# CHAPTER 1
# EXECUTIVE SUMMARY

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# New Jersey Chromium Workgroup Report

## CHAPTER 1

## Executive Summary and Recommendations

### Executive Summary

### A. Overview

In response to a request by Commissioner Bradley Campbell, The New Jersey Department of Environmental Protection (Department) convened an internal workgroup to review and discuss the applicability of current and proposed cleanup criteria for chromium, specifically as they apply to chromium ore processing residue (COPR) waste sites in New Jersey. The request emanated from concerns raised to the Commissioner by the Hudson County community where most of the chrome ore processing residue waste sites are located. The workgroup was comprised of experts from various programs of the Department, one representative from the NJ Department of Health and Senior Services and one representative from the NJ District of the US Geological Survey. The group worked intensively for six months outlining the details of the issues for examination and making recommendations to the Department for improving the cleanup criteria and/or the application of the cleanup criteria. The criteria are presented in Table 1.1. This document summarizes the issues and recommendations discussed by the workgroup members. The report reflects the combined contribution of staff of the Department and other government scientists. For some aspects of the report, consensus was not possible, as the individuals serving on the work groups were polarized in their professional judgement about some of the issues. This report has attempted to outline those issues for which evidence was presented that demonstrate the theoretical possibility of a phenomenon occurring. However, recommendations have been made only for issues where definitive scientific evidence was presented. The report is intended to serve as an informational resource to the Department and as a foundation for future cleanup decisions at COPR sites in the state to reduce the environmental and public health impacts of chromium contamination. The recommendations are not intended to result in any retroactive application of any new criteria/standards.

The overall charge to the workgroup, as identified by Commissioner Campbell:

**The workgroup will review the application of the current chromium standards and any revised standards.**

The workgroup was charged with specific questions (memos outlining the charges to the group are included as an appendix of this report). The questions were:

- Analytical: the Site Remediation Program currently accepts results of chromium analyses using a non-certified method. It has been recommended that the NJDEP-certified analytical method for hexavalent chromium be used.

- Interconversion of trivalent chromium to hexavalent chromium and site-specific chemistry: Due to the differing toxicity of chromium depending on its valence state (tri- or hexavalent), it is vital to understand the interconversions of these two species. Investigation of this chemistry is needed.

- Concentration due to capillary action: Hexavalent chromium may concentrate on surfaces due to it solubility and transport in ground water. This phenomenon needs examination.

- Carcinogenicity of hexavalent chromium via ingestion: It has been suggested that this form of chromium, known to be carcinogenic via inhalation, may also induce cancers when ingested. This route of exposure needs further investigation.

This list of questions was developed into specific charges, and four subgroups were identified and formed to address the charges:

1. Risk Assessment Subgroup
2. Analytical Chemistry Subgroup
3. Air and Dust Transport Subgroup
4. Chromium Environmental Chemistry Subgroup

**1. Risk Assessment Subgroup charges:**

- Carcinogenicity via ingestion: Do toxicological studies show that hexavalent chromium is carcinogenic when ingested? Should the exposure route be altered to address potential ingestion carcinogenicity?

- Contact Dermatitis: The procedure for site specific allergic contact dermatitis criteria includes the assumption that exposure to hexavalent chromium occurs in solution because the approved threshold is solution-based. If this is not appropriate, suggest another mechanism, and a method for quantifying dose-response and exposure.

- Exposure Pathways: Are the exposure pathways for chromium adequately addressed in the soil standards, particularly as they relate to alternate remediation standards?

**2. Analytical Chemistry Subgroup Charges**

- Certified Method: The Site Remediation Program has been accepting analytical results for hexavalent chromium using a non-NJDEP certified analytical method for Cr(VI) digestion. There is an USEPA-certified method available (Method 3060A). Should the Department mandate use of the USEPA method for hexavalent chromium determinations? What should the Department do about data obtained by the non-certified method the Site Remediation Program has been using for site decisions?

- Data Review and Acceptance: What should the Department policy be on analytical data where the associated quality assurance protocols are outside method limits?

- Additional Analytical Methods: USEPA Method 6800 "Elemental and Speciated Isotope Dilution Mass Spectrometry" is approved and included in SW846 for the analysis of speciated metals, including chromium. The Office of Quality Assurance (OQA) does not currently offer certification for USEPA Method 6800. Should the OQA offer certification for USEPA Method 6800? If so, what should be the extent of its potential applications?

- Method Deficiencies: There is a question that the methods for the regulatory-approved methods of preparation and analysis of hexavalent chromium (USEPA Methods 3060a, 7196a and 7199) underestimate its in-situ concentration in certain types of soil. What are the circumstances where the low bias in hexavalent chromium measurements exist? Are there any conditions under which high bias (resulting from oxidation of Cr(III) to Cr(VI)) in sample preparation and/or measurement occurs?

- Quality Assurance Tools: The Department has proposed a collaboration with USEPA, National Institute of Standards and Technology (NIST) and the Environmental and Occupational Health Sciences Institute (EOHSI) to develop a reference material of defined Cr(VI) concentration using a source material from Hudson County, New Jersey that can be used to assess the efficacy of future Cr(VI) measurements. Should such a reference material be developed?

- Other Measurement Options: Is it possible to develop a commercially available, NJDEP-certifiable method to replace the current method (Method 3060A)? If not, should speciation of hexavalent chromium continue to be performed should only total chromium be measured? Are there any known biases to the measurement of total chromium in soil that would prevent its use in establishing chromium remediation standards?

**3. Air and Dust Transport Subgroup**

- Exposure Pathways: The protocol for the development of alternate remediation standards for chromium needs to include the physical mechanism by which dust gets into the air and reach humans via inhalation. Are the mechanisms for this transport adequately calculated?

**4. Chromium Environmental Chemistry Subgroup**

- Nature of COPR: The interconversion question is imbedded in the larger problem of the nature of chromite ore processing residue (COPR). The physical (micropore) structure of chromite ore processing residue may be the rate-limiting factor in the release of hexavalent chromium. What is the nature of this waste material and how does it influence what we know about chromium chemistry?

- Transport to Groundwater: What concentration of chromium in the soil at the chromate ore processing residue sites results in chromium levels above the drinking water standard in ground water? Do the NJDEP clean up standards currently under development adequately protect groundwater?

- Interconversion: What is the capacity of trivalent chromium to convert to hexavalent chromium in the soil of the chromate ore processing residue sites? Do the current remediation standards adequately account for this interconversion? If not, recommend some options the Department should pursue to address any discrepancy or inadequacy, including research.

- Concentration effect: Enrichment of concentrated hexavalent chromium have been observed on soils and in structures at the sites. Soluble hexavalent chromium dissolves in ground water and can move throughout the soil column. The chromium becomes concentrated as the water evaporates. Rainfall events and movement of groundwater levels can change the location of these concentrated evaporative fronts. Can the concentration of chromium in the enrichment areas be anticipated and modeled? Is there a concentration in the soil that protects against elevated levels of hexavalent chromium from being deposited in this way?

After six months of meetings and review, the NJDEP Chromium Workgroup has determined that the cleanup criteria for Cr(III) and Cr(VI), initially proposed in 1998 (Table 1.1), are based on the science currently available. The group recommends that the Department continue to support and review new and upcoming research that may improve the understanding of chromium toxicity and its fate and transport in the environment, as there are several studies and reviews currently underway in the scientific and regulatory community. Each individual subgroup has summarized its findings and recommendations in the chapters of this report.

**Table 1.1. Soil Cleanup Criteria for Trivalent and Hexavalent Chromium (proposed 1998)**

| Exposure Pathway | Trivalent Chromium (ppm) | | Hexavalent Chromium (ppm) | |
|---|---|---|---|---|
| | Residential | Nonresidential | Residential | Nonresidential |
| Allergic contact dermatitis | None[1] | None[1] | Site specific, but not to exceed 400[4] | Site specific, but not to exceed 400[4] |
| Inhalation | None[2] | NR[2] | 270[5] | 20[5] |
| Ingestion | 120,000 ppm[3] | NR[3] | 240 | 6,100 |
| Impact to Groundwater | None[1] | None[1] | Site specific[6] | Site specific[6] |

*1 – Under normal environmental conditions, trivalent chromium is insoluble in water.*
*2- Noncancer toxicological data for trivalent chromium does not exist for this exposure pathway.*
*3- For the nonresidential scenario, ingestion of trivalent chromium does not pose an unacceptable risk.*
*4- The 400 ppm maximum is a new criterion being recommended in this report.*
*5- Due to the effects of vehicular traffic, the nonresidential scenario soil cleanup criterion will be lower than the residential criterion.*
*6- The model used to develop a generic impact to ground water remediation criterion for Cr(VI) is not appropriate for COPR, which will require remediation in accordance with N.J.A.C. 7:26E requirements. A site-specific criterion for Cr(VI) in COPR-soil mixtures can be developed with Departmental review and approval.*

The Risk Assessment subgroup examined new information pertaining to the development of cancer by Cr(VI) ingestion. The current cleanup criteria are based on cancer due to inhalation. The most recent study (Davidson et al., 2004) investigated the occurrence of skin tumors on mice caused by the interaction of Cr(VI) and UV-radiation. The group determined that while the implication of the study are important, it is not sufficient by itself to support the

development of an ingestion-based soil cleanup value for Cr(VI). Another issue examined by the subgroup concerned the ability of ingested Cr(VI) to cause allergic dermatitis. It was determined that none of the studies individually or together provide a sufficient basis for the development of an ingestion-based soil cleanup value for allergic dermatitis. However, the group concluded that Cr(VI) could elicit allergic contact dermatitis on the skin without being solubilized first. Originally, it was assumed that Cr(VI) had to be dissolved in water in order to cause this effect. From the studies reviewed, it appears that even solid Cr(VI) can be mobilized into the skin. The group therefore concluded that it was reasonable to consider an exposure scenario based on loading of Cr(VI) in soil on the skin without prior solubilization. The group further agreed that this could result in risk-based approach quantified in terms of $\mu g$ Cr(VI)/$cm^2$ skin surface. This would correspond to a soil cleanup value of 400 ppm of Cr(VI). This does not however invalidate the previous approach based on Cr(VI) in solution. Both approaches have applicability under different environmental conditions.

