%
D3	27685	1503	5.4%
D4	18514	465	2.5%
E1	12611	283	2.2%
E7	16432	780	4.7%
F1	11288	4031	35.7%
F2	9217	578	6.3%
F3	13197	3351	25.4%
F4	14785	1228	8.3%
G1	23081	4389	19.0%
G2	24187	1982	8.2%
G3	24767	2747	11.1%
G4	27131	4055	14.9%
H1	33669	2595	7.7%
H5	25100	2348	9.4%
H7	12706	38	0.3%
I5	28323	144	0.5%
I7	12771	998	7.8%
J1	45518	1645	3.6%
J2	40609	204	0.5%
J3	35769	1147	3.2%
J4	33627	1322	3.9%
		All data	9.6%
		exclude outliers	7.7%

*Outliers marked in red

Table 4. Accuracy of measurement of Cr^{6+}

Sample	Cr^{6+}(mg/kg)				Relative error
	Our results		Certified value		
	Average	SD	Average	SD	
SQC012	87.49	19.29	116.96	17.66	25%
SRM2701	540	81	551	34.5	2%

Table 5. The particle size distribution in terms of number of particles

Particle Diameter(µm)	Distribution (%)				
	D3	E3	F3	G3	H3
0.5-1	23.6	36.3	33	30.4	37
1-2.5	48.1	48.1	49.9	50.7	51.8
2.5-5	19.6	11.6	10.6	14.4	8.9
5-7.5	4.9	2.7	3.8	3.1	1.7
7.5-10	2	0.5	1.3	1	0.3
>10	1.8	0.7	1.5	0.5	0.3

Table 6. The ratio of Cr^{6+} in each particle size vs. Cr^{6+} in the unsized soil sample

Sampling Site	Cr^{6+} at each size/Cr^{6+} in unsized portion						
	Unsized	250 µm	75 µm	38 µm	30-10 µm	10-2.5 µm	2.5 µm
IMTT1	1.0	2.1	2.4	1.8	14	17	61
IMTT Fenceline	1.0	2.8	4.8	5.1	2.8	36	48
IMTT3	1.0	15	16	23	133	164	318
Nicholas Truck	1.0	6.7	10.3	6.3	8.3	11	18
Garfield	1.0	1.7	2.2	2.2	4.6	9.6	27
Liberty Park	1.0	3.5	3.9	4.8	6.8	12	34
Colony Diner	1.0	1.1	0.5	1.4	1.1	0.9	1.1
Honeywell 0-6	1.0	1.0	1.7	2.6	1.5	6.2	2.8
Honeywell 6-12	1.0	1.1	1.9	4.2	2.7	4.8	3.0
Honeywell 1	1.0	1.2	2.0	3.1	NA	NA	NA
Honeywell 10 feet	1.0	1.6	1.9	1.1	NA	NA	NA

The IMTT-1 refers to the sample collected across the street of the IMTT site, and IMTT-Fence refers to the sample collected by the Fenceline of the IMTT, and IMTT-3 refers to the location right besides the IMTT.

No fractions of 30-10 µm, 10-2.5 µm, and < 2.5 µm for Honeywell 1 (cement like sample) and Honeywell 10 feet (with little quantity of sample).

Table 7. The percentage of Cr^{6+} in total Cr in different particle size at different sampling site

Sampling Site	Cr^{6+} in each size/Cr total in each size (%)						
	Unsized	250 µm	75 µm	38 µm	30-10 µm	10-2.5 µm	2.5 µm
IMTT1	5.6	2.6	2.1	1.2	2.9	2.6	7.3
IMTT Fenceline	1.2	2.8	2.4	2.1	2.8	4.2	5.7
IMTT3	0.5	3.2	2.7	4.0	20	23	28
Nicholas Truck	0.3	1.7	2.7	2.5	1.6	3.6	17.7
Garfield	0.8	0.9	1.6	1.4	5.1	6.7	15.8
Liberty Park	0.2	1.1	0.8	0.9	0.6	2.6	11.4
Colony Diner	27	29	13	32	27	23	28
Honeywell 0-6	5.2	6.8	11.9	20	11	45	38
Honeywell 6-12	3.5	4.8	8.0	15	20	48	49
Honeywell 1	7.5	10	19	31	NA	NA	NA
Honeywell 10 feet	NA	NA	NA	NA	NA	NA	NA

The IMTT-1 refers to the sample collected across the street of the IMTT site, and IMTT-Fence refers to the sample collected by the Fenceline of the IMTT, and IMTT-3 refers to the location just besides the IMTT.

NA: data not available.

Table 8. Concentration of Cr^{6+} detected at different particle size for chromium waste laden soils at all sites

Size(µm)	N	Cr^{6+}(mg/kg)				
		GM	GSD	Min	Median	Max
unsized	11	134	32	1	95	6220
250	11	307	18	4	492	9573
75	11	384	18	4	757	11350
38	11	460	21	3	464	11040
10-30	9	347	11	5	437	6739
10-2.5	9	706	9	31	835	11026
2.5	9	1068	5	94	1337	7033

Table 9. The ratio of total Cr in each particle size vs. total Cr in the unsized soil sample

Sampling Site	Total Cr at each size/ Total Cr in unsized portion						
	Unsized	250 µm	75 µm	38 µm	30-10 µm	10-2.5 µm	2.5 µm
IMTT1	1.0	4.4	6.7	8.4	5.0	NA	46.7
IMTT Fenceline	1.0	1.2	2.3	2.9	1.2	NA	10.0
IMTT3	1.0	2.2	2.8	2.7	1.5	NA	5.3
Nicholas Truck	1.0	1.4	1.3	0.9	1.8	NA	0.4
Garfield	1.0	1.4	1.0	1.2	0.7	NA	1.3
Liberty Park	1.0	0.7	0.9	1.1	2.4	0.9	0.6
Colony Diner	1.0	1.0	1.1	1.2	0.0	NA	0.0
Honeywell 0-6	1.0	0.8	0.7	0.7	0.7	NA	0.4
Honeywell 6-12	1.0	0.8	0.8	0.9	0.5	NA	0.2
Honeywell 1	1.0	0.9	0.8	0.7			
Honeywell 10 feet	NA	NA	NA	NA			

The IMTT-1 refers to the sample collected across the street of the IMTT site, and IMTT-Fence refers to the sample collected by the Fenceline of the IMTT, and IMTT-3 refers to the location just besides the IMTT.

NA: data not available.

Table 10. Concentration of total Cr detected at different particle size for chromium waste laden soils at all sites

Size(µm)	N	Total Cr (mg/kg)				
		GM	GSD	Min	Median	Max
unsized	10	4864	16	33	17324	59695
250	10	6048	11	143	20498	49466
75	10	6793	8	217	18079	49240
38	10	7009	8	272	16545	55601
10-30	8	3959	13	161	14653	38958
2.5	8	4963	3	875	7981	16432

Table 11. The ratio of Cr^{3+} in each particle size vs. Cr^{3+} in the unsized soil sample

Sampling Site	Cr^{3+} at each size/Cr^{3+} in unsized portion						
	Unsized	250 µm	75 µm	38 µm	30-10 µm	10-2.5 µm	2.5 µm
IMTT1	1.0	4.5	6.9	8.8	4.4	NA	45.8
IMTT Fenceline	1.0	1.2	2.3	2.9	1.2	NA	9.5
IMTT3	1.0	2.1	2.7	2.6	0.9	NA	3.8
Nicholas Truck	1.0	1.4	1.3	0.8	1.8	NA	0.3
Garfield	1.0	1.4	1.0	1.2	0.6	NA	1.1
Liberty Park	1.0	0.7	0.9	1.0	2.4	0.9	0.5
Colony Diner	1.0	1.0	1.3	1.1	0.0	NA	NA
Honeywell 0-6	1.0	0.8	0.7	0.6	0.7	NA	0.2
Honeywell 6-12	1.0	0.8	0.8	0.8	0.4	NA	0.1
Honeywell 1	1.0	0.9	0.7	0.5			
Honeywell 10 feet	NA	NA	NA	NA			

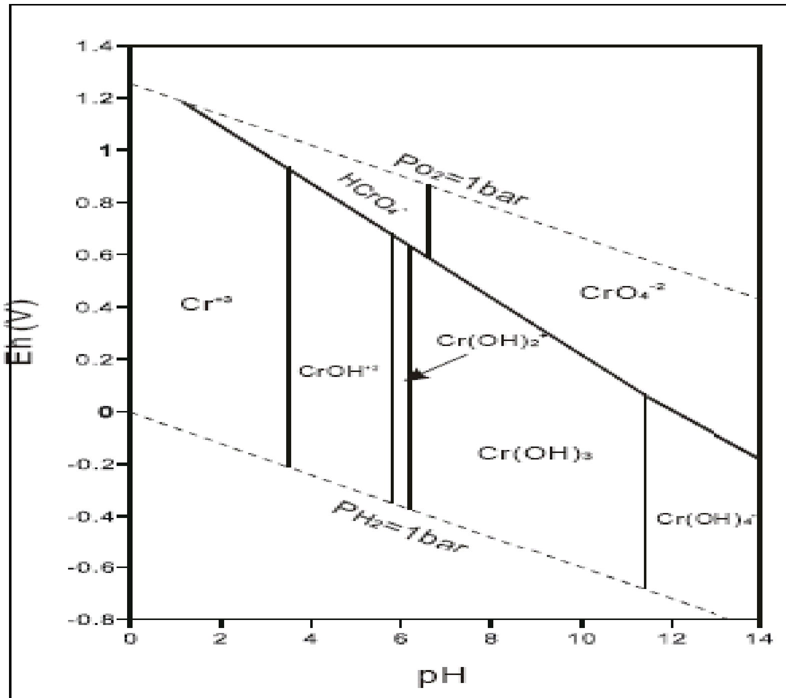
The IMTT-1 refers to the sample collected across the street of the IMTT site, and IMTT-Fence refers to the sample collected by the Fenceline of the IMTT, and IMTT-3 refers to the location just besides the IMTT.

NA: data not available.