The Analytical Chemistry subgroup examined several issues regarding the extraction of Cr(VI) from soils, the analysis of Cr(VI) by instrumentation, and the usability of "qualified"[1] data submitted to the Department. The subgroup concurred with the recent Site Remediation and Waste Management Programs recommendation to use only USEPA Method 3060A to prepare samples for the analysis of Cr(VI) and that the Department should implement this policy immediately, pending certification availability. The subgroup also recommended that samples be analyzed for Cr(VI) using a tiered approach that includes analytical options USEPA Method 7196A, USEPA Method 7199 and USEPA Method 6800 to ensure that accurate and precise measurements are made. In the past, the Department has accepted and used qualified data submitted by responsible parties. While the Department does have Standard Operating Procedures for the acceptance and validation of analytical data, there is no such formal document for the usability of this type of data. The subgroup recommends that a Departmental Workgroup be established to define the data usability policy to be followed in the remediation decision processes. This protocol will be used for future determinations of data acceptance and is not retroactive. It would be useful to have speciated reference materials to be used when analyzing for Cr(VI) in non-aqueous sample matrices, and the subgroup recommends that a project be initiated that develops such material.

The Air Transport subgroup evaluated the protocol for the development of alternative remediation standards (ARS) for the inhalation pathway. The group determined that the evaluation of ARS and the process for selecting the one that drives the selection of the final Remedial Action should be fully documented and be readily available upon request. The current review process does not require this, and, as a result, it was difficult to replicate the derivation of many of the ARS that had been developed in the past. The USEPA methodology for predicting emissions has changed over the past few years, so that the impacts from truck traffic and fugitive dust have drawn closer together. Therefore, future soil remediation standards and ARS should be calculated on the basis of impacts from both.

[1] A qualified data point is one has not passed the full quality assurance/ quality control criteria developed for the method.

The Environmental Chemistry subgroup examined four major issues. The first involved defining the nature of COPR. COPR contains a number of hexavalent chromium-bearing minerals that were created in a high temperature industrial process and are not found in nature. Over time, these Cr(VI)-bearing minerals slowly dissolve, thereby acting as a continuing source of hexavalent chromium to the surrounding environment. It is important that distinctions between pure COPR and COPR-soil mixtures be developed immediately because COPR slag behaves very differently (dissolution) than a COPR-soil mixture (adsorption-desorption). By re-defining COPR and COPR-soil mixtures, the options for remedial strategies can be better selected and used by the Department. The subgroup also has refined the impact to groundwater protocols contained in the Department Interested Party Review for proposed soil remediation standards to create a chromium-specific scenario. The refined scenario is presented in Chapter 6 of this report. The chief difference pertains to instances where groundwater is not currently impacted by overlying chromium waste material. In the new proposal, an investigation is required to determine why such impacts have not been observed and to demonstrate that conditions at the site will continue to prevent groundwater impacts as long as the source material is present. The third issue examined by the subgroup is the potential oxidation of Cr(III) to Cr(IV) at COPR sites. It is established that the COPR sites in New Jersey contain very high levels of Cr(III) and that the cleanup levels for this form of chromium is high compared to that for Cr(VI). The concern here is that the Cr(III) can oxidize to the more toxic hexavalent form over time and therefore cleanups based solely on the concentration of Cr(VI) at a site will not be protective into the future. The subgroup reviewed many studies in the literature. Some of the studies show that the oxidation reaction is so slow as to be insignificant in conditions similar to those found at the New Jersey COPR sites, while others indicate that oxidation can occur over a period of less than a decade. While it was agreed that conditions favoring reduction occur at COPR sites, it was not agreed to what extent conditions may favor oxidation. After much discussion within the subgroup, it appears that there is not a preponderance of evidence in the published literature to warrant change in the determination of soil cleanup levels based on oxidation reactions. Nevertheless, further study is needed to effectively resolve the issue for COPR sites. The final issue examined by the subgroup is the phenomenon of enrichment of Cr(VI) on structures, land surface, and on small particles. This phenomenon, occurring as visible blooms, has been documented at the COPR sites in New Jersey where Cr(VI) levels are high. Whether Cr(VI) salts deposit at levels too low to result in visible blooms but high enough to be of an inhalation risk is not known. The subgroup determined that given the complexity of the factors involved, it is difficult at this time to develop a predictive model for this transport mechanism. It is recommended that the Department continue to study the issue through New Jersey-specific research. Regarding the enrichment of Cr(VI) on small, respirable particles, the subgroup found equivocal information. Again, there is not enough data to suggest a change in the application of the generic model, but the subgroup did recommend that ARS petitions submitted for the inhalation pathway provide more detailed information on Cr(VI) concentration by particle size distribution, which can be used in the approval process by NJDEP.

## B. Recommendations

There are several patterns inherent in the recommendations submitted by each subgroup. Overall, the members found that while the current proposed generic cleanup numbers (Table

1.1.) are based on the science currently available, there were some administrative areas in the application of those numbers that need to be improved. Most of these programmatic types of recommendations focus on making the processes by which the Department accepts data or information pertaining to an Alternative Remediation Standard (ARS) be more formal and transparent.

Many of the recommendations provided in this report seek to improve the procedures and operating practices of the application of the human health-based cleanup levels for chromium. Representatives from the Site Remediation and Waste Management Program agreed to implement the programmatic recommendations immediately. Recommendations for further research can be implemented with availability of funding.

While many recommendations were suggested by the subgroups, only the top priorities are presented in this summary. The subgroup chapters describe both the program and research recommendations in full.

**Risk Assessment**

- The results of the Davidson et al. (2004) study of the co-carcinogenicity of UV radiation and Cr(VI) ingestion should not form the basis of a revised soil cleanup value for Cr(VI). Nonetheless, this study raises the possibility that the cancer risk posed by exposure to Cr(VI) could be larger than that currently used by the NJDEP in the derivation of its soil standards. Therefore, additional research on the oral carcinogenicity of Cr(VI) would be valuable and any additional data should be rapidly evaluated to determine whether they provide sufficient additional evidence of oral carcinogenicity for Cr(VI).

- The NJDEP should consider adopting a cleanup value based on the Nethercott et al. (1994) study and USEPA's current guidance on reasonable maximum soil adherence on skin as developed in this document. Based on the assessment of this group, a value of 400 ppm Cr(VI) is recommended for direct contact with soil. This value should be applied under the assumption of 100% bioavailability.

**Analytical Chemistry**

- Comparison of analytical methods used to detect Cr(VI) in soil samples

A research project should be designed to answer the following question:
After the digestion of soil samples containing Cr(III) and Cr(VI) using USEPA Method 3060A, which of the following three analytical methods best responds to the interconversion of Cr(III) and Cr(VI) in reducing and oxidizing soils?

Method 6800, Elemental and Speciated Isotope Dilution Mass Spectroscopy
Method 7199, Determination of Hexavalent Chromium in Drinking Water
Method 7196A, Chromium (Colorimetric)

- Evaluation of analytical methods that can determine Cr(III) and Cr(VI) in reducing and oxidizing soils without digestion is needed. It is necessary to investigate the availability of methods that do not involve wet chemistry to address the concerns

with interconversion and matrix spike recoveries. Researchers have investigated the use of a wide range of X-Ray methods for in-situ metals measurements. This research project should include use of the COPR matrix. These techniques would be able to determine worst case scenarios without first digesting the COPR waste into the aqueous phase where reduction and/or oxidation could potentially inter-convert between the species present.

- Examination of other digestion methods that will remove chromium from soil without changing the indigenous content of Cr(III) and Cr(VI). A detailed search of the literature should be conducted to identify other possible methods. If methods are found, research should be conducted to determine if these methods are improvement over USEPA Method 3060A.

**Air**

- The Subgroup found that it was very difficult to compile the history of how an ARS was developed and the final decision-making process that led to the selection of a remedy. All information used in the decision process of accepting an ARS by the Department should be contained in a formal document and made publicly available.

- It is recommended that future soil remediation standards and of alternative remediation standards (ARS) include both traffic-generated dust and wind-blown dust in the calculation. In cases where no traffic is anticipated, an ARS should be based on exposure to windblown dust at a hypothetical residence located at property fenceline (the default being 270 mg/kg at the moment).

**Environmental Chemistry**

- Recommend that the Department consider defining COPR waste material and soil with larger amounts of COPR waste material as a continuing source of contamination to ground water that will require remediation in accordance with the Department's Technical Requirements for Site Remediation (N.J.A.C. 7:26E).

- To address the question of whether or not vadose zone transport can cause blooms at low soil chromium concentrations, it is recommended that a study be conducted to investigate the potential occurrence of surface enrichment due to capillary transport of hexavalent chromium. Theoretically, enrichment on surfaces can occur at any Cr(VI) concentration, but it is not known definitively whether or not there is a threshold concentration. Specifically, COPR material and COPR-soil mixtures containing various Cr(VI) concentrations should be studied for potential evaporative enrichment via capillary action toward the goal of determining whether there is a threshold concentration in soil where evaporative enrichment via capillary action does or does not occur. It is especially important to evaluate the possibility of capillary transport at sites so that the Department is better able to evaluate the effectiveness of remedial strategies.

- Information in the published literature (Kitsa et al., 1992 and Falerios et al., 1992) and site data (PPG) present limited data on enrichment of Cr(VI) on smaller soil particles. Research is recommended to clarify whether particle size enrichment is or is not of concern due to the limited data available to address this issue. Systematic, specific research is needed to definitely determine levels of hexavalent chromium on smaller particle in bloom areas, chromium-contaminated areas, and background areas. The mineralogy of small particles in chromium-contaminated areas needs to be determined. The design of the study should be determined by an appropriate group of people from the Department and unbiased external researchers with expertise in this research area. The study should include sample sites from several COPR sites in New Jersey. The Kitsa et al. (1992) study is the only one that approaches this need, but it is dated and limited. The work by Falerios et al. (1992) does not demonstrate that more chromium is present on the smaller particles. The data are equivocal. Therefore, it appears that further investigation of this matter, as a human health issue, is warranted. A larger and more current investigation than the two described here could illuminate the issue for the state and better inform the soil standard setting process. At the very least, measurements of Cr(VI) on small soil and bloom particles, as well as the routine measurements on bulk samples, could be considered as an important step in assessing human health risks from COPR. Mineralogical characterizations should be completed on samples used in experiments. It might be helpful to compare the concentrations resulting from such a study with those collected from a deep soil core for variation. Several sites plus a control site would need to be included in the study.