Table 12. Concentration of Cr^{3+} detected at different particle size for chromium waste laden soils

Size(µm)	N	Total Cr (mg/kg)				
		GM	GSD	Min	Median	Max
unsized	10	4596	16	31	15347	57625
250	10	5640	10	139	17170	47100
75	10	6343	8	212	16748	45322
38	10	6172	7	269	16261	47000
10-30	8	3428	14	136	13475	38345
2.5	8	3818	3	631	6387	13830

FIGURES



Note: The stability region for water is shown by the dotted lines in this diagram

Figure 1. Eh-pH Diagram for Chromium (Adapted from Ball et al, 1998)

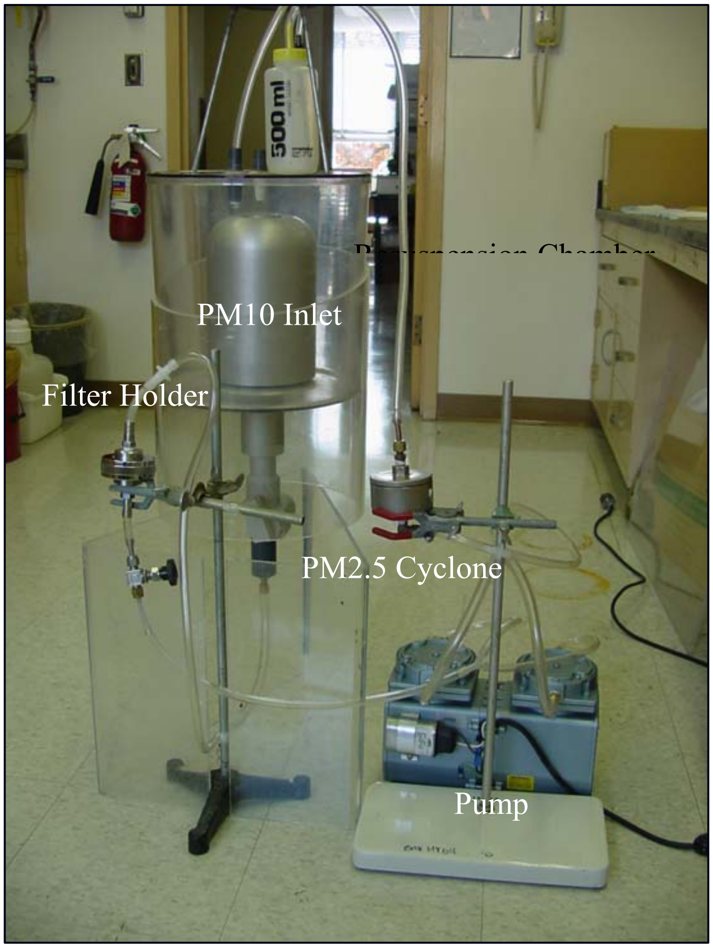


Figure 2. Elutriation System for size segregating

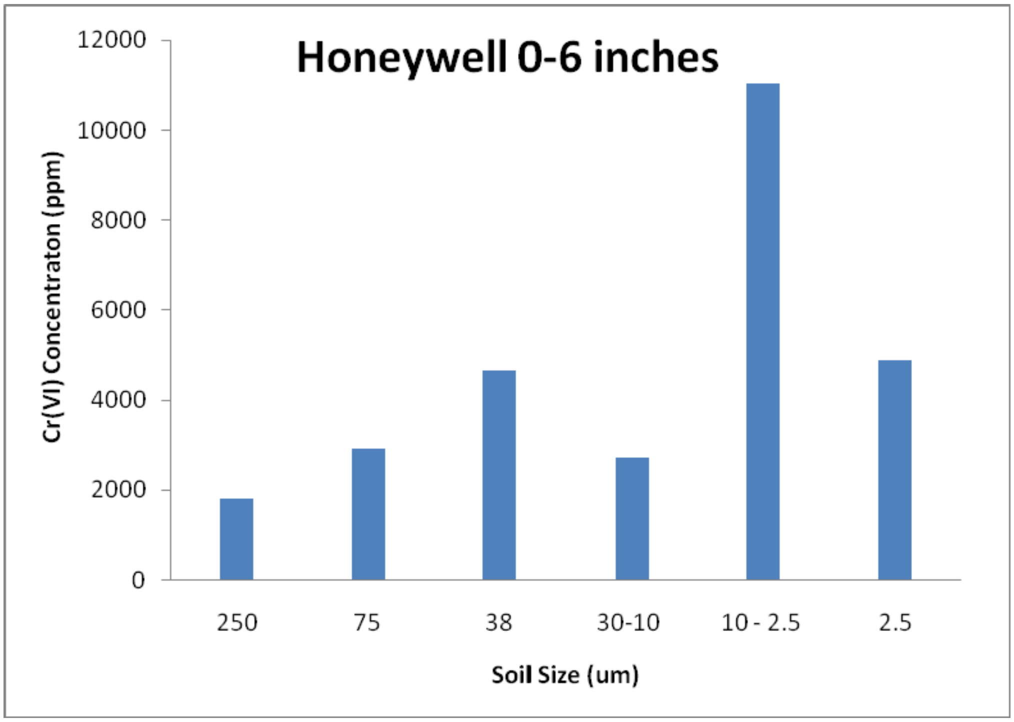


Figure 3. Hexavalent chromium size distribution in Honeywell 0-6 inches soil samples

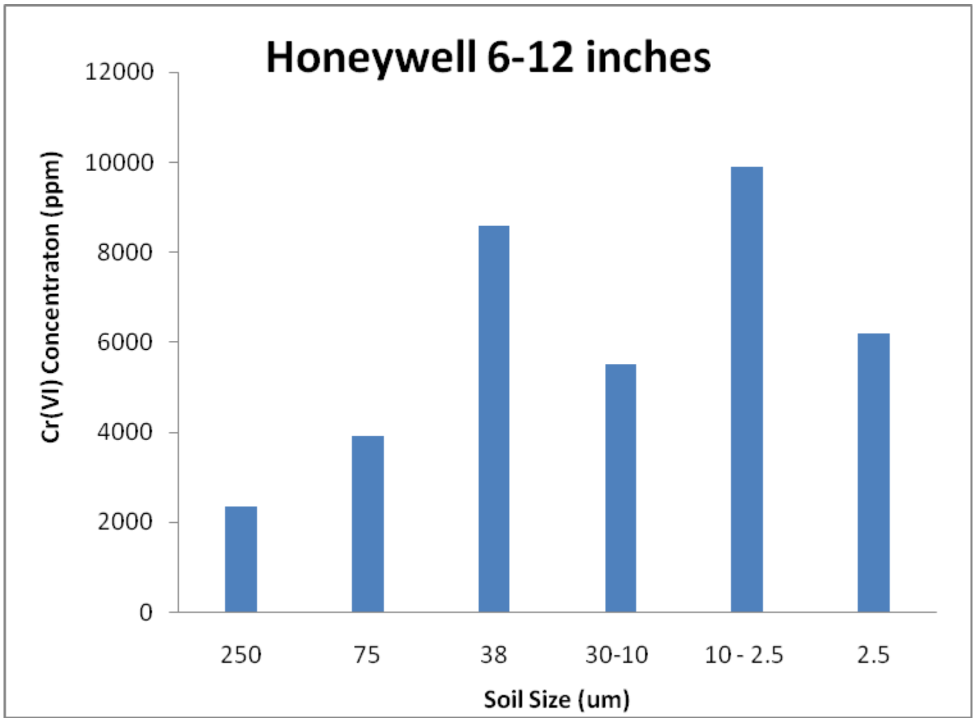


Figure 4. Hexavalent chromium size distribution in Honeywell 6-12 inches soil samples

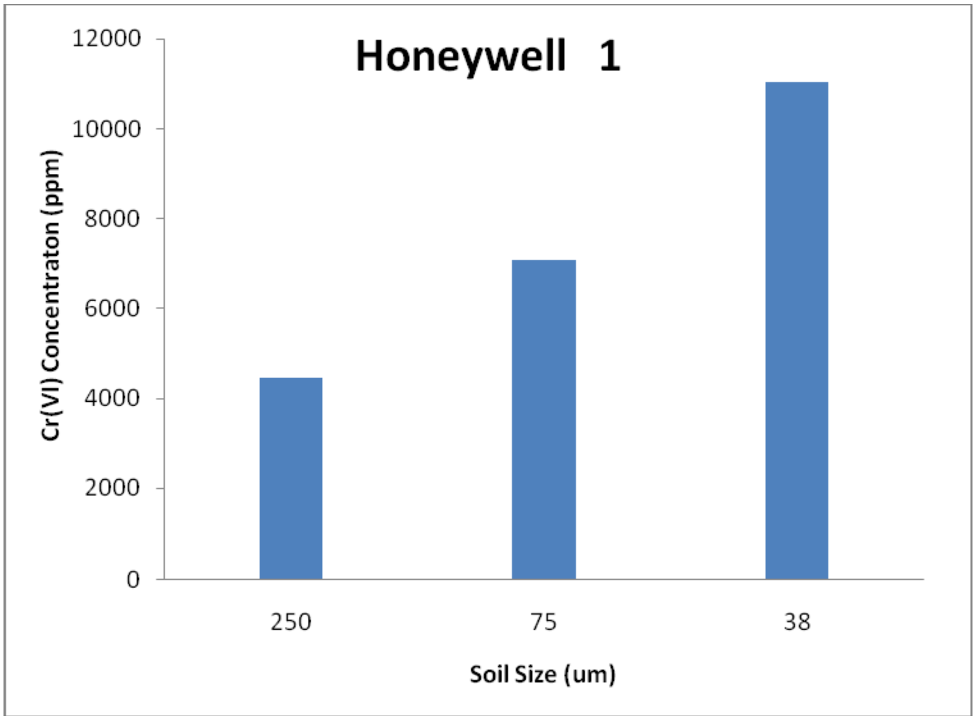


Figure 5. Hexavalent chromium size distribution in Honeywell1 soil samples

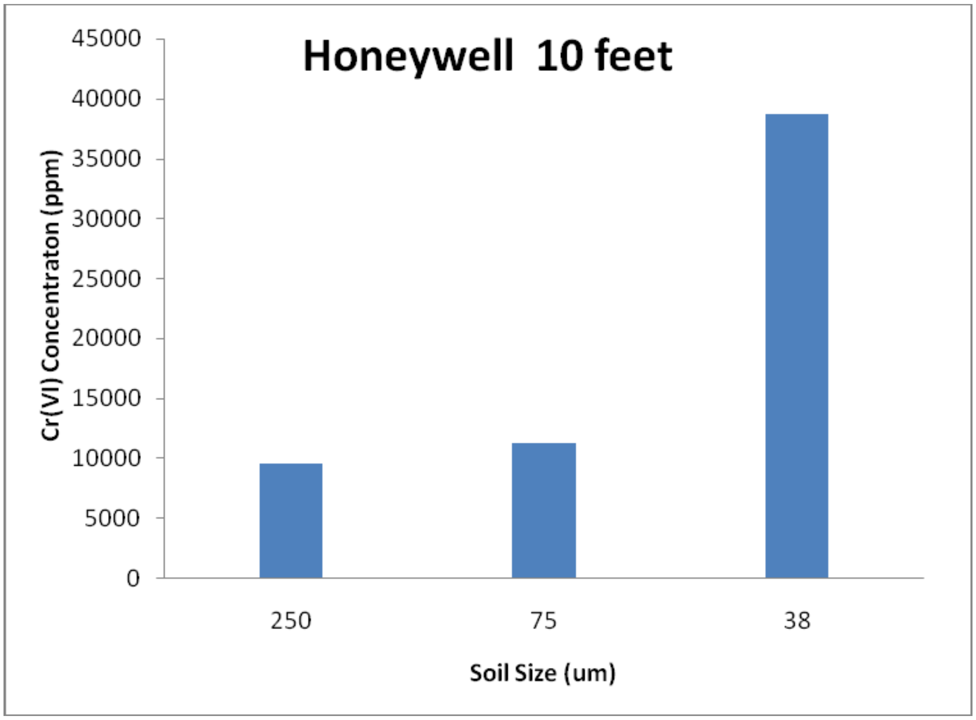


Figure 6. Hexavalent chromium size distribution in Honeywell 10 feet soil samples