References:

Davidson T, Kluz T, Burns F, Rossman T, Zhang Q, Uddin A, Nadas A, Costa M. (2004) Exposure to chromium (VI) in the drinking water increases susceptibility to UV-induced skin tumors in hairless mice. *Toxicol. Appl. Pharmacol*. 19:431-437.

# CHAPTER 2
# INTRODUCTION

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# New Jersey Chromium Workgroup Report

## CHAPTER 2

## Introduction

### A. Background and Context

In response to a request by Commissioner Bradley M. Campbell, staff from The New Jersey Department of Environmental Protection (Department) convened an internal workgroup to review and discuss the applicability of current and proposed cleanup criteria for chromium as they apply to chromium ore processing residue (COPR) waste sites in New Jersey. The request emanated from concerns raised to the Commissioner by the Hudson County community where most of the chrome ore processing residue waste sites are located. The group worked intensively for six months outlining the details of the issues for examination and making recommendations to the Department for improving the cleanup criteria and/or the application of the cleanup criteria.

The overall charge to the workgroup, as identified by Commissioner Campbell:

**The workgroup will review the application of the current chromium standards and any revised standards.**

The workgroup was charged with specific questions (memos outlining the charges to the group are included as an appendix of this report). The questions were:

- Analytical: The Site Remediation and Waste Management Program currently accepts results of chromium analyses using a non-certified digestion method. It has been recommended that the NJDEP-certified digestion method for hexavalent chromium be used.

- Interconversion of trivalent chromium to hexavalent chromium and site-specific chemistry: Due to the differing toxicity of chromium depending on its valence state (tri- or hexa-valent), it is vital to understand the interconversions of these two species. Investigation of this chemistry is needed.

- Concentration due to capillary action: Hexavalent chromium may concentrate on surfaces due to its solubility and transport in groundwater. This phenomenon needs examination.

- Carcinogenicity of hexavalent chromium via ingestion: It has been suggested that this form of chromium, know to be carcinogenic via inhalation, may also induce cancers when ingested. This route of exposure needs further investigation.

This list of questions was developed into specific charges, which were assigned to each of the four subgroup components. The subgroups and their charges are:

**Risk Assessment Subgroup**

Carcinogenicity via ingestion: Do toxicological studies show that hexavalent chromium is carcinogenic when ingested? Should the exposure route be altered to address potential ingestion carcinogenicity?

Contact Dermatitis: The procedure for site specific allergic contact dermatitis criteria includes the assumption that exposure to hexavalent chromium occurs in solution because the approved threshold is solution-based. If this is not appropriate, suggest another mechanism, and a method for quantifying dose-response and exposure.

Exposure Pathways: Are the exposure pathways for chromium adequately addressed in the soil standards, particularly as they relate to alternative remediation standards?

**Analytical Chemistry Subgroup**

Certified Method: The Site Remediation and Waste Management Program has been accepting analytical results for hexavalent chromium using a non-NJDEP certified analytical method for Cr(VI) digestion. There is an USEPA-certified method available (Method 3060a). Should the Department mandate use of the USEPA method for hexavalent chromium determinations? What should the Department do about data obtained by the non-certified method the Site Remediation and Waste Management Program has been using for site decisions?

Data Review and Acceptance: What should the Department policy be on analytical data where the associated quality assurance protocols are outside method limits?

Additional Analytical Methods: USEPA Method 6800 "Elemental and Speciated Isotope Dilution Mass Spectrometry" is approved and included in SW846 for the analysis of speciated metals, including chromium. The Office of Quality Assurance (OQA) does not currently offer certification for USEPA Method 6800. Should the OQA offer certification for USEPA Method 6800? If so, what should be the extent of its potential applications?

Method Deficiencies: There is a question that the methods for the regulatory-approved methods of preparation and analysis of hexavelent chromium (USEPA Methods 3060a, 7196a and 7199) underestimate its in-situ concentration in certain types of soil. What are the circumstances where the low bias in hexavalent chromium measurements exist? Are there any conditions under which high bias (resulting from oxidation of Cr(III) to Cr(VI)) in sample preparation and/or measurement occurs?

Quality Assurance Tools: The Department has proposed a collaboration with USEPA, National Institute of Standards and Technology (NIST) and the Environmental and Occupational Health Sciences Institute (EOHSI) to develop a reference material of defined Cr(VI) concentration using a source material from Hudson County, New Jersey, that can be used to assess the efficacy of future Cr(VI) measurements. Should such a reference material be developed?

Other Measurement Options: Is it possible to develop a commercially available, NJDEP-certifiable method to replace the current method (Method 3060a)? If not, should speciation of hexavalent chromium continue to be performed should only total chromium be measured? Are there any known biases to the measurement of total chromium in soil that would prevent its use in establishing chromium remediation standards?

**Air Transport Subgroup**

Exposure Pathways: The protocol for the development of alternative remediation standards for chromium needs to include the physical mechanism by which dust gets into the air and reach humans via inhalation. Are the mechanisms for this transport adequately calculated?

**Environmental Chemistry Subgroup**

Nature of COPR: The interconversion question is imbedded in the larger problem of the nature of chromium ore processing residue (COPR). The physical (micropore) structure of the residue may be the rate-limiting factor in the release of hexavalent chromium. What is the nature of this waste material and how does it influence what we know about chromium chemistry?

Transport to Groundwater: What concentration of chromium in the soil at the COPR sites results in chromium levels above the drinking water standard in ground water? Do the NJDEP cleanup standards currently under development adequately protect groundwater?

Interconversion: What is the capacity of trivalent chromium to convert to hexavalent chromium in the soil of the COPR sites? Do the current remediation standards adequately account for this interconversion? If not, recommend some options the Department should pursue to address any discrepancy or inadequacy, including research.

Concentration Effect: Enrichment of concentrated hexavalent chromium has been observed on soils and in structures at the sites. Soluble hexavalent chromium dissolves in groundwater and can move throughout the soil column. The chromium becomes concentrated as the water evaporates. Rainfall events and movement of groundwater levels can change the location of these concentrated evaporative fronts. Can the concentration of chromium in the enrichment areas be anticipated and modeled? Is there a concentration in the soil that protects against elevated levels of hexavalent chromium from being deposited in this way?

This document summarizes the issues and recommendations discussed by the workgroup members and reflects the combined contribution of staff of the Department. It is intended to serve as an informational resource to the Department and as a foundation for future cleanup decisions at chromium ore processing residue (COPR) sites in the state to reduce the environmental and public health impacts of chromium contamination.

## B. Properties of Chromium

Chromium is a naturally occurring metallic element found in the earth's crust. Chromium exists in several oxidation states, although only the trivalent, Cr(III), and the hexavalent, Cr(VI), forms are common in the natural environment. The predominant form of chromium in crustal rocks is chromite ore, which contains a mixture of Cr(III) oxides. It is the only commercial source of chromium. Very small releases of naturally occurring chromium to the aquatic environment can occur as a result of weathering and erosion. The predominant source of chromium contamination in environmental media is industrial uses and discharges. Raw metallic chromium is used mainly for making steel and other alloys. Chromium compounds, in either the Cr(III) or Cr(VI) forms, are used for chrome plating, the manufacture of dyes and pigments, leather and wood preservation, and treatment of cooling tower water. Smaller amounts are used in drilling mud, textiles, and toner for copying machines.

Occupational exposure to chromium occurs from chromate production, stainless-steel production, chrome plating, and leather tanning. Occupational exposure can be two orders of magnitude higher than exposure to the general population (ATSDR 1998, OSHA 1998). People who live in the vicinity of chromium waste disposal sites or chromium manufacturing and processing plants have a greater probability of elevated chromium exposure than the general population. These exposures are generally to both Cr(VI) and Cr(III).

*Trivalent*

Trivalent chromium occurs naturally in the environment and is the most stable of the forms of chromium both in nature and in biological systems. Cr(III) is an essential micro-nutrient in humans, necessary to promote the action of insulin in body tissues so that sugar, protein, and fat can be used by the body. Without Cr(III) in the diet, the body loses its ability to use sugars, proteins, and fat properly, which may result in weight loss or decreased growth, improper function of the nervous system, and a diabetic-like condition. Therefore, Cr(III) compounds have been used as dietary supplements and are beneficial if taken in recommended dosages. The dietary daily recommendation is 50 to 200 µg/d for adults. The general population is exposed to Cr(III) by eating food, drinking water, and inhaling air that contains the chemical. The average daily intake from air, water, and food is estimated to be approximately 0.2 to 0.4 micrograms (µg), 2.0 µg, and 60 µg, respectively (ATSDR 1998, USEPA 1998a, WHO 1998).

*Hexavalent*

Exposure to the hexavalent form of chromium has been shown to cause both cancer and noncancer health effects. The respiratory tract is the major target for Cr(VI) following inhalation exposure in humans. Other effects noted from acute inhalation exposure to very high concentrations of Cr(VI) include gastrointestinal and neurological effects, while dermal exposure causes skin burns in humans (USEPA 1998b, 1999b). Epidemiological studies of workers have clearly established that inhaled chromium is a human carcinogen, resulting in an increased risk of lung cancer. Although chromium-exposed workers were exposed to both Cr(III) and Cr(VI) compounds, only Cr(VI) has been found to be carcinogenic in animal studies, causing lung

tumors via inhalation, so USEPA has concluded that only Cr(VI) should be classified as a Group A carcinogen (known human carcinogen) by the inhalation route of exposure (ATSDR 1998, USEPA 1999b). Hexavalent chromium, when inhaled over a period of many years, can also cause a variety of noncancer health effects including damage to the nose, blood disorders, lung disease including asthma, and kidney damage. Noncancer health effects can also result from the ingestion of Cr(VI), although the health effects would not be likely to occur unless the ingested soil contained a considerable amount of hexavalent chromium. These health effects are liver damage and relatively minor changes in blood cells.

USEPA used a mathematical model, based on data from an occupational study of chromate production workers, to estimate the probability of a person developing cancer from continuously breathing air containing a specified concentration of chromium. The "acceptable" risk used by USEPA is calculated to be that level of Cr(VI) which causes no more than one-in-a-million cancer in the population of exposed individuals exposed to it. More details on the development of Cr(VI) risk levels are presented in Chapter 3 (Risk Assessment Subgroup) of this report.

## C. Development of Cleanup Standards

- Generic

The Legislature directed the Department to develop human health based soil remediation standards that protect human health for constituents present at contaminated sites. Specifically, the standards are to be developed according to the way the land is or will be developed - residential and nonresidential (N.J.S.A. 58:10-1 et seq.). Within these scenarios, the standards are further refined by exposure route – ingestion, inhalation, impact to groundwater (drinking water), and skin contact. To prevent the unacceptable risk to human health exposure due to contaminated sites, the Department has developed generic soil remediation standards for a number of contaminants, including trivalent and hexavalent chromium. Considered in the development of these generic standards are human health effects for both carcinogenic and noncarcinogenic endpoints. The Legislature determined that standards would be set at one additional cancer risk in one million ($1x10^{-6}$) for carcinogens and a hazard quotient not to exceed one (1) for noncarcinogens. The generic Soil Remediation Standards are to be used at any site regardless of site conditions. However, the Department recognizes that the inclusion of site-specific conditions may be appropriate in determining alternative remediation standards. The central principle employed in developing the generic standards was to establish viable methodologies for calculating values and to apply these to the full range of exposure scenarios and contaminants that need to be assessed. Conservative estimates (though not worst case estimates) were used when establishing parameters to include in the models used to generate the generic standards.

Generic numbers are used as defaults; that is, in instances where conditions at a site are unknown, generic (or very general), assumptions are made about the site. These assumptions are used in determining conservative conditions under which exposure to contamination may occur.

- Alternative Remediation Standards (ARS)

Site-specific characteristics may be substituted for default inputs in the algorithm in order to calculate alternative remediation standards for the site. The site-specific factors that may be substituted are discussed further in the Basis and Background documents developed by the Department for each exposure route. The Basis and Background documents are detailed descriptions of the methodologies used to develop the generic standards. Throughout the documents are sections describing instances where site-specific parameters may be substituted in the development of the alternative remediation standards.

In instances where data on a particular site is available, that site-specific information is used in lieu of the more conservative generic default values. Alternative Remediation Standards (ARS) are specific to the site and the pathway for which they are developed. The procedures to develop ARS's are based on site specific conditions and are contained in each exposure or transport pathway basis and background document. ARS's may be developed so that they are appropriate for nonresidential or residential uses. After an ARS is developed for a given pathway, it must be compared to the generic standards for the remaining exposure pathways. The lower of the generic standards or ARS becomes the remediation standard.

## D. The Site Cleanup Process

Whenever a contaminated site is investigated or remediated, there are two options available with respect to soil cleanup criteria. One option is to use the already available generic numbers that apply to all sites in New Jersey. The other option is to develop an alternative remediation standard that incorporates site-specific conditions and information.

There are a number of factors that will determine how the soil remediation standards (either generic or ARS) will be applied for a contaminant at a site. How they are applied is intimately related to the phase of remediation. The phases of remediation are:

- **Memorandum of Agreement (MOA):** A written voluntary agreement between NJDEP and one or more persons concerning remedial activities planned for a contaminated site.

- **Preliminary Assessment (PA):** Identifies all contaminated and potentially contaminated areas of concern (including historic) that will require a formal site investigation.

- **Site Investigation (SI):** Determines if any contaminants are present above applicable remediation standards/criteria through sampling and analysis. During this step, the site is assessed for general use information (e.g., residential or nonresidential use). When analytical results of sampling become available, they are compared to the generic soil standards for each pathway (standards may vary based on the exposure route, i.e., inhalation, and by the use of the site, i.e., residential):
  - Ingestion-dermal exposure pathway (residential/nonresidential use)
  - Inhalation exposure pathway (residential/nonresidential use)
  - Impact to ground water exposure pathway

If the site investigation sample results of all suspected contaminants are **lower** than the soil remediation standards for all exposure pathways, a No Further Action (NFA) letter may be

issued for the site. If the site investigation sample results show levels of contaminant(s) **higher** than the lowest soil remediation standards then a remedial investigation must be conducted.

- **Remedial Investigation (RI):** Entails gathering data necessary to determine the nature and extent of contamination at the site, establishing the remedial response criteria and identifying remedial action alternatives, which are described in the statutes (described in the following section). Remedial options include treatment, removal, or control via institutional and/or engineering controls.

- **Remedial Action (RA):** The physical action consistent with the selected remedy to correct a release or threatened release of a hazardous substance into the environment. The term, often referred to as a cleanup action or construction project, includes but is not limited to: engineering controls, confinement, dredging, neutralization, recycling, removal, reuse and storage or treatment of hazardous substances. Sampling is conducted during this phase to document the completion of the treatment or removal remedial action.

- **No Further Action (NFA)/Covenant Not to Sue:** A No Further Action (NFA) designation is given when all remedial activities that were necessary to address an environmental concern have been completed. This designation is given when it is determined that regulatory requirements have been satisfied at a site, including instances when no contamination is found above applicable criteria or when it is determined that no additional remedial work is required at the site. A **conditional NFA** is obtained when all remedial work has been completed at a site, but a Deed Notice, Classification Exception Area or engineering control is required because some contamination above appropriate standards or criteria remains. Also, a **conditional NFA** is obtained when only a portion of an entire site has been addressed in an unrestricted, limited restricted or restricted manner. The Department designates an NFA-A for a partial area of a site and an NFA-E for an entire site. An NFA-A or NFA-E can have restrictions or institutional controls such as a Deed Notice or Classification Exception Area if soil or groundwater contamination remains above applicable standards.

There are several types of no further actions that the Department can issue.

- **Full Site No Further Action:** A determination by the Department that, based upon evaluation of the historical uses and/or investigation of a site or subsite, there are no contaminants present, or that any discharged contaminants that were present at the site or subsite have been remediated.

- **Limited Restricted:** This remedial action type includes a deed notice that provides notice of the residual soil contamination and limits human activities. Properties must be restricted when contamination will remain above the residential soil cleanup criteria. A notice requires a property owner's concurrence and documents the location and concentration of all contaminants and how they must be controlled or maintained and monitored, if applicable.

- **Restricted:** This remedial action type includes both engineering controls and a deed notice at sites with soil contamination remaining.

- **Classification Exception Area (CEA):** Serves to provide notice that groundwater contamination in exceedance of the Department's GroundWater Quality Standard exists in a particular location.

A **Deed Notice** (formerly called a Declaration of Environmental Restriction) is imposed for sites having a limited restricted or a restricted use designation. This notice ensures the disclosure of site conditions to future owners and the maintenance of required engineering controls. Certain exceptions for affected ground water also can be obtained depending upon its use. A **Classification Exception Area** is established at sites when groundwater contaminant levels exceed state groundwater quality criteria, but there is an expectation that over time, standards will be met. This designation must be established as part of an approved remedy to protect groundwater resources. The intent of a CEA is to ensure the uses of a designated aquifer in a specific area are restricted until contaminant levels are measured below appropriate standards.

**E. Statutory Authority for Site Cleanups**

The Brownfield and Contaminated Site Remediation Act ("Act") is detailed regarding remedy selection.

- The Act at NJSA 58:10B-12g(1) states "Unrestricted use remedial actions, limited restricted use remedial actions and restricted use remedial actions shall be allowed except that unrestricted use remedial actions and limited restricted use remedial actions shall be preferred over restricted use remedial actions. The department, however, may not disapprove the use of a restricted use remedial action or a limited restricted use remedial action so long as the selected remedial action meets the health risk standard established in subsection d. of this section, and where, as applicable, is protective of the environment. The choice of the remedial action to be implemented shall be made by the person performing the remediation in accordance with regulations adopted by the department and that choice of the remedial action shall be approved by the department if all the criteria for remedial action selection enumerated in this section, as applicable, are met. The department may not require a person to compare or investigate any alternative remedial action as part of its review of the selected remedial action."

- The Act at NJSA 58:10B-12g(2) states "Contamination may, upon the department's approval, be left onsite at levels or concentrations that exceed the minimum soil remediation standards for residential use if the implementation of institutional or engineering controls at that site will result in the protection of public health, safety and the environment at the health risk standard established in subsection d. of this section and if the requirements established in subsections a., b., c. and d. of section 36 of P.L.1993, c.139 (C.58:10B-13) are met. "

- The Act at NJSA 58:10B-13f states "Whenever the department approves or has approved the use of engineering controls for the remediation of soil, groundwater, or surface water, to protect public health, safety or the environment, the department may require additional remediation of that site only if the engineering controls no longer are protective of public health, safety, or the environment."

In accordance with the Brownfield and Contaminated Site Remediation Act, N.J.S.A. 58:10B-12, the draft soil remediation standards are developed for the protection of human health and therefore, are not specifically developed to be protective of ecological resources. However, high levels of contamination must be evaluated, on a site by site basis, for potential ecological impacts as well as for the presence of free and residual product pursuant to the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

### F. History of the Development of Cleanup Criteria for Chromium and Status of Chromium Sites in New Jersey

Soil cleanup criteria have been developed for two valence states of chromium: trivalent chromium and hexavalent chromium. Different criteria have been established due to the differences in toxicity and solubility between the two valence states.