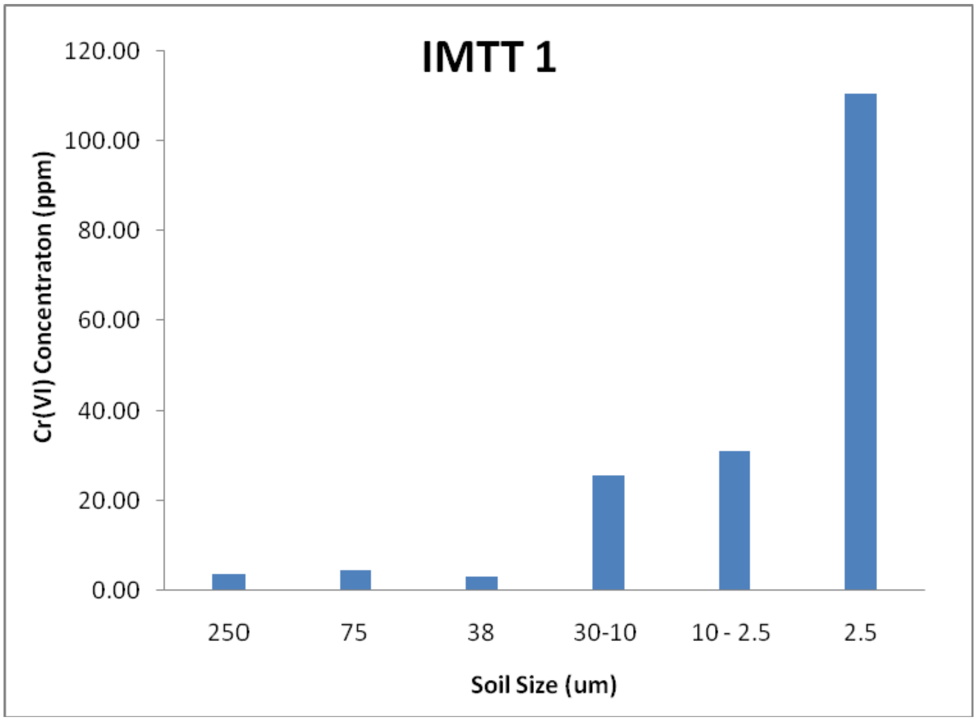


Figure 7. Hexavalent chromium size distribution in IMTT1 soil samples

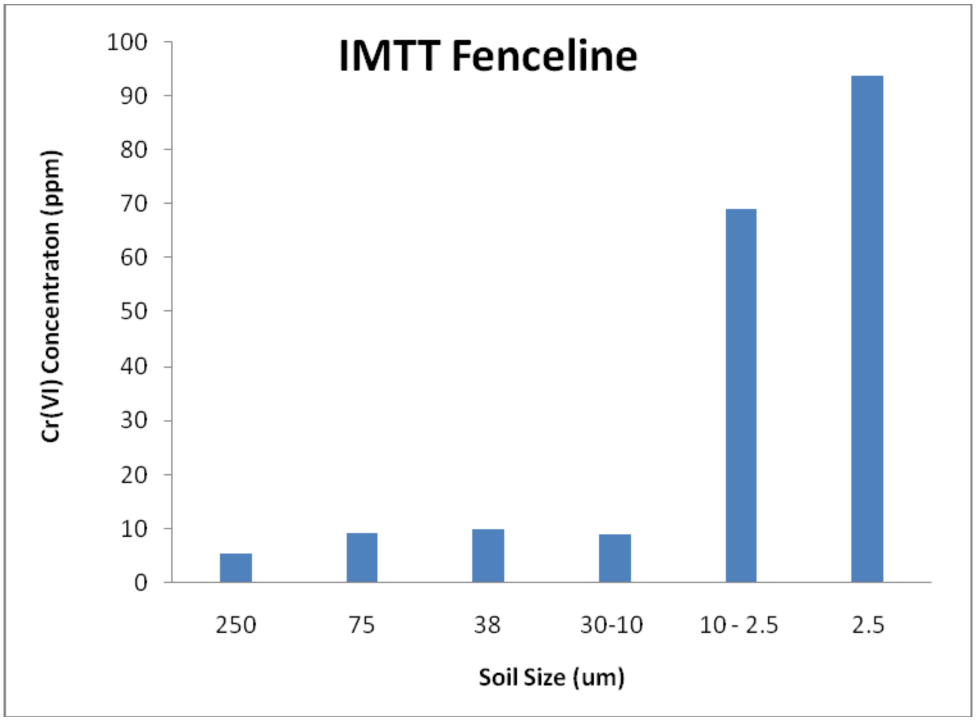


Figure 8. Hexavalent chromium size distribution in IMTT Fencelline soil samples

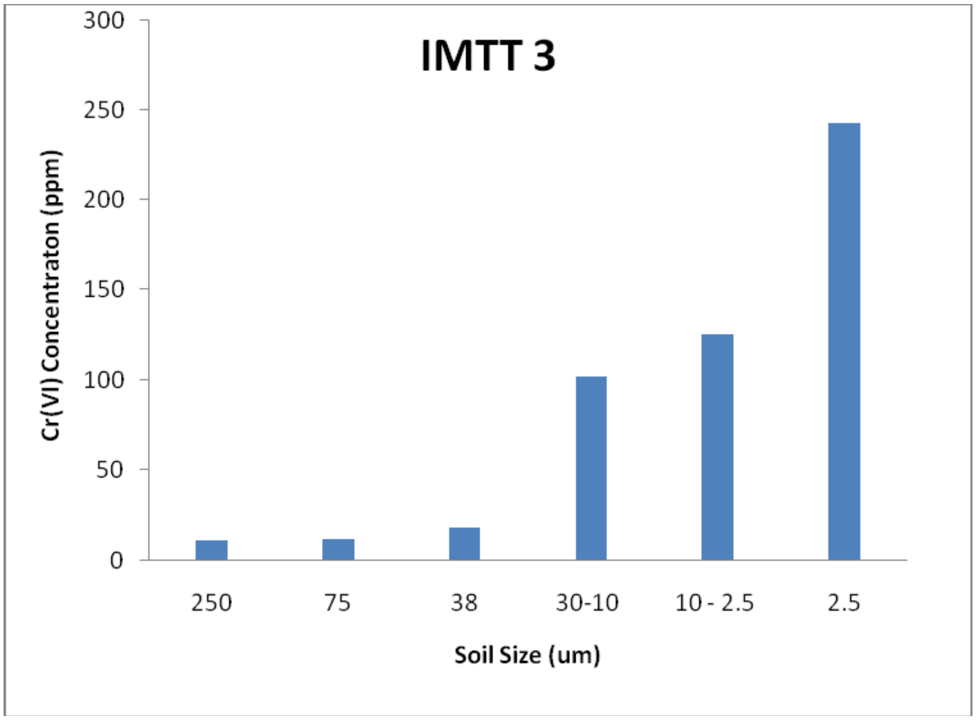


Figure 9. Hexavalent chromium size distribution in IMTT3 soil samples

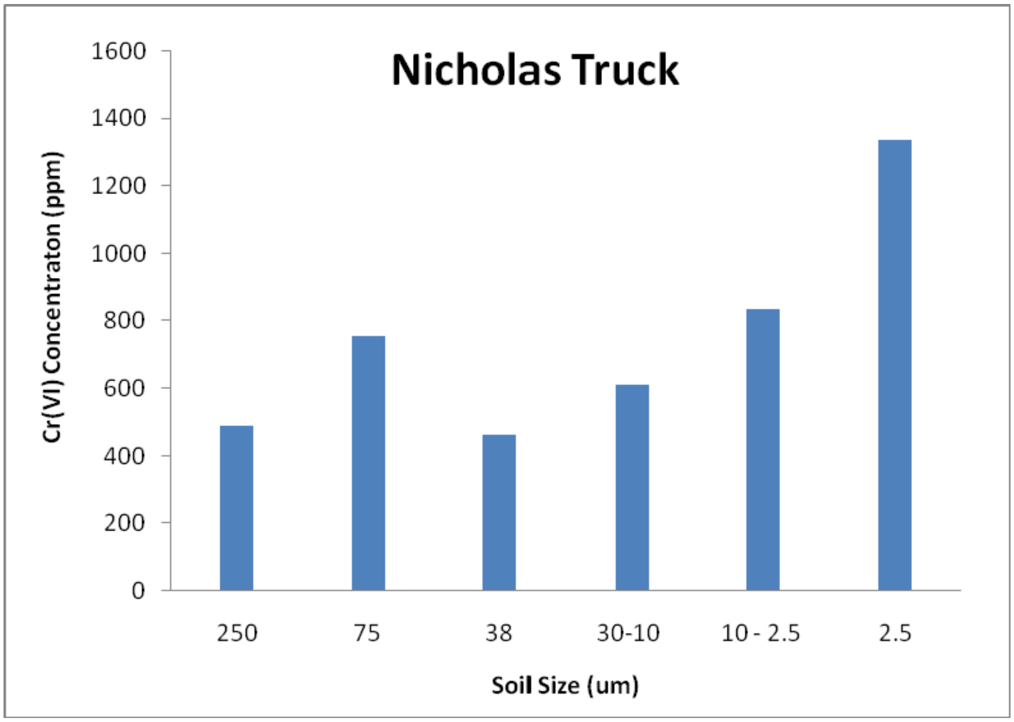


Figure 10. Hexavalent chromium size distribution in Nicholas Truck soil samples

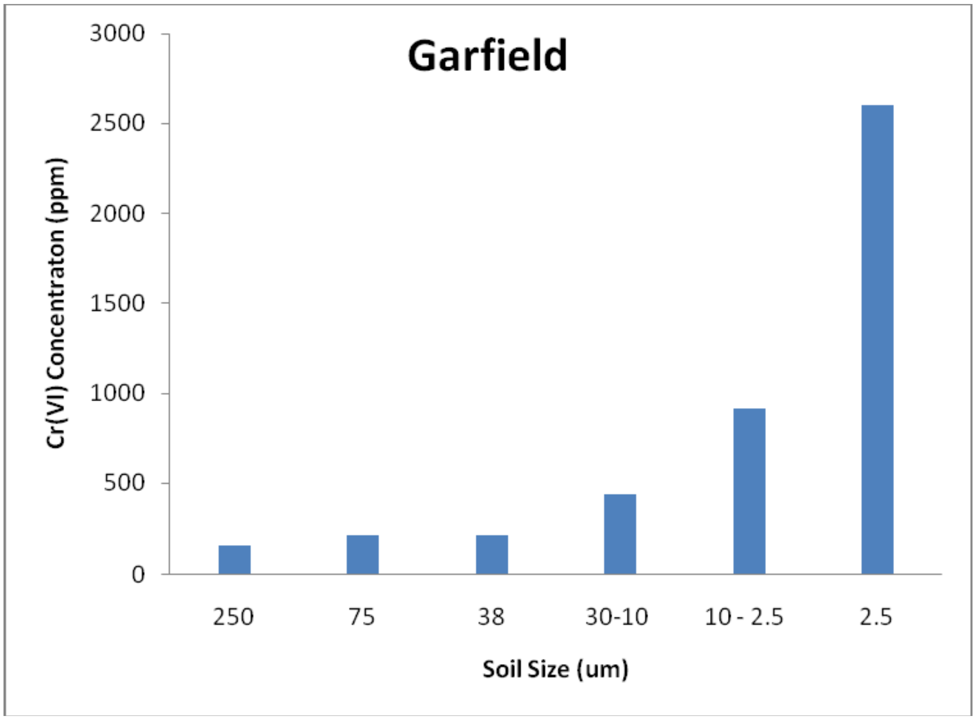


Figure 11. Hexavalent chromium size distribution in Garfield soil samples

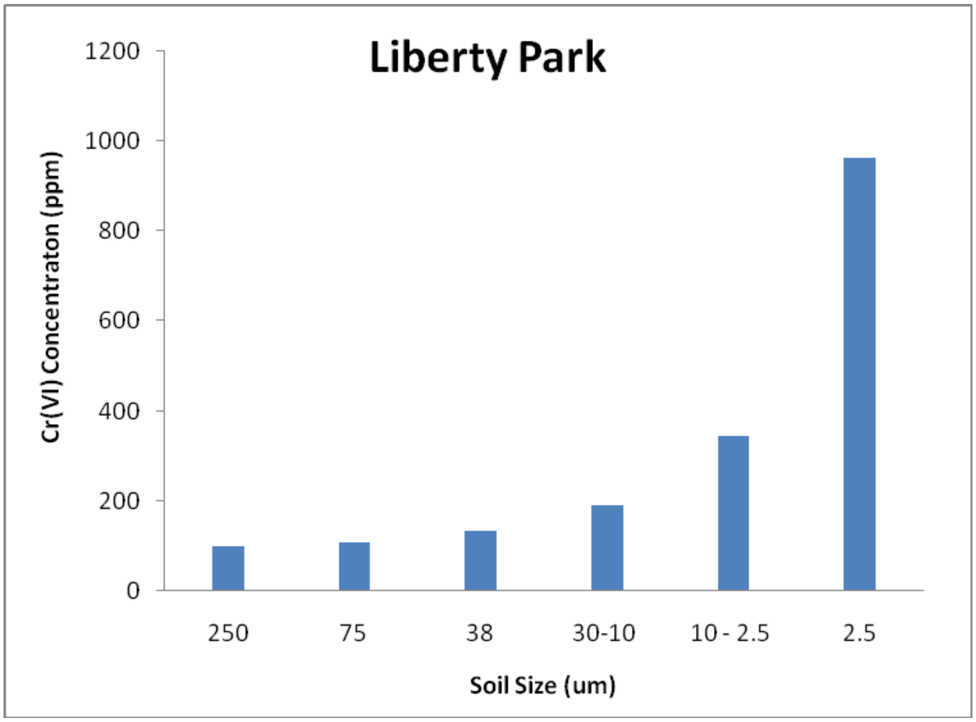


Figure 12. Hexavalent chromium size distribution in Liberty Park soil samples

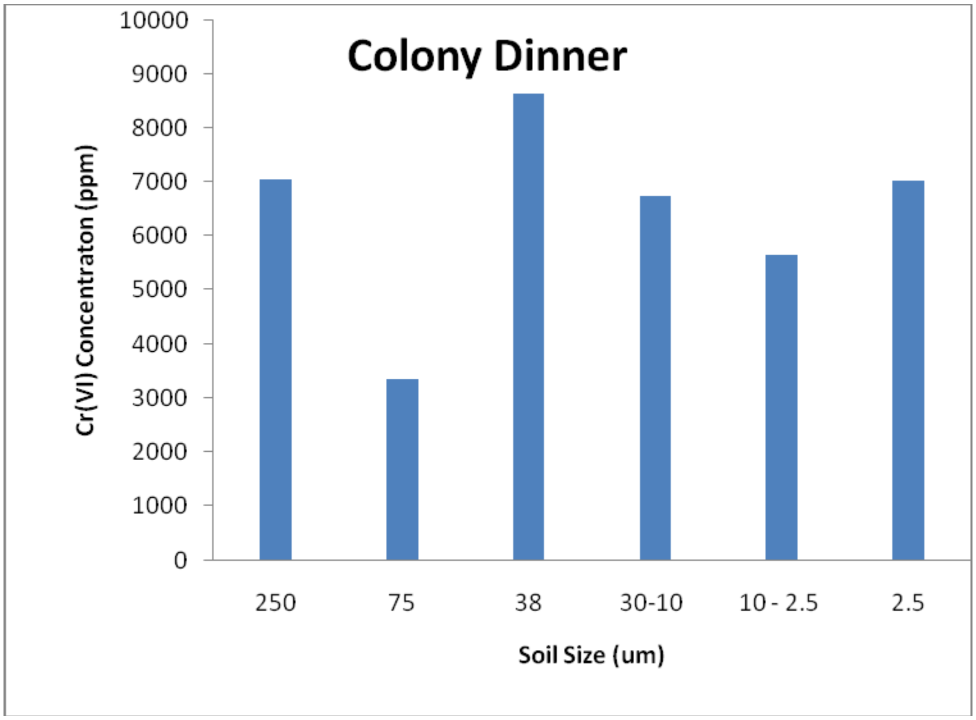


Figure 13. Hexavalent chromium size distribution in Colony Dinner soil samples

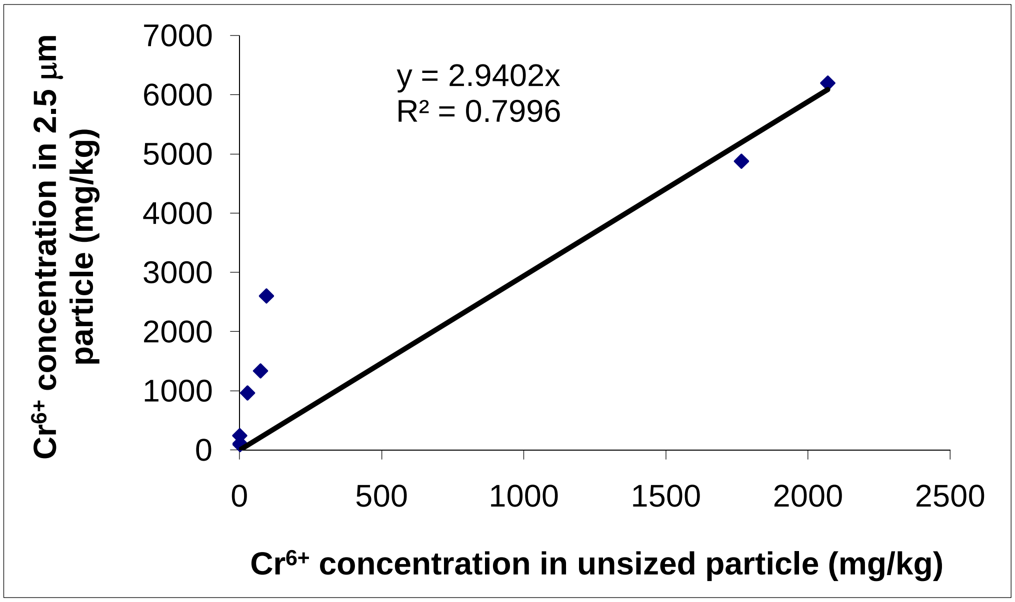


Figure 14. Hexavalent chromium concentration measured in the 2.5 µm fraction as a function of that in the unsized particles (n=8).

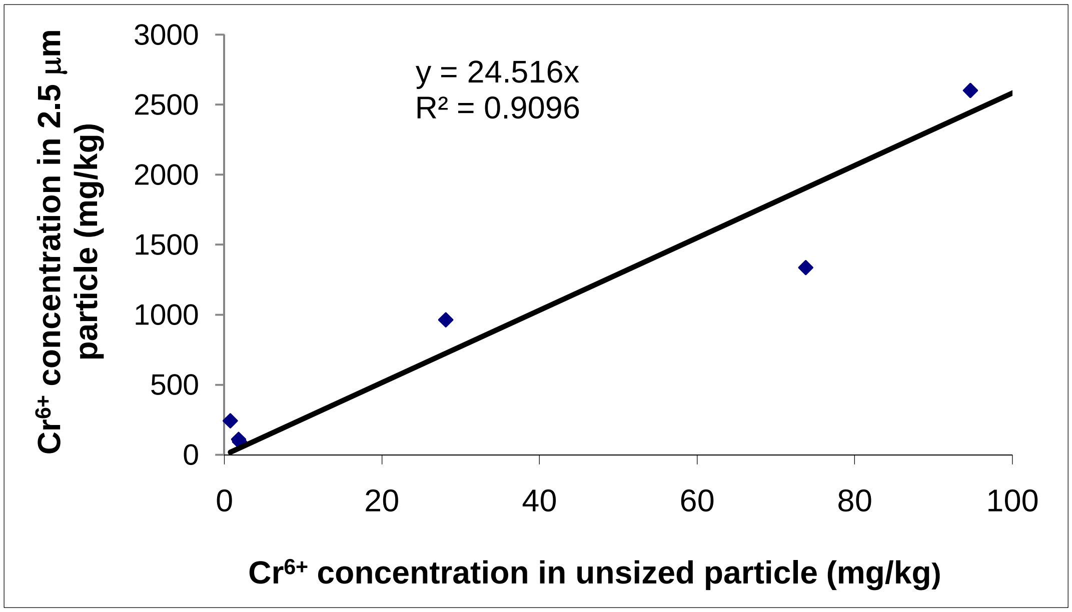


Figure 15. Hexavalent chromium concentration at 2.5µm fraction as a function of at unsized particles (n=6, exclude 2 high concentration at Honeywell site).

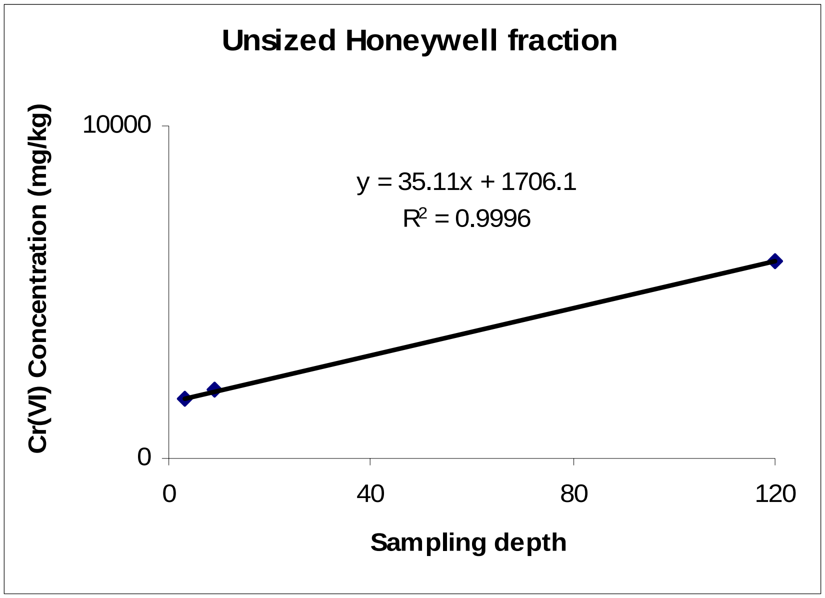


Figure 16. Hexavalent chromium concentration for unsized fraction as a function of sampling depth at Honeywell site.

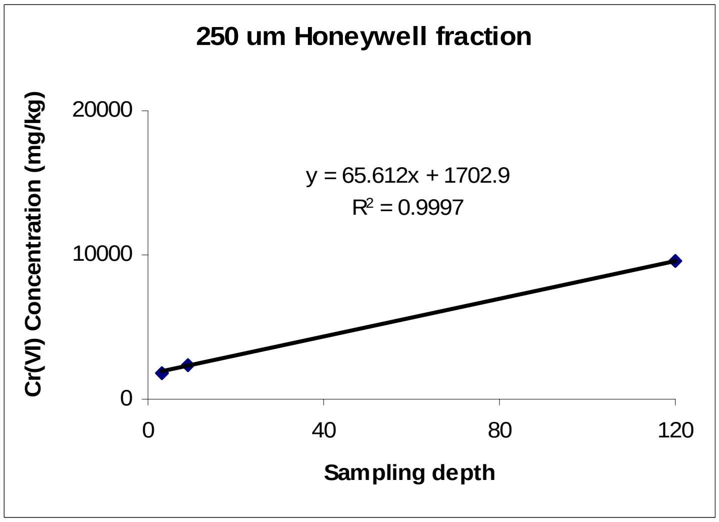


Figure 17. Hexavalent chromium concentration for 250 µm fraction as a function of sampling depth at Honeywell site.