The Department has refined its guidance for chromium soil cleanup levels based upon changes and developments in the applicable science over the years. Table 2.1 shows the cleanup levels from 1989 through the present. Table 1.1 shows the 1998 proposed cleanup levels. A discussion about how the Department derived the cleanup criteria described in the table is available at the Departments Chromate Project website (http://www.state.nj.us/dep/srp/siteinfo/chrome/cr_criteria.htm). A brief synopsis is presented here.

**Table 2.1. History of Chromium Soil Cleanup Levels in New Jersey**

| Year | Chromium Cleanup Level, mg/kg dry weight (ppm) |
|---|---|
| 1989 | 75 ppm total Cr |
| 1993 | 10 ppm soil Cr(VI)<br>500 ppm soil Cr(III) |
| 1998 | Multiple exposure pathway proposal for Cr(VI) and Cr(III) announced by Department. See Table 1.1. |

Prior to 1989, the Department used a 100 mg/kg[1] action level for total chromium. This action level was based on New Jersey background total chromium soil concentrations derived from Rutgers University data and also took into account qualitative toxicological information available at the time.

The Department established subsequent guidance on a total chromium cleanup level in 1989 with a value of 75 mg/kg to account for allergic contact dermatitis (ACD). USEPA does not use the ACD endpoint in its standard-setting process. The guidance was developed in New Jersey for total chromium to protect exposure to the hexavalent form, which is the toxic form. A suitable digestion method did not exist at the time specific for hexavalent chromium in soil, so a total chromium level was established.

[1] mg/kg: milligram total chromium per kilogram of dry weight soil (equivalent to parts per million or ppm)

From 1993 until September 3, 1998, the soil cleanup criterion for Cr(III) was 500 mg/kg, based on an allergic contact dermatitis health endpoint. As this health condition results from short-term or acute exposures to chromium, the same criterion was applicable to both residential and nonresidential land use scenarios. On September 3, 1998, the Department proposed to delete this criterion and establish a soil cleanup criterion based on a soil ingestion exposure pathway using USEPA exposure pathway models, exposure assumptions, and toxicology data. This resulted in a new residential soil cleanup criterion of 78,000 ppm for Cr(III). Using USEPA models and assumptions, there is no unacceptable risk from Cr(III) exposure under the nonresidential land use scenario. As such, the Department chose not to regulate Cr(III) under a nonresidential land use scenario. From 1993 until 1998, the soil cleanup criterion for Cr(VI) was 10 mg/kg.

In addition, the Department proposed to establish separate Cr(VI) soil cleanup criteria for the following exposure pathways:

Soil ingestion
Inhalation of soil particles
Impact of soil contamination on ground water quality

Soil Ingestion

For the ingestion and inhalation soil exposure pathways, the Department again proposed to establish soil cleanup criteria using USEPA exposure pathway models, toxicology data, and exposure assumptions (substituting New Jersey specific data where applicable). As the existing toxicology data for the ingestion and inhalation exposure pathways were based on long-term or chronic exposures to Cr(VI), different criteria could be developed for residential and nonresidential land use scenarios. The Department had proposed on September 18, 1998, to use 240 ppm and 6,100 ppm Cr(VI) for the soil ingestion pathway under the residential and nonresidential land use scenarios, respectively.

Inhalation of Soil Particles

Based on data in the IRIS (Integrated Risk Information System) database, a value of 20 ppm Cr(VI) was proposed for the cancer inhalation endpoint for a nonresidential setting and 270 ppm Cr(VI) for a residential setting.

Impact of Soil Contamination on GroundWater Quality

For the impact to ground water exposure pathway, the Department proposed on September 18, 1998, the use of USEPA exposure pathway models and the Department groundwater quality standard for Cr(VI) to develop a site-specific cleanup criterion. Due to highly variable soil conditions throughout the State, it is not possible at this time to develop a generic soil impact to groundwater cleanup criterion for Cr(VI). As the groundwater quality standard for Cr(VI) is the same throughout the state, different soil cleanup criteria cannot be developed for residential and nonresidential land use scenarios.

Current Sites

A site status report for the COPR sites in New Jersey is presented in Table 2.2.

**Table 2.2 Chromite Ore Processing Residue Sites Status (September 17, 2004)**

| Organization | Active Sites<br>RI or RA Phase | NFA* | Total Sites |
|---|---|---|---|
| Honeywell | 20 | 2 | 22 |
| Occidental Chemical | 22 | 18 | 40 |
| PPG Industries | 23 | 38 | 61 |
| Exxon | 2 | 0 | 2 |
| Developer/Owner | 1 | 3 | 4 |
| **Sub-Total Responsible Party** | **68** | **61** | **129** |
| Allied Directive | 24 | 0 | 24 |
| NJDEP | 0 | 1 | 1 |
| NJDEP Orphan Site #1 | 13 | 1 | 14 |
| NJDEP Orphan Site #2 | 15 | 0 | 15 |
| **Sub-Total Publicly Funded** | **52** | **2** | **54** |
| **Sites Investigated and Not Contaminated** | 0 | 0 | 27 |
| **SUBTOTAL** | **120** | **63** | **183** |
| **TOTAL** | **120** | **63**** | **210** |

* Sites Cleaned-Up with "**Entire Site - No Further Action (NFA-E) Determinations**" (37 Residential and 26 Non Residential). Approximately 34% of all confirmed Hudson County Chromium Sites have been investigated and cleaned up.

**Remedy Selection Summary:

- 48 - Excavation
- 6 – Alternative Remediation Standard developed & No remedial action necessary
- 4 - Cap and Deed Notice
- 2 – Iron Sulfate & Portland Cement Treatment
- 2 - No remedial action necessary
- 1 - Deed Notice only

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# CHAPTER 3
# RISK ASSESSMENT – SUBGROUP

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# New Jersey Chromium Workgroup Report

## CHAPTER 3

## Risk Assessment Subgroup

### Charges Being Addressed

1. Ingestion Carcinogenicity

1. There are currently no standards or guidelines from either the federal government, or from any state government for protection of human health based on ingestion carcinogenicity of hexavalent chromium [Cr(VI)].

2. The National Toxicology Program (NTP) is currently conducting a chronic cancer bioassay (ingestion exposure) for Cr(VI). However, the results of that study are not expected for at least two years.

3. It appears that the State of California is currently considering approaches to development of on oral cancer potency factor for Cr(VI), but these are not available, and it is not known when they will become available.

4. Individual historical occupational studies provide weak evidence for Cr(VI) ingestion carcinogenicity. It does not appear likely that, given the inherent limitations of the available studies, a meta-analysis across studies would yield a useful estimate of cancer potency.

5. There are only two animal studies that potentially provide data on the ingestion carcinogenicity of Cr(VI). The first, Borneff et al. (1968) is severely flawed by a concurrent viral infection of the animals, by use of only a single Cr(VI) dose, and by unclear reporting of data. It is, therefore, not suitable for quantitative risk assessment.

6. The second, Davidson et al. (2004), a study of the interaction of Cr(VI) and ultra violet (UV) radiation in the production of skin tumors is a scientifically valid study. The uncertainties resulting from differences in the administered UV radiation compared to UV radiation from ambient sunlight appear relatively minor. The data on total tumors (but not malignancies *per se*) can be used for dose-response modeling. However, given that this study was conducted in a single species and a single sex, and that the findings were confined to a single study, the study is not sufficient by itself to support the development of an ingestion-based soil cleanup value for Cr(VI). Nonetheless, this study raises the possibility that the cancer risk posed by exposure to Cr(VI) could be larger than that currently used by the NJDEP in the derivation of its soil standards. Therefore, additional research on the oral carcinogenicity of Cr(VI) would be valuable and any additional data should be rapidly evaluated to determine whether they provide sufficient additional evidence of oral carcinogenicity for Cr(VI).

## 2. Allergic Contact Dermatitis

1. Cr(VI) appears to be capable of eliciting allergic dermatitis in sensitive subjects with ingestion. However, none of the studies individually or together provide a sufficient basis for the development of an ingestion-based soil cleanup value for allergic dermatitis.

2. It is not necessary that Cr(VI) be, *a priori*, in an aqueous solution to elicit allergic contact dermatitis (ACD). Based on observations of solid Cr(VI) crystals in petrolatum, it appears that even solid Cr(VI) can be mobilized into the skin. The group therefore concluded that it was reasonable to consider an exposure scenario based on loading of Cr(VI) in soil on the skin without prior solubilization. The group further agreed that this could result in a risk-based approach quantified in terms of $\mu$g Cr(VI)/cm$^2$ skin surface. For a given loading of soil on the skin surface, this would correspond to mg Cr/kg soil on the skin surface.

3. Three studies were identified that provide dose-response data for elicitation of ACD based on the mass of Cr (VI) on the skin surface (Hansen et al., 2003; Wass and Wahlberg, 1991; Nethercott et al., 1994). These studies appear to be show a relatively consistent dose-response relationship. Of these, the Nethercott et al.(1994) study is the most appropriate for quantitative risk assessment because of its relatively large sample size.

4. Benchmark dose modeling of the data from Nethercott et al. (1994) gives an estimate of the $BMDL_{10}$ (i.e., the lower 95% confidence limit on the dose corresponding to a 10% response among sensitized individuals) of 0.08 $\mu$g Cr(VI)/cm$^2$ skin. This value is appropriate for the development of a soil cleanup value.

5. Based on a review of the various recommended values for adherence/loading of soil on skin, a reasonable upper bound (RME) value of 0.2 mg soil/cm$^2$ skin was selected. This value is appropriate for children and adults in a residential setting, and for adults in an occupational/industrial setting.

6. Combining the Cr(VI) loading and the soil loading results in a concentration of Cr(VI) in soil adhering to the skin of 400 ppm. It is assumed that this concentration corresponds to the concentration of Cr(VI) in the parent soil.

7. There are uncertainties about the availability of the Cr(VI) in the Nethercott et al. (1994) patches, as well as with the potential availability of Cr(VI) in contaminated soil. Thus, it is not clear that the dose-response relationship derived from the Nethercott et al. (1994) either over-estimates or under-estimates the dose-response relationship that would be seen with Cr(VI)-contaminated soil. Furthermore, the observation that solid Cr(VI) can be mobilized into the skin and can result in elicitation of ACD means that solubility is not a unique determinant of bioavailability with respect to ACD. Therefore, it is most appropriate to apply the dose-response relationship derived from Nethercott et al. (1994) under the assumption of 100% bio-availability of Cr(VI) in the soil. This leads to direct application of the value of 400 ppm as a soil cleanup value.

8. The current approach for calculating an ACD-based Cr(VI) soil cleanup value based on the concentration of Cr(VI) in solution reflects a reasonable exposure scenario and a valid dose-response relationship for that scenario. It therefore continues to constitute a valid approach for deriving a Cr(VI) soil cleanup value.

**Responses to Charges**

The Risk Assessment Subgroup was initially charged with three objectives:

1. Carcinogenicity by Ingestion

Do toxicological studies show that hexavalent chromium is carcinogenic when ingested? Should the exposure route be altered to address potential ingestion carcinogenicity?

2. Contact Dermatitis

The procedure for site specific allergic contact dermatitis criteria includes the assumption that exposure to hexavalent chromium occurs in solution because the approved threshold is solution-based. If this is not appropriate, suggest another mechanism, and a method for quantifying dose-response and exposure.

3. Exposure Pathways

Are the exposure pathways for chromium adequately addressed in the soil standards, particularly as they relate to alternate remediation standards?

Subsequently, it was agreed that the third charge was not unique to the Risk Assessment Sub-Group, and related more directly to the Air and Dust Transport Group as well as to the Environmental Chemistry Group. Therefore, with the agreement of the Workgroup Chair, and the members of the sub-group the third charge was revised to read as follows:

Revised charge #3 - Provide guidance in risk assessment and/or exposure assessment to other COPR sub-groups to assist in their assessment of various exposure pathways as requested.

Informal assistance to both the Air and Dust Transport and the Environmental Chemistry sub-groups was provided upon request, but no formal deliberations occurred within the Risk Assessment sub-group regarding these issues. Therefore, this report will address the findings and recommendations of the sub-group relative to charges 1 and 2.

**Charge 1 - Ingestion Carcinogenicity**

*Background*

Cr(VI) has long been known as a respiratory carcinogen via inhalation (USEPA, 2004) . However, there are few data from which to draw conclusions about its ingestion carcinogenicity. Some *in-vitro* studies suggest that reduction of Cr(VI) in the gastro-intestinal track is rapid, and

that reduction is complete in the blood. However, a human *in-vivo* study gave equivocal results with one of four subjects showing a sustained red blood cell (RBC) concentration of Cr (indicative of Cr(VI) absorption across the RBC membrane) with oral dosing (Kerger et al., 1996). For the most part, studies of occupational cohorts exposed to Cr(VI) have concentrated on respiratory cancers. Reporting of cancers at other locations has been spotty and has mostly come from older studies with high exposure levels and poor industrial hygiene measurements. In addition to these occupational epidemiology studies, the group identified only two controlled studies that potentially bear directly on the ability of Cr(VI) to cause cancer in humans by ingestion. The group also contacted the USEPA, the National Toxicology Program (NTP), and various state risk assessment programs (through the Federal and State Toxicology and Risk Assessment Committee (FSTRAC) to determine what relevant research is expected and what, if any, parallel efforts are or have been undertaken by other states.

*Ongoing and recent research*

The NTP is currently in the early stages of a chronic rodent bioassay of Cr(VI) ingestion. However, results from this study that may be useful for qualitative and/or quantitative determinations of ingestion carcinogenicity are not expected for at least two years and possibly longer. With the exception of the recent paper by Davidson et al. (2004), discussed in detail below, the group was unable to identify other peer-reviewed studies directly relating to the carcinogenic potential of ingested Cr(VI).

*Risk assessment efforts by other states*

Through discussions with staff at Cal-EPA, we are aware that California is also undertaking an assessment of the ingestion carcinogenicity of Cr(VI) as part of their efforts to develop a drinking water Public Health Goal. While we have no formal description of their efforts, California's efforts appear to focus on two approaches. One is the derivation of a cancer potency from the mouse study of Borneff et al. (1968), discussed in detail below, and the other is a meta-analysis of various occupational epidemiologic studies. No other past or current risk assessment efforts relating to Cr(VI) ingestion carcinogenicity by any other state was identified.

*Review of Occupational Studies*

Since the 1950s, epidemiologic studies of occupational exposure to Cr(VI) compounds have found strong associations with an increased risk of respiratory cancers. These studies have been reviewed, summarized and evaluated by several national and international agencies (DHSS, 2002; ATSDR, 2000; USEPA, 1998; IARC, 1990; WHO, 1988). After the initial epidemiologic links were established in worker cohorts in several parts of the world, improvements in industrial conditions reduced exposure levels. Worker cohorts employed after these improvements were made appear to be at much lower risk of respiratory cancer than cohorts exposed prior to that time.

Elevated risks of respiratory cancer have been observed in several chromium-related industries, including chromate manufacturing, chromate pigment production, and chrome plating. Studies of cancer risk in workers in ferrochromium alloy manufacturing and stainless steel welding have

shown inconsistent results. There is uncertainty regarding the relative carcinogenic potency of different chromium compounds. Based on the epidemiologic evidence and supporting experimental animal studies, the International Agency for Research on Cancer (IARC) has classified Cr(VI) as carcinogenic to humans (Group 1), the US Department of Health and Human Services (DHSS) has classified Cr(VI) compounds as known to be human carcinogens, and the US Environmental Protection Agency (USEPA) has classified Cr(VI) as a known human carcinogen by the inhalation route of exposure (Group A).

Workers may be exposed to Cr(VI) through the ingestion route of exposure via hand-to-mouth contact and via clearance of chromium from the respiratory tract. Some occupational studies reported elevated numbers of stomach or other gastrointestinal cancers in Cr(VI)-exposed cohorts. However, agency reviews have concluded that there is insufficient epidemiologic evidence of an association between oral exposure to chromium and the development of stomach or gastrointestinal cancers. IARC (1990) concluded, "For cancers other than of the lung and sinonasal cavity, no consistent pattern of cancer risk has been demonstrated among workers exposed to chromium." The USEPA (1998) stated, "At present, the carcinogenicity of hexavalent chromium by the oral route of exposure cannot be determined." Most recently, the DHHS (2002) concluded that, "The incidences of cancers at other [than the lung] sites may also be increased in such [chromium-exposed worker] populations…"

There are other reviews of chromium carcinogenicity that have evaluated the oral exposure route. According to Yassi and Nieboer (1988), "An excess of cancers at sites other than the lung has been reported in chromate production workers, chrome platers, chromate pigment producers, and ferrochromium production workers. Specifically, cancers of the gastrointestinal tract, as well as nasal and laryngeal cancers have been noted to be slightly increased in various investigations. Such findings, however, have not been consistently found in all studies, and no firm conclusions are possible." In a review of carcinogenic mechanisms, Cohen et al (1993) concluded that, "For cancers other than those of the lungs and sinonasal cavity, no consistent pattern of cancer risk has been demonstrated in those workers exposed to chromium." Langard (1990) wrote that, "Some epidemiologic studies indicate increase of cancer at other sites, e.g., gastrointestinal tract and kidneys, but none of these studies could rule out possible confounding by other exposure factors." The most recent analysis of the literature, by Proctor et al. (2002), arrives at a similar conclusion.

While there are suggestions of ingestion carcinogenicity from studies of some worker cohorts, there is only weak evidence from the occupational epidemiologic literature that oral exposure to Cr(VI) exposure increases the risk of gastrointestinal cancer. For risk assessment purposes, it should be noted that oral dose estimates for exposed workers would be difficult to estimate from measurements or models of historical air levels, heightening uncertainty in a quantitative dose-response determination.

Based on this analysis, the group concluded that there is insufficient evidence from any individual occupational epidemiological study to conclude that Cr(VI) is carcinogenic by ingestion. The group also concluded that it did not seem likely that a meta-analysis across these studies would provide a clear qualitative determination of ingestion carcinogenicity or provide a useful cancer potency estimate. The group recognizes that this conclusion is speculative, and

that a firm determination of the usefulness of a meta-analysis requires a close examination and quantitative analysis of the individual and aggregate studies. However, the committee also recognizes that such an examination and analysis could not be completed within the allotted time frame. It is recommended that California's efforts toward such a meta-analysis be followed and evaluated when it becomes available for review and comment.

*Review of Animal Studies*

The group identified two animal studies of Cr(VI) ingestion carcinogenicity with the potential to yield a cancer potency factor.

Borneff et al. (1968)
The original of this paper is in German. The group reviewed two different translations of the Borneff et al. (1968) study. In its intended design, 480 female and 40 male mice (total = 520) were exposed through drinking water to potassium chromate at a nominal concentration of 550 ppm in detergent, or detergent alone, in two groups each of 120 females and 10 males. The authors noted that the Cr(VI) was not stable and tended to reduce to Cr(III) after several days. New Cr(VI) solutions were, therefore, provided weekly. However, it is not known what the range of actual exposure concentrations were over the course of a week. There were also groups of mice exposed to benzo(a)pyrene in detergent and benzo(a)pyrene + potassium chromate in detergent in drinking water. The intended exposure period was 880 days (approximately 29 months). The mice were mated during exposure to produce an F1 generation. During the 8$^{th}$ month of exposure, the mice colony experienced a mouse-pox epidemic in which 512 mice died. A second round of breeding occurred producing an F2 generation. It is not clear whether this resulted from re-mating of F0 mice, mating of F1 mice, or cross breeding of F0 and F1 mice. In total, 101 mice exposed to Cr(VI) + detergent, and 126 mice exposed to detergent alone survived for assessment of tumors. It appears that only stomach tumors were noted. It is not known if this is because no other organs were examined or because no other sites showed tumors. The authors note that Cr(VI)-exposed mice engaged in cannibalism probably due to the unpalatability of the Cr(VI)-containing drinking water. Among the Cr(VI)-exposed mice there were 10/101 benign stomach tumors, and 2/101 carcinomas of the stomach. In contrast in the detergent-only mice, there were 5/126 benign stomach tumors, and 0/126 stomach carcinomas. The differences in numbers of benign tumors between the two groups was not statistically significant.