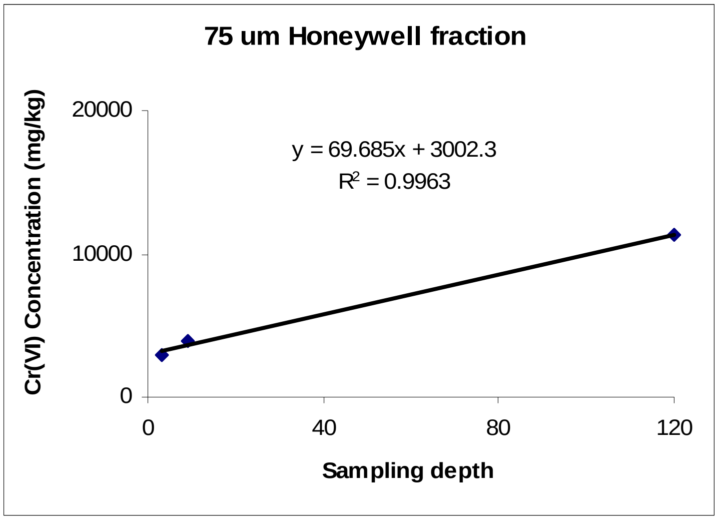


Figure 18. Hexavalent chromium concentration for 75µm fraction as a function of sampling depth at Honeywell site.

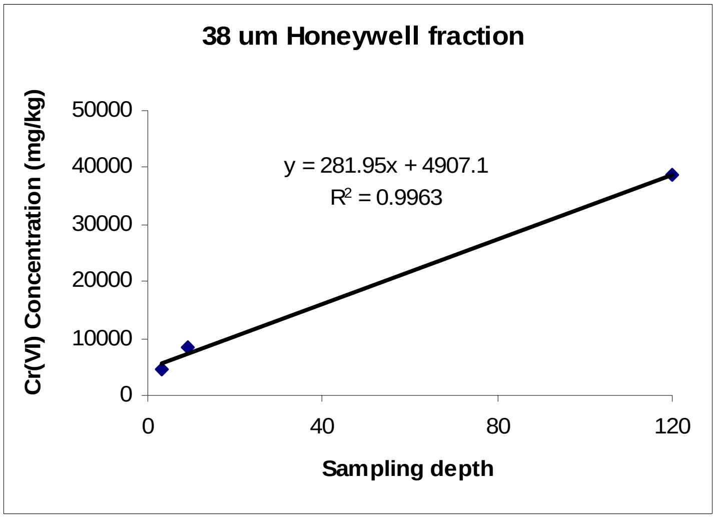


Figure 19. Hexavalent chromium concentration for 38µm fraction as a function of sampling depth at Honeywell site.

APPENDICES

Appendix I

Report of Results: MVA6948

Soil, Garfield and Honey Well, NJ Chromium Project

INTRODUCTION

This report includes the results of scanning electron microscopy (SEM) particle elemental analysis and polarized light microscopy (PLM) analysis of two soil samples delivered to MVA Scientific Consultants on 30 November 2007. Upon receipt the samples were assigned the following identification numbers:

MVA ID	**EOHSI ID**
S1697	Honey Well 0-6 Inch, 2.5 g
S1698	Garfield, 75 um, 2.4 g

MVA was asked to provide information about the composition and morphology of the samples.

Analyses were performed at MVA Scientific Consultants during the period 05 December through 13 December 2007.

METHODS

The sample was prepared for particle analysis by suspending a portion of the sample in 100ml of 20ppm methylcellulose solution and sonicating the suspension for ~5 minutes. Aliquots of the suspension were then filtered onto 0.2µm pore-size polycarbonate membrane filter. Sections of the filters were prepared for examination by scanning electron microscopy-energy dispersive x-ray spectrometry (SEM/EDS). The analyses were performed using a JEOL Model JSM-6500F field emission scanning electron microscope operating in automated mode under the control of a Thermo Noran System Six x-ray analysis system. Elemental composition were collected using x-ray analysis for 18 elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb. Data were obtained for approximately 1000 particles. The data are tabulated in two ways: by number of particles that contain an element in significant amounts and by element groupings that show predominate elemental associations in the particles.

To aid with the interpretation of the data, additional analysis by polarized light microscopy was also performed on each sample. The methodology used in this analysis is similar to what was previously used for a sample analyzed by MVA in February/March 2007 (see report issued 01 March 2007). The samples were examined under an Olympus SZ-40 stereomicroscope at magnifications from 7 to 40 times. Particles from the sample were mounted in 1.55 RI Cargille liquid for analysis by polarized light microscopy using an Olympus BH-2 polarized light microscope with a magnification range from 100 to 1000X.

RESULTS AND DISCUSSION

Sample S1697. Stereobinocular analysis shows that the sample consists of a fine gray powdery material. PLM analysis shows that it is composed of soil minerals including quartz grains that are encrusted with fine material (10-20%), construction-type material (including carbonate/lime and/or Portland cement) (10-20%), yellow hexagonal crystals (10-15%), opaque brown particles/polycrystalline aggregates (50-70%), and acicular to rod shaped crystals (Trace –1%). Representative photographs of the sample particulate are presented in Figures A1-1 and A2-2. The high amount of material not specifically identified by PLM (primarily opaque brown particles or aggregates) in Sample S1697 appears to correspond to the high concentration of magnesium/aluminum-rich particles found by SEM-EDS. This material is not typical of soil minerals and may be particles (remnants) of a magnesium-aluminum alloy. Ten of 992 particles (1%) contain measurable amounts of chromium (at least 5% of the x-ray counts accumulated for the 18 elements chosen). Many of the chromium containing particles also contained iron suggesting a possible steel alloy particle.

Sample S1698. Stereobinocular analysis shows that the sample consists of a fine brown powder. PLM analysis shows that it is composed of soil minerals including amphibole, feldspar, mica and quartz grains, many of which are encrusted with fine material (20-40%), construction-type material (including carbonate/lime and/or Portland cement) (20-40%), rust/metal flakes (20-40%), and non-magnetic opaque black particles. A representative photograph of the sample is presented in Figure A1-3. Sample S1698 contains a significant concentration of magnesium/aluminum-rich particles found by SEM-EDS. This material is not typical of soil minerals and may be particles (remnants) of a magnesium-aluminum alloy. Twenty-six of 1001 particles (2.6%) contain measurable amounts of chromium (at least 5% of the x-ray counts accumulated for the 18 elements chosen). The chromium containing particles also contained iron suggesting a possible steel alloy particle.

The data in Table A1-1 show that the samples are significantly different from one another in terms of chemical composition. The Honey Well, NJ sample is richer in particles containing Mg and particles containing Ca than the Garfield, NJ sample. The Garfield, NJ sample contains more particles that are Si-rich (with Al and Fe) and Fe-rich. Table A1-2 shows that magnesium-aluminum-rich particles make up the majority of the particles in the Honey Well, NJ sample (S1697). The Garfield, NJ sample (S1698) is composed primarily of silicon, aluminum and iron rich particles, typical of soil silicate minerals. Table A1-2 shows that magnesium-aluminum-rich particles make up the second highest group of the particles in the Garfield, NJ sample (S1698).

The large number of unclassified particles in Sample S1698 (approximately 10%) is likely the result of the presence of varying mixtures of minerals aggregated together. Individual sample particle size and element data sets are available in Excel format upon request.

Table A1-1. Occurrence of Particles by Element*

	Honey Well, NJ (S1697)		**Garfield, NJ (S1698)**	
Element	**Number**	**Percent**	**Number**	**Percent**
Na	0	0.0	0	0.0
Mg	216	71.8	42	11.4
Al	2	0.7	11	3.0
Si	37	12.3	170	46.1
P	0	0.0	0	0.0
S	0	0.0	1	0.3
Cl	0	0.0	0	0.0
K	0	0.0	0	0.0
Ca	42	14.0	19	5.1
Ti	1	0.3	6	1.6
V	0	0.0	0	0.0
Cr	0	0.0	0	0.0
Mn	0	0.0	0	0.0
Fe	3	1.0	120	32.5
Ni	0	0.0	0	0.0
Cu	0	0.0	0	0.0
Zn	0	0.0	0	0.0
Pb	0	0.0	0	0.0

*Presence of an element was based on over 40 weight % of the particle based on the 18 elements determined by x-ray analysis.

Table A1-2. Groupings of Elements in Particles

	Honey Well, NJ (S1697)		Garfield, NJ (S1698)	
Type	**Number**	**Percent**	**Number**	**Percent**
Al-rich	0	0.0	5	0.4
Ca+Fe	30	3.9	3	0.3
Ca-rich	6	0.8	14	1.2
Ca-rich silicate	160	20.6	21	1.8
Fe-rich	3	0.4	87	7.6
KAlSi	7	0.9	23	2.0
Mg+Al-rich	380	49.0	329	28.9
Mg-rich	36	4.6	1	0.1
Mixed Si	5	0.6	48	4.2
Si+Al+Fe	119	15.3	490	43.0
Si-only	0	0.0	3	0.3
Unknown	30	3.9	115	10.1
	776		1139	

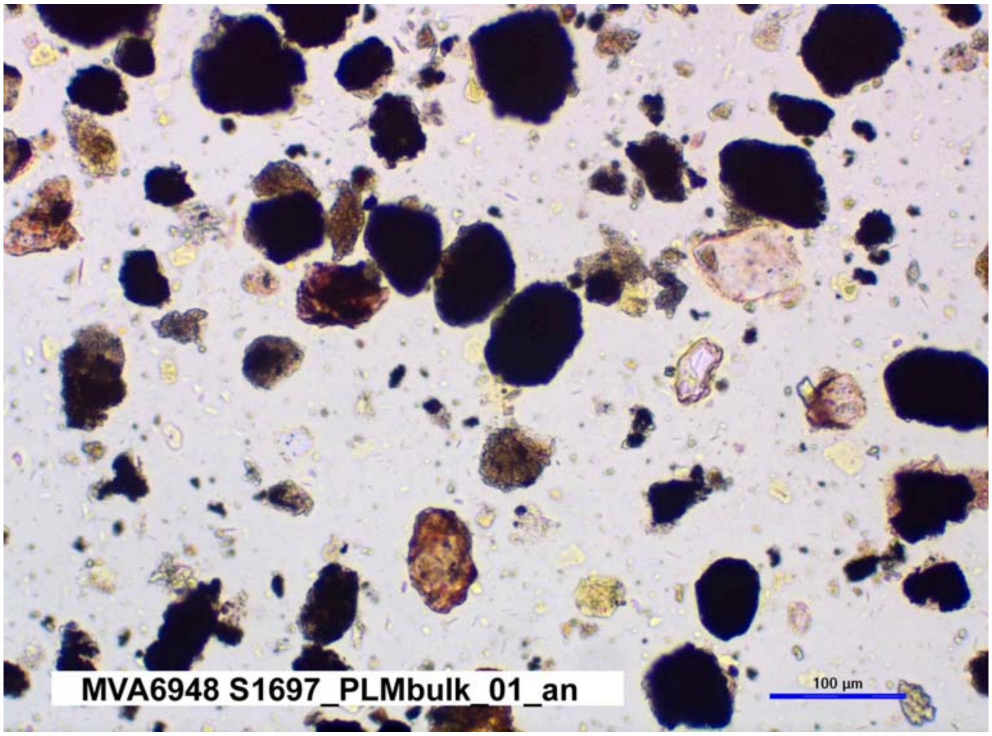


Figure A1-1. Particles in Sample S1697, transmitted light.