The group reviewed the Borneff et al. (1968) study and concluded that the study was not useful for risk assessment purposes for several reasons. The study was not clearly reported, leading to several important uncertainties (this does not appear to be a translation issue). There was only a single Cr(VI) dose, and the effect of the detergent exposure is unknown. However, the primary problem is that the mouse-pox epidemic calls into question whether there was an independent effect from the Cr(VI) exposure. In particular, both the F0 and F1 generations were exposed to the virus with the highest mortality occurring in the F0 generation. Essentially all the elevation in tumors (benign + malignant) was in the F0 generation (controls – F0 2/54, F1 1/24, F2 2/43; exposed – F0 9/32, F1 1/21, F2 2/36). This suggests a biologically significant effect of the pox virus on Cr(VI) carcinogenicity, and precludes making an independent assessment of Cr(VI). The authors, themselves, state that the results do not indicate unequivocal carcinogenicity.

Davidson et al. (2004) - In this study, hairless mice were exposed for six months to UV light at a constant energy of 1.2 kJ/m$^2$, and to potassium chromate in drinking water at 0.5, 2.5, and 5.0 ppm. The purpose of this study was to investigate the joint effects of Cr ingestion and UV light exposure on skin tumor formation. The authors report that UV light alone results in tumor development, while mice exposed to Cr-only had no tumors. Compared to exposure to UV light alone, there was a statistically significant increase in skin tumors (benign + malignant) >2 mm for the Cr + UV exposed mice. They also report a significant increase in the number of malignant tumors per mouse for the 5 ppm Cr exposure compared to UV alone. This work follows on a model of arsenic ingestion and UV exposure conducted by the same laboratory (Rossman et al., 2001; Burns et al., 2004). In this model, Cr(VI) appears to be acting as a co-carcinogen with UV light rather than as an independent carcinogen.

The group found that, overall, the Davidson et al. (2004) study was scientifically valid in its design and in the conclusions reached by the authors, but raised several issues about the study. The group found that the reporting of data in the Davidson et al. (2004) paper is incomplete, and further found that the reporting based on tumors per mouse was not appropriate for consideration of risk assessment. Therefore, the group requested and received from the authors the raw data on tumor occurrence. These data were re-analyzed in-house. The full report of that analysis is included in Appendix A of this report. Based on the analysis, the group reached the following conclusions:

- There is a consistent dose-response for total tumors >2 mm based on the number of tumors/mouse, or on the number of mice with at least one tumor.

- The analysis of malignancies is problematic due to the fact that not all mice and not all tumors were analyzed for malignancy. Sampling for malignancy was reported to be randomized with respect to tumors rather than with respect to mice. Therefore, it might be expected that mice with more tumors would be oversampled. This does not appear to have been the case. While the apparent absence of such a bias is desirable, it raises questions as to the how the randomization procedure was conducted and to what extent the reported data on the occurrence of malignancies can be used to support quantitative risk assessment.

- Based on the proportion of mice with malignancies at each Cr concentration, neither inclusion nor exclusion of mice with no malignancies resulted in a statistically significant trend. However there is an apparent (but not significant) trend when mice with no malignancies are excluded.

- Based on the proportion of malignant tumors per mouse, neither inclusion nor exclusion of mice without malignancies resulted in a clear trend. This analysis, however, is highly dependent on the randomization procedure used in the selection of tumors for determination of malignancy.

- Overall, the interpretation of malignancies in this study is difficult due to the partial collection of data on malignancies. Quantitative estimates based on the probability of malignancy are, therefore, not appropriate.

- Tumors >2 mm are likely to progress to malignancy in this system. Of 21 mice with tumors that were examined for malignancies, 18 had malignancies. Thus, non-malignant tumor production appears to be predictive of malignant tumor development.

The group also investigated the relationship of the artificial UV light exposures in the study to environmental exposures. The results of an in-house review of the physics and health effects of UV radiation as they relate to the Davidson et al. (2004) study are presented in Appendix B of this report. Based on the information provided by this review, the group concluded the following:

- UV wavelength is grouped in UV-C, UV-B, and UV-A in order of increasing wavelength. Sunlight contains about 96% UVA (Learn et al., 1993). UV-C from the sun does not reach the surface of the earth at the elevation of New Jersey. The radiation in Davidson et al. (2004) came from two different types of UV bulbs. One bulb (Westinghouse solar FS-20), produced 85% UV-B light, 4% UV-A light, <1% UV-C, and the remainder in the visible range. The other bulb (General Electric F-20T12-BL) produced only UV-A and visible light.

- The authors give the UV dose as 1.1-1.3 $kJ/m^2$. UV radiation has a range of effects. Erythema (sunburn) potential is usually expressed in terms of the minimal erythematous dose (MED). This value varies depending on the wavelength of the UV radiation. Data from a number of studies give the minimum erythema dose for UV-B in humans as about 15 $mJ/cm^2$ (0.15 $kJ/m^2$). Therefore, in terms of UV-B radiation, the exposure in Davidson et al. (2004) was about 10 times the MED. However, for equal energy, UV-A is much less effective in producing erythema, with UV-A at 320 nm being only about 1% as effective as UV-B at 300 nm (see Appendix B of this report). Thus, while the exact proportion of UV-B and UV-A in Davidson et al. (2004) is not known, it appears that the UV dose was within the range of the MED, and therefore relevant to outdoor human exposure with respect to erythema.

- The UV-C radiation delivered by one of the lamp types is not relevant to human UV exposure at most altitudes including all of those in New Jersey. While UV-C is more effective at equal energy levels in producing erythema than UV-B or UV-A, the relevant metric for consideration of Davidson et al. (2004) is tumor production. Erythema potential does not correlate with tumorogenic potential. UV-C at 250 nm is about 10% as effective as UV-B at 300 nm in tumor production (see appendix B, Fig. B.2). Therefore, since UV-C contributed <1% of the total UV energy it is likely to contribute considerably less than 1% to the tumor production seen in Davidson et al. (2004).

- The group, therefore, concluded that the UV exposures in Davidson et al. (2004) were relevant to consideration of human exposure.

- On the basis of these considerations, the group concluded that the Davidson et al. (2004) study was a methodologically sound study with potential relevance to human co-exposure to environmental UV radiation and Cr(VI).

The group considered the applicability of the Davidson et al.(2004) study for quantitative cancer risk assessment with respect to current USEPA guidance. There are currently two draft versions

of the USEPA's Guidance for Carcinogen Risk Assessment extant (USEPA, 1999; 2003). The only guidance that is considered final by the USEPA is the 1986 version. While the 1999 and 2003 versions are similar in many respects, they are substantially different in terms of risk assessment methodology from the 1986 guidance. USEPA currently recommends using the 1999 guidance on an interim basis, but does not recommend using the 2003 guidance. With respect to the applicability of the EPA guidance to quantitative risk assessment based on Davidson et al. (2004), the group concluded the following:

- The data on the occurrence of malignant tumors are incomplete and difficult to interpret. However, the dose-response for total tumors (benign + malignant) is statistically significant and robust. Furthermore, the benign tumors produced in this study appear likely to progress to malignancy. Therefore, the guidance for the use of benign tumor data in the 1999 EPA document is applicable. This states: "...the default is to include benign tumors observed in animal studies in the assessment of animal tumor incidence if they have the capacity to progress to the malignancies with which they are associated." The group, therefore, concluded that dose-response assessment using the total tumor data from Davidson et al. (2004) would be consistent with current EPA guidance.

- With respect to the 1986 EPA guidelines, the group agreed that, based on the Davidson et al. (2004) study, Cr(VI) would likely be classified as a group C chemical - "possible human carcinogen"- defined as "...agents with limited evidence of carcinogenicity in animals in the absence of human data. It includes a wide variety of evidence, e.g., (a) a malignant tumor response in a single well-conducted experiment that does not meet conditions for sufficient evidence, (b) tumor responses of marginal statistical significance in studies having inadequate design or reporting, (c) benign but not malignant tumors with an agent showing no response in a variety of short-term tests for mutagenicity, and (d) responses of marginal statistical significance in a tissue known to have a high or variable background rate." Under the 1999 guidelines, which dispense with the letter classification scheme, the group agreed that the classification would likely be "Suggestive Evidence of Carcinogenicity, but Not Sufficient to Assess Human Carcinogenic Potential." This classification applies when "...evidence from human or animal data is suggestive of carcinogenicity, which raises a concern for carcinogenic effects but is judged not sufficient for a conclusion as to human carcinogenic potential. Examples of such evidence may include: a marginal increase in tumors that may be exposure-related, or evidence is observed only in a single study, or the only evidence is limited to certain high background tumors in one sex of one species. ...Further studies would be needed to determine human carcinogenic potential."

- For substances classified as having "suggestive evidence of carcinogenicity," the 1999 guidelines state that "Dose-response assessment is not indicated for these agents." The group noted, however, that this statement does not appear in the 2003 guidelines. Therefore, strict adherence to the currently recommended version of the EPA's carcinogen guidance would preclude development of a quantitative cancer potency based on the Davidson et al. (2004) study. However, the 1999 guidelines technically have the status of a draft document, notwithstanding the EPA's current recommendation for their use. Furthermore, the more recent (2003) version of the guidelines do not specifically preclude such a step. Finally, while the NJDEP is required to consider EPA guidance, it is not strictly bound by that guidance. For these reasons, the group

agreed to investigate linear dose-response modeling of the Davidson et al. (2004) data to provide general information on the carcinogenic potential of Cr(VI) in this system.