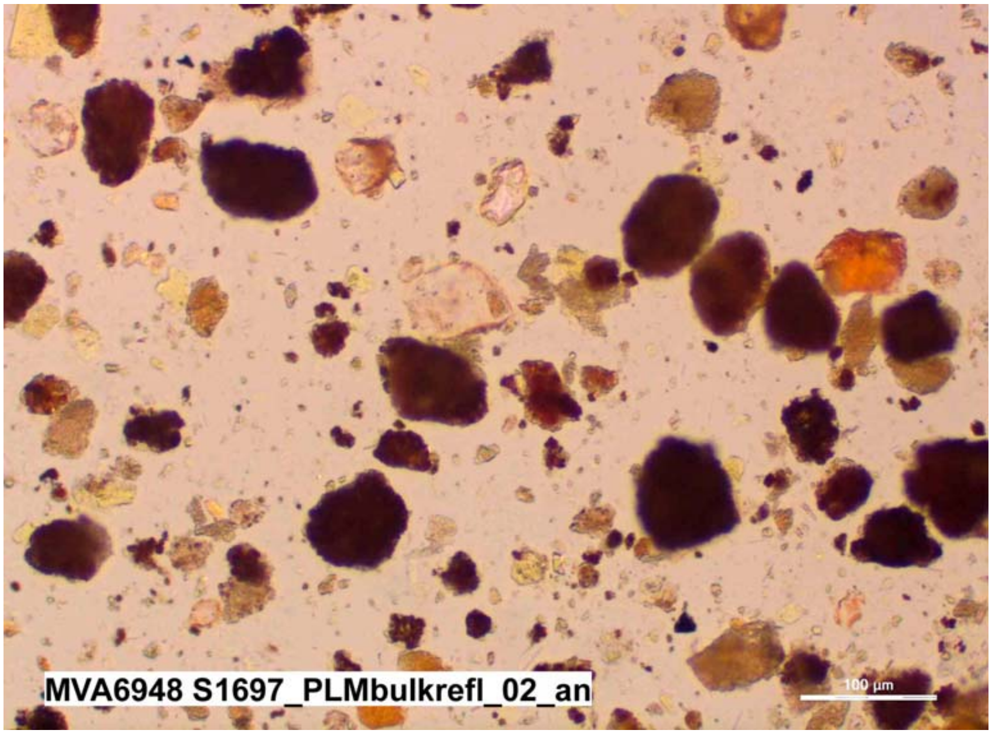


Figure A1-2. Particles in Sample S1697, reflected light.

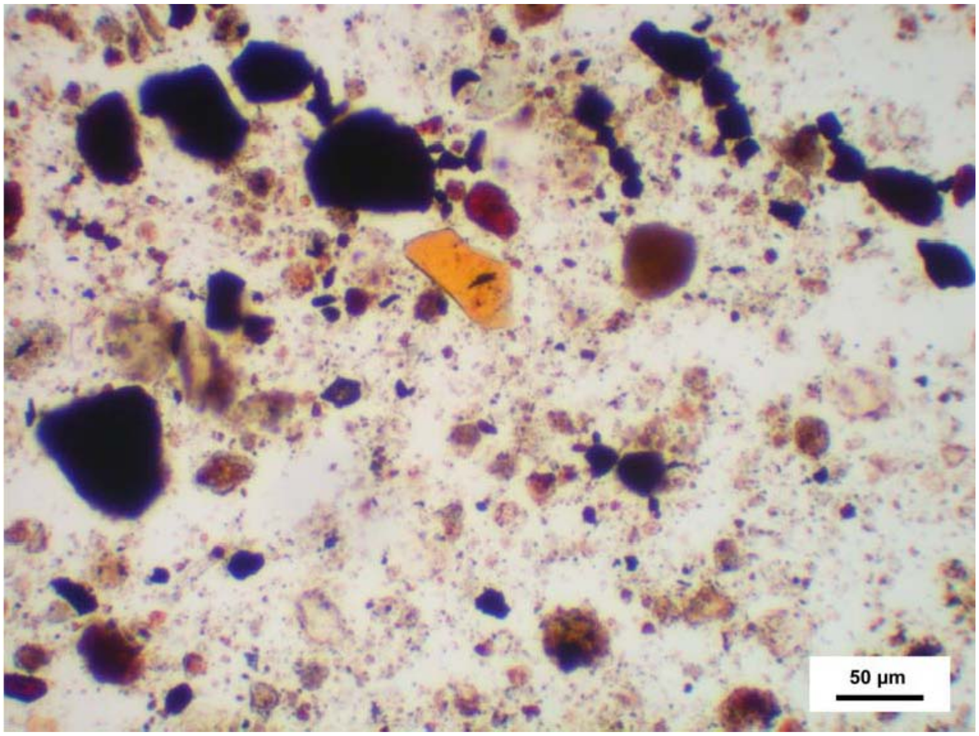


Figure A1-3. Particles in Sample S1698, transmitted light.

Appendix II

Report of Results: MVA6948

Soil, Hudson County, NJ Chromium Project

INTRODUCTION

This report includes the results of scanning electron microscopy (SEM) particle size and elemental analysis and polarized light microscopy (PLM) analysis of two soil samples delivered to MVA Scientific Consultants on 27 April 2007. Upon receipt the samples were assigned the following identification numbers:

MVA ID	EOHSI ID
S0380	Nicholas Trucking Site, 75µm, 2.0614g
S0381	Liberty State Park, 75µm, 2.0946g

MVA was asked to provide information about the composition and particle size distribution of the samples.

Analyses were performed at MVA Scientific Consultants during the period 8 May through 15 May 2007.

METHODS

The sample was prepared for particle size analysis by suspending 0.05g of the sample in 100ml of 20ppm methylcellulose solution and sonicating the suspension for ~5 minutes. Aliquots of the suspension were then filtered onto 0.2µm pore-size polycarbonate membrane filter. Sections of the filters were prepared for examination by scanning electron microscopy-energy dispersive x-ray spectrometry (SEM/EDS). The analyses were performed using a JEOL Model JSM-6500F field emission scanning electron microscope operating in automated mode under the control of a Thermo Noran System Six x-ray analysis system. Particle size data and elemental composition using x-ray analysis for 25 elements (Al, As, Ba, Br, Ca, Cl, Cr, Cu, Fe, Ga, Ge, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, Ti, V, and Zn which were automatically selected as possible elemental peaks by the analysis software during acquisition) were obtained for between 1500 and 2000 particles. The data are tabulated in three ways: by particle size, by number of particles that contain an element in significant amounts and by element groupings that show predominate elemental associations in the particles. To aid with the interpretation of the data, additional analysis by polarized light microscopy was also performed on each sample. The methodology used in this analysis is similar to what was previously used for a sample analyzed by MVA in February/March 2007 (see report issued 1 March 2007).

The samples were also examined under an Olympus SZ-40 stereomicroscope at magnifications from 7 to 40 times. Particles from the sample were mounted in 1.55 RI Cargille liquid for analysis by polarized light microscopy using an Olympus BH-2 polarized light microscope with a magnification range from 100 to 1000X.

RESULTS AND DISCUSSION

Sample S0380. Stereobinocular analysis shows that the sample consists of a fine red-brown powder. PLM analysis shows that it is composed of soil minerals including quartz, mica, carbonate, and zircon (20-40%), rust/metal flakes, many of which are magnetic (60-80%) and acicular to prismatic crystals of an unknown material (1-5%). A trace amount of plant material was also detected. A representative photo of the sample is presented in Figure A2-1.

Sample S0381. Stereobinocular analysis shows that the sample consists of a fine red-brown powder. PLM analysis shows that it is composed of soil minerals including quartz, mica, carbonate, amphibole, and feldspar (40-60%), rust/metal flakes, many of which are magnetic (40-60%) and trace amounts (<1%) of glass fibers, plant fragments, aerosol particles, and possible coal/coke particles. A representative photo of the sample is presented in Figure A2-2.

Table A2-1 shows the particle size distribution for the samples in terms of number of particles and by volume. As might be expected with soil samples, a high percentage of the particles were in the smaller diameter ranges (0.5-2.5 micrometers) while the majority of the volume is contributed by a few particles greater than 10 micrometers in diameter.

Tables A2-2 and A2-3 show that calcium-rich particles (probably limestone related) and particles containing iron, magnesium, aluminum and/or silicon (common to soil minerals) make up the majority of the particles in both samples. The data also show that the samples have significantly different amounts of some elements. The Nichols Trucking Site sample is richer in Mg, Ca, and Fe than the Liberty State Park sample. The Liberty State Park sample contains more particles that are Si-rich. The Liberty State Park sample also contained numerous Ti-rich particles and Fe plus Cr-rich (1.4%) particles (Figures A2-3 and A2-4).

The large number of unclassified particles (approximately 10%) is likely the result of the presence of varying mixtures of limestone and other minerals. Individual sample particle size and 24 element data sets are available in Excel format upon request.

Table A2-1. Particle Size Distribution in Terms of Number of Particles and Particle Volume in Size Ranges

Nicholas Trucking Site (S0380)				
Diameter (mm)	**Number**	**Number %**	**Volume**	**Volume %**
0.5-1.0	400	23.6	170.2	0.2
1.0-2.5	817	48.1	2420.7	2.7
2.5-5.0	333	19.6	7678.2	8.7
5.0-7.5	83	4.9	9096.2	10.3
7.5-10.0	34	2.0	9477.1	10.7
>10.0	31	1.8	59747.2	67.4
Total Particles	1698			

Liberty State Park (S0381)				
Diameter (mm)	**Number**	**Number %**	**Volume**	**Volume %**
0.5-1.0	604	33.0	237.9	0.4
1.0-2.5	914	49.9	2146.9	3.8
2.5-5.0	194	10.6	4316.2	7.6
5.0-7.5	69	3.8	7584.5	13.4
7.5-10.0	24	1.3	3687.1	6.5
>10.0	27	1.5	38545.7	68.2
Total Particles	1832			

Table A2-2. Occurrence of Particles by Element*

	Nicholas Trucking Site (S0380)		Liberty State Park (S0381)	
Element	**Number**	**Percent**	**Number**	**Percent**
Na	0	0.0	0	0.0
Mg	366	21.6	12	0.7
Al	0	0.0	0	0.0
Si	134	7.9	470	25.7
P	1	0.1	0	0.0
S	0	0.0	0	0.0
Cl	0	0.0	0	0.0
K	0	0.0	0	0.0
Ca	160	9.4	33	1.8
Ti	1	0.1	10	0.5
V	0	0.0	0	0.0
Cr	0	0.0	0	0.0
Mn	1	0.1	0	0.0
Fe	826	48.6	612	33.4
Ni	0	0.0	0	0.0
Cu	0	0.0	0	0.0
Zn	0	0.0	0	0.0
Ga	0	0.0	0	0.0
Ge	0	0.0	0	0.0
As	0	0.0	0	0.0
Br	0	0.0	0	0.0
Sr	0	0.0	0	0.0
Mo	0	0.0	0	0.0
Ba	0	0.0	0	0.0
Pb	1	0.1	0	0.0

*Presence of an element was based on over 40 weight % of the particle based on the 25 elements determined by x-ray analysis.

Table A2-3. Groupings of Elements in Particles

	Nicholas Trucking Site (S0380)		**Liberty State Park (S0381)**	
Type	**Number**	**Percent**	**Number**	**Percent**
Al+Si	79	4.7	305	16.6
Ca+Fe	9	0.5	0	0.0
Ca-rich	114	6.7	33	1.8
Ca-rich Silicate	49	2.9	11	0.6
Fe-rich	709	41.8	463	25.3
KAlSi	5	0.3	24	1.3
Mg+Al	4	0.2	7	0.4
MgAlSiFe	150	8.8	235	12.8
Mg-rich	272	16.0	5	0.3
Mixed Si	37	2.2	140	7.6
Si+Al+Fe	2	0.1	20	1.1
SiAlMgFe	79	4.7	366	20.0
Si-only	2	0.1	0	0.0
Ti-only	0	0.0	10	0.5
Fe+Cr	0	0.0	26	1.4
Unclassified	187	11.0	187	10.2
Total Particles	1698		1832	

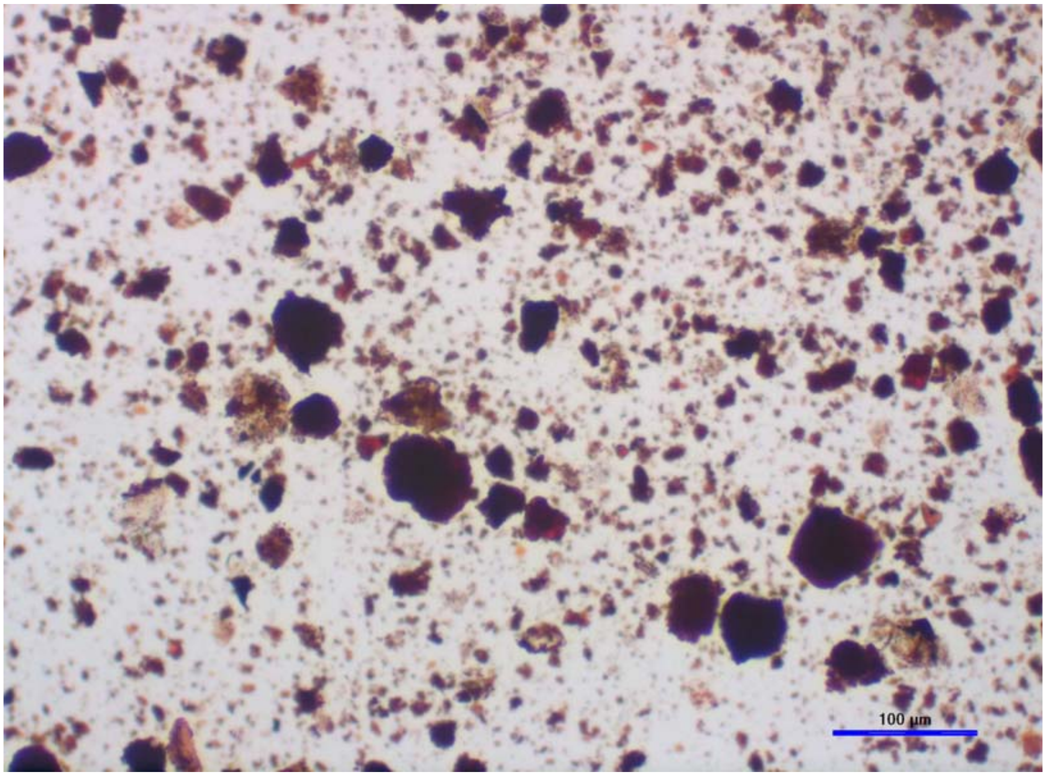


Figure A2-1. Rust/metal flakes, soil minerals in Sample S0380, transmitted light.

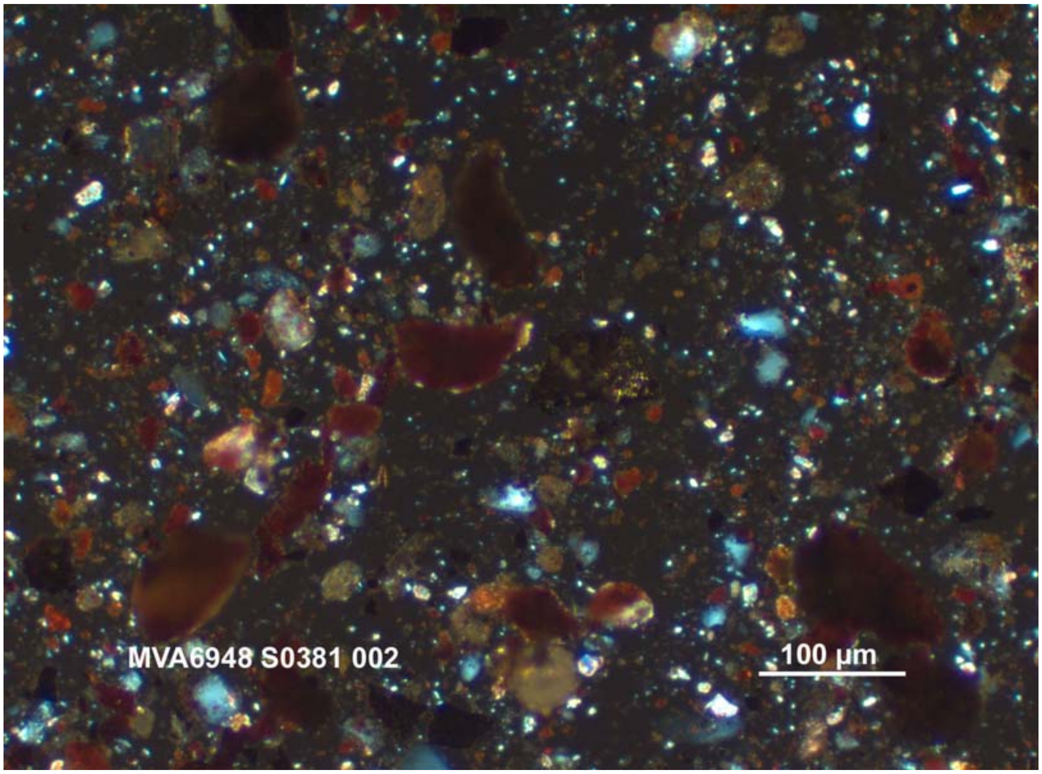


Figure A2-2. Rust/metal flakes, soil minerals in Sample S0381, crossed polars (with reflected light).

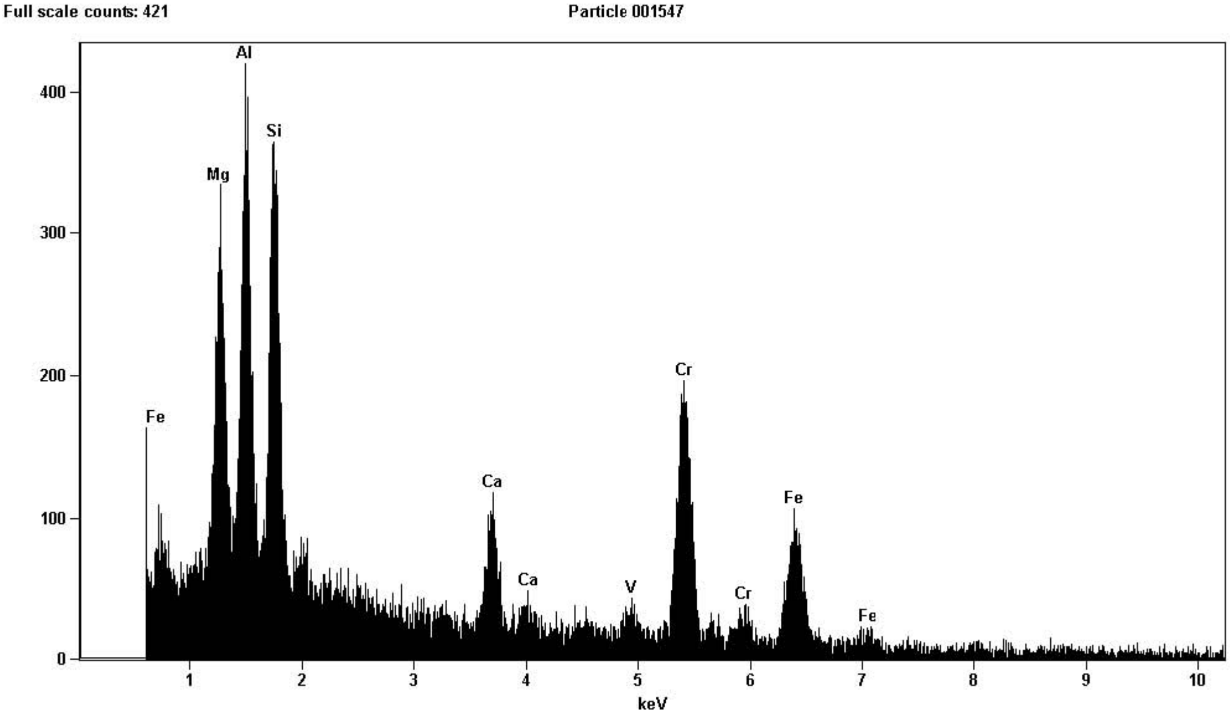


Figure A2-3. EDS spectrum (collected from 0.6 to 20KeV) of iron and chromium-rich particle observed in Liberty State Park sample (S0381).

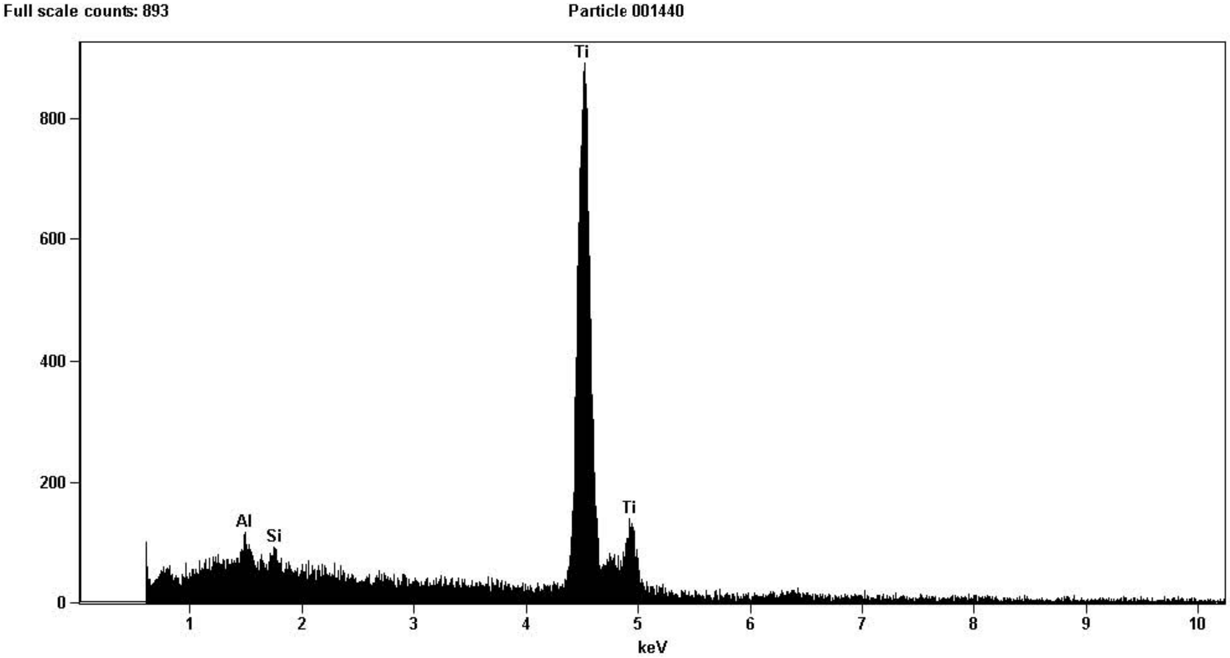


Figure A2-4. EDS spectrum (collected from 0.6 to 20KeV) of titanium-rich particle observed in Liberty State Park sample (S0381).

Appendix III

Report of Results: MVA6948

Soil, Hudson County, NJ Chromium Project

INTRODUCTION

This report includes the results of particle size analysis of one soil sample delivered to MVA Scientific Consultants on 9 February 2007. The sample was identified as “Colony Diner, 2.05g/75µm” and assigned MVA identification number S0148. We were asked to determine the particle size distribution of the sample and to determine the chemical composition of the particles.

Analyses were performed at MVA Scientific Consultants during the period 15 through 20 February 2007.

METHODS

The sample was prepared by suspending 0.05g of the sample in 50ml of 20ppm methylcellulose solution and sonicating the suspension for ~5 minutes. Aliquots of the suspension were then filtered onto 0.2µm pore-size polycarbonate membrane filter. Sections of the filters were prepared for examination by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS). The analyses were performed using a JEOL Model JSM-6500F field emission scanning electron microscope operating in automated mode under the control of a ThermoFisher Scientific, Noran System Six

x-ray analysis system. Particle size data and elemental composition using x-ray analysis for 21 elements (Al, Ba, Ca, Cd, Cl, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si, Ti, V, Zn, and Zr) were obtained for 1716 particles. The data are tabulated in three ways: by particle size, by number of particles that contain an element in significant amounts and by element groupings that show predominate elemental associations in the particles. To aid with the interpretation of the data, additional analysis by polarized light microscopy was also performed on the sample.

RESULTS AND DISCUSSION

Table A3-1 shows the particle size distribution for the Colony Diner Sample (S0148) in terms of number of particles and by volume. As might be expected with soil samples,

a high percentage of the particles were in the smaller diameter ranges (0.5-2.5 micrometers) while the majority of the volume is contributed by a few particles greater than 10 micrometers in diameter.

Tables A3-2 and A3-3 show that calcium-rich particles (probably limestone related) and particles containing iron, magnesium, aluminum and/or silicon (common to soil minerals) make up the majority of the particles.

The finding of metal particles other than iron based in soil samples is unusual. The presence of two individual particles with high concentrations of chromium (Cr) and lead (Pb) were confirmed and the EDS spectra from these particles are shown in Figures A3-1 and A3-2. Although the data are very limited (2 of 1716 particles), the spectra suggest that the chromium-containing particles are of at least two types. Figure A3-1 shows chromium associated with typical soil mineral elements (Mg, Al, Si, Ca, Fe, and K) and Figure A3-2 is suggestive of a lead-chromate paint particle.

The large number of unclassified particles is likely the result of the presence of varying mixtures of limestone and other minerals. The great amount of variation makes classifying mixed particles based on elemental groupings very difficult.

The polarized light microscopy analysis showed that the soil sample contained approximately 30-50% carbonate and 30-50% soil minerals such as quartz, feldspar and amphibole. There were also traces (less than 1%) of rust/metal flakes, yellow isotropic particles, black porous material (possibly cinder) and a fine red material (probably an iron compound, mostly coating individual grains).

Table A3-1. Particle Size Distribution in Terms of Number of Particles and Particle Volume in Size Ranges for Colony Diner Sample (S0148)

Diameter (μm)	**Number**	**Percent**	**Volume**	Volume %
0.5-1.0	521	30.4	198.7	0.2
1.0-2.5	870	50.7	2111.7	1.8
2.5-5.0	247	14.4	5253.6	4.5
5.0-7.5	53	3.1	5162.1	4.5
7.5-10.0	17	1.0	4333.0	3.7
>10.0	8	0.5	98742.6	85.3
Total Particles	1716			

Table A3-2. Occurrence of Particles by Element* from Colony Diner Sample (S0148)

Element	Number of Particles	Percent
Ca	301	17.5
Fe	146	8.5
Mg	85	5.0
Si	80	4.7
Al	43	2.5
Ti	1	0.1
Cr	1	0.1
Cu	1	0.1
Pb	1	0.1
Na	0	0.0
P	0	0.0
S	0	0.0
Cl	0	0.0
K	0	0.0
V	0	0.0
Mn	0	0.0
Ni	0	0.0
Zn	0	0.0
Zr	0	0.0
Cd	0	0.0
Ba	0	0.0

*Presence of an element was based on over 40 weight % of the particle based on the 21 elements determined by x-ray analysis.

Table A3-3. Groupings of Elements in Particles from Colony Diner Sample (S0148)

Type	Number	Percent
Ca-rich silicate	356	20.7
Si+Al+Fe	324	18.9
Mg+Al	292	17.0
Unclassified	249	14.5
Ca-rich	213	12.4
Fe-rich	97	5.7
Ca+Fe	75	4.4
Mg-rich	57	3.3
Mixed Si	22	1.3
Al-rich	20	1.2
K+Al+Si	8	0.5
Cu+Zn	1	0.1
Pb-rich	1	0.1
Cr-rich	1	0.1
Total Particles	1716	

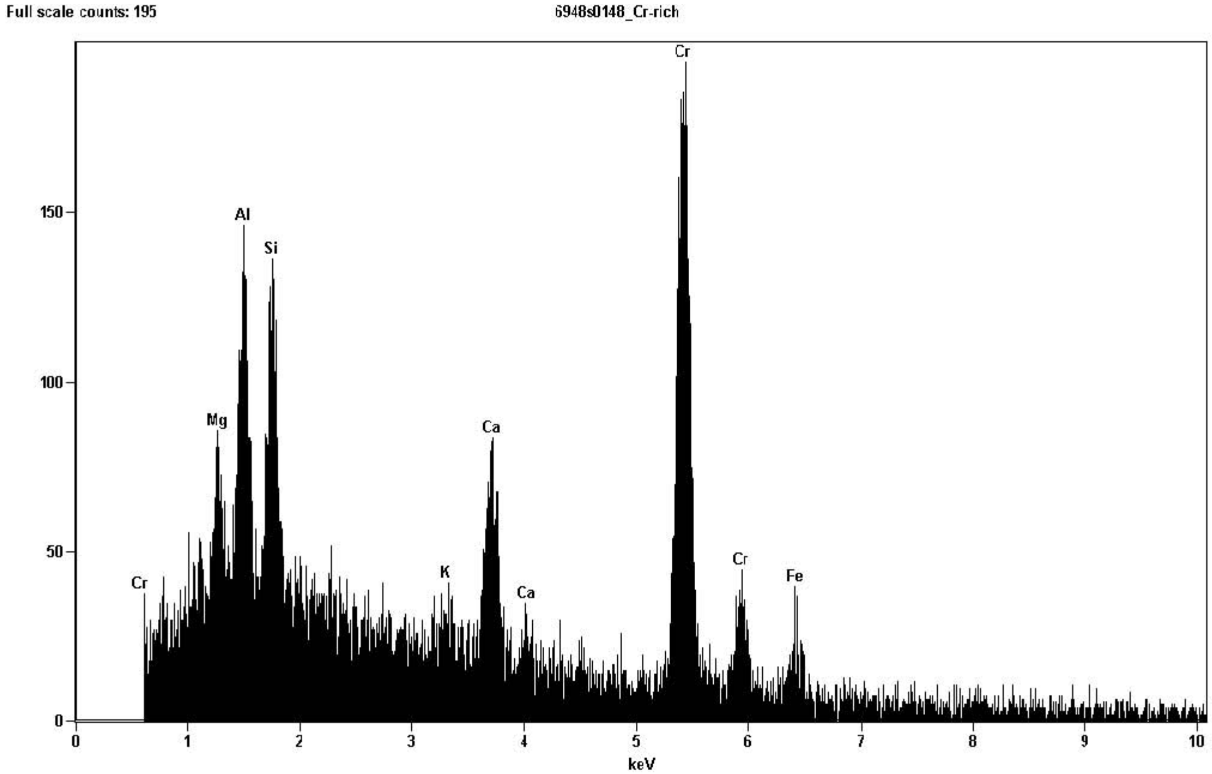


Figure A3-1. EDS spectrum of chromium-rich particle observed in Colony Diner sample (S0148).

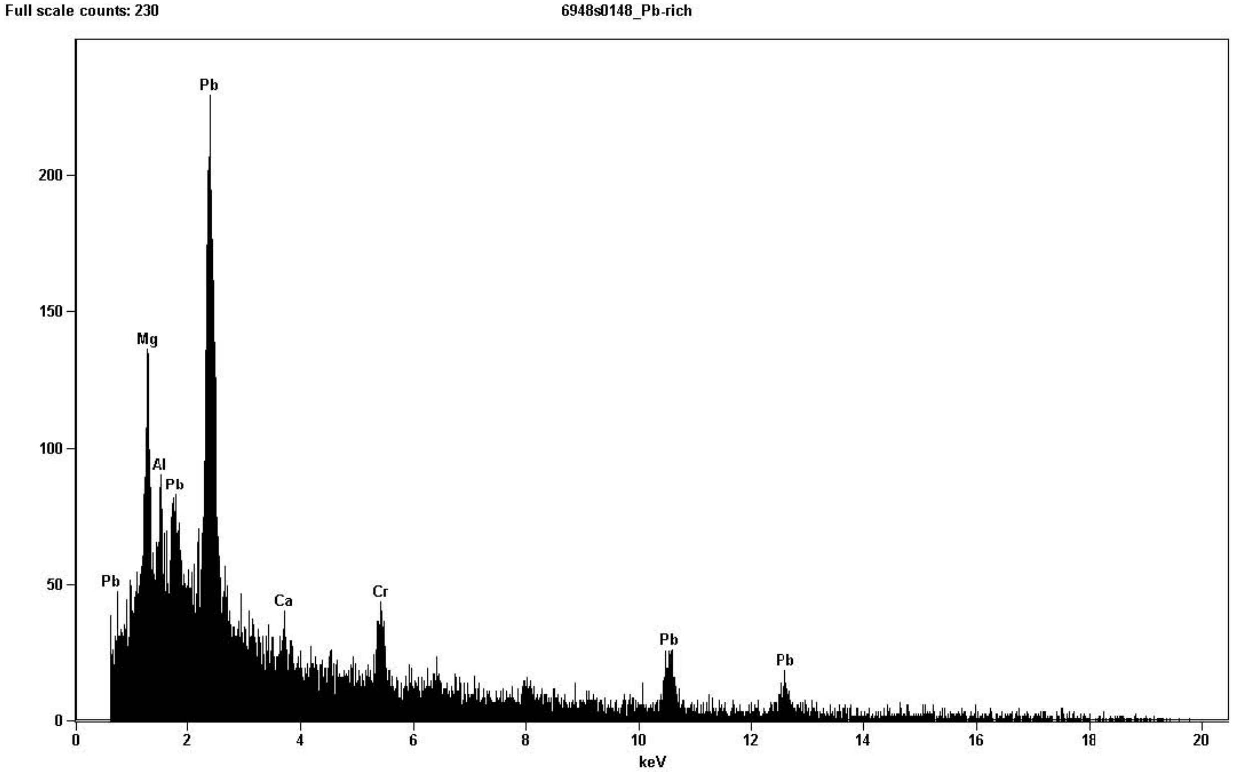


Figure A3-2. EDS spectrum of lead-rich particle observed in Colony Diner sample (S0148). The particle contains chromium as well.