The group conducted linear dose response modeling of the Davidson et al. (2004) complete data set using the linear-from-point-of-departure (POD) approach outlined in the 1999 EPA guidelines. This analysis was carried out using the concentrations of Cr(VI) in the drinking water as reported in the paper. The EPA 1999 guidance states that the default approach for development of a quantitative cancer potency factor (cancer slope factor) is the linear-from-point-of-departure approach. In this approach, a point-of-departure (POD) is a point on a dose response curve that lies close to the lower end of the observed data, and which is a reliable point from which to extrapolate the dose response relationship downward. The 1999 guidance suggests that for linear extrapolation, the POD be the lower bound on the default dose (e.g., an $LED_{10}$ , the lower confidence bound on the dose corresponding to a 10% response). Benchmark dose modeling was used to derive a $BMDL_{7.5}$, and this value was taken as the POD. Given the recommendation of the group that it is not appropriate to derive cleanup guidance based on the Davidson et al. (2004) study, and support for this conclusion from the peer-reviewers, the result of that calculation is not presented here, so as not to create confusion as to the appropriate application of the Davidson et al. (2004) study. The committee agreed, however, that it is likely that a dose-based cancer potency factor from these data would be consistent with the range of cancer slope factors currently seen for the majority of recognized environmental carcinogens.

The group also noted that the hairless mouse model for UV-Cr(VI) has not been characterized with respect to the mechanism involved in tumor initiation or promotion. This includes lack of characterization of the this strain of mouse with respect to its potential for specific sensitivity to either UV or Cr(VI). In the absence of such characterization, it is difficult to predict to what extent this model may be relevant to humans. While a similar system has been shown to produce skin tumors in this strain of mouse with co-exposure to UV and arsenic, the group notes that arsenic is a known human skin carcinogen. There are no reports of skin cancer in humans associated with Cr.

In addition, the group noted that there are several reports in the literature of the production of genotoxic endpoints in animals following oral administration of Cr(VI) (e.g., Coogan et al., 1991; Bagchi et al., 1995; 1997; 2001). These studies are consistent with the hypothesis that Cr(VI) can, at some doses, be transported to tissues distant from the initial point of contact, and can result in effects that may be predictive of the production of tumors. However, genotoxicity is not necessarily predictive of tumor formation. Furthermore, such studies provide no basis for the derivation of a dose-response relationship that would be useful for risk assessment.

Based on consideration of the foregoing, the group reached the following conclusions regarding the applicability of the Davidson et al. (2004) study for the development of Cr(VI) cleanup standards.

- The Davidson et al. (2004) study is a scientifically valid study. Although the mechanism of the co-carcinogenicity of UV radiation and Cr(VI) is not known, and although there is some uncertainty regarding the exact proportions of the different UV wavelengths used in the study,

the study has potential implications for human health under conditions of Cr(VI) ingestion and background environmental levels of UV radiation.

- Given that the Davidson et al. (2004) study was conducted in a single species, and a single sex, and that the findings were confined to a single study, the study is not sufficient by itself to support the development of an ingestion-based soil cleanup standard for Cr(VI).

## Charge 2 – Allergic Contact Dermatitis

*Background*

The NJDEP has previously recognized the potential of Cr(VI) to elicit allergic contact dermatitis (ACD) in sensitized individuals, and has further recognized that Cr allergy is among the most common dermal allergies in the population. For these reasons, the NJDEP developed a soil cleanup approach based on elicitation of ACD by Cr(VI). The basis for this approach was developed in a paper by Stern et al. (1993). This approach was based on a concentration-response relationship derived from a meta-analysis of studies that determined the ability of patches containing various concentrations of Cr(VI) in solution (i.e., µg Cr(VI)/L) to elicit ACD in sensitized individuals. With the application of benchmark-dose modeling, the lower confidence limit on the solution concentration of Cr(VI) that resulted in a 10% response rate was derived. The underlying rationale for this approach was that soluble Cr(VI) contamination in soil could leach out of the soil during a rain, and become dissolved in water that was on the soil surface, or was loosely associated with wet soil. Direct contact with this water could then result in an ACD reaction. While this rationale and risk assessment methodology still appear to be valid, this approach presents several practical difficulties. Because the risk assessment is based on solution concentration, but the soil standard is based on a soil concentration (i.e., mg Cr(VI)/kg soil), it is necessary to convert from the one metric to the other using an extraction procedure. However, there is no unique relationship between a given concentration in solution and a soil concentration that will give rise to that solution concentration. This depends on a number of factors including the volume of water, the volume of soil, the solubility of the Cr(VI), and the pH of the mixture. It has, therefore, been necessary to make several reasonable, but not unique assumptions in order to define the default extraction procedure. In addition, problems have arisen in attempting to standardize the solubilization procedure.

Since the adoption of the solution-based approach, the NJDEP has become aware of studies in which ACD is elicited from skin contact with non-aqueous material and from solid material. Such studies present the possibility of deriving an ACD criterion that does not require prior solubilization. Such a criterion could be defined in terms of mg Cr(VI)/kg of carrier material. In these studies, the carrier material is not soil *per se*. However, the mechanisms of movement of Cr(VI) from the carrier material to the skin surface are likely to be sufficiently similar to the mechanisms occurring with soil on the skin surface that the concentration can be directly extrapolated between media. In addition, in Stern et al. (1993), it was noted that several studies had observed the elicitation of ACD through ingestion of Cr(VI). A soil cleanup standard derived for this exposure pathway would be identical in approach with the ingestion-based

standards currently employed by the NJDEP. The group therefore agreed to re-examine the applicability of these studies for derivation of a risk-based cleanup standard.

*Risk assessment efforts by other states*

The group is aware of only one other state that employs an ACD-based approach for Cr(VI). Massachusetts (Zewdie, 1998) employs a soil standard based on the study of Nethercott et al. (1994) (see below). While the group did not reject the MADEP approach, the consensus of the group was that insufficient information was provided in the Zewdie (1998) document to support the development of a standard.

*Review of studies of elicitation of Cr allergy by Cr(VI) ingestion*

A search of the scientific and medical literature identified four papers that present data on Cr(VI) ingestion allergy. These are the same four papers that were available and were discussed in Stern et al. (1993), and by the MADEP (Zewdie, 1998). They are summarized below.

Goitre et al. (1982) - A 52 year old building worker presented with a 20 yr history of Cr ACD on hands and patch test sensitivity. He was given an oral dose of potassium dichromate (25 mg as Cr). Local itching of active sites increased two days later. Subsequently a "double dose" resulted in lesions on the hands with complications 12 hr later.

Kaaber and Veien (1977) – Thirty one Cr(VI) patch-test positive subjects mostly with ACD on hands and feet were identified. Potassium dichromate (7.1 mg, equivalent to 2.5 mg as Cr) or a placebo were given orally in a double blind test. The sequence of Cr and placebo was randomized and each was given 1-2 weeks apart. 11/31 (35%) had a response only to Cr. 1/31(3%) had response to Cr and placebo, and 3//31 (10%) had a "questionable" response to both Cr and placebo, 2/31 (6%) had response to placebo only, and 14/31 (45%) had no response to Cr or placebo. In addition, two subjects administered only Cr had a reaction. Responses (mostly itching) occurred 5-24 hr after dosing. Some subjects experienced eruptions in areas of skin previously affected.

Schleiff (1968) - (Based on in-house translation). Twenty subjects who were patch-test positive for potassium dichromate, were given of 1 and/or 10 mg potassium dichromate orally. "In almost all cases" there was a reaction at dormant and/or active sites of dermal Cr allergy including patch-test sites. Reactions lasted 2-5 days.

Fregert (1965) - Five Cr-sensitive subjects were given an oral dose of 50 μg potassium dichromate (18 μg as Cr). Each developed reactions on palms and one developed a generalized (i.e., whole-body) eruption. (Note: this report is provided by the author as part of a review article. There does not appear to be a primary research paper describing these results.).

Based on consideration of these studies, the group concluded that ingestion of Cr(VI) can cause elicitation of Cr allergic dermatitis in sensitized individuals. The group considered whether some or any of the primary studies were sufficient and appropriate for the derivation of an (oral) RfD based on elicitation of Cr-allergic dermatitis by ingestion. All of the studies appeared to

employ a single dose of Cr(VI). The studies of Goitre, Kaaber and Veien, and Schleiff all gave lowest-observed-effect-levels (LOELs) in the range of 6-50 μg/kg. However the Fregert study gives a NOEL of 0.26 μg/kg. This wide range of doses combined with the lack of detail in the Fregert (1965) paper creates significant uncertainty. The group concluded that despite the qualitative plausibility of Cr allergic elicitation from this exposure route, the data are insufficient to support quantitative risk assessment

*Consideration of the plausibility of elicitation of ACD from non-aqueous media*

In order to ascertain whether Cr(VI) must be dissolved in an aqueous solution (the scenario underlying the current ACD soil cleanup criterion) to elicit ACD, the group searched for and reviewed studies in which non-aqueous vehicles were used to deliver Cr(VI) either in patch testing of sensitive individuals, or in *in-vitro* skin permeation. These studies are summarized below.

Skog and Wahlberg (1968) - Patch testing with potassium dichromate was conducted on 46 subjects with a known Cr (VI) sensitivity. Cr(VI) was contained in three different carriers, pH 12 buffered solution, distilled water, and petrolatum (petroleum jelly). In the petrolatum, the Cr(VI) was present as micro-crystals and was not dissolved. All 46 subjects were tested with all three carrier preparations across eight concentrations. The mean elicitation threshold was determined to be 0.08%, 0.27%, and 0.15% for pH 12 buffer, distilled water and petrolatum respectively. Petrolatum was, therefore, effective in elicitation of ACD, and was more effective than distilled water. This was the case even though the Cr(VI) was contained in the carrier as a solid material.

Wahlberg (1973a) - Cr-sensitive subjects were patch tested with either potassium chromate (n = 31), or potassium dichromate (n = 21) in pH 12 buffer, distilled water and petrolatum. All subjects were tested with a range of concentrations across all three carriers. For potassium chromate, the alkaline buffer gave the lowest mean elicitation threshold, but water and petrolatum were not significantly different, and the number of subjects with thresholds in the lowest three dilutions was the same for water and petrolatum. For potassium dichromate, alkaline buffer gave the lowest mean threshold, but the mean threshold for petrolatum was significantly less than that for water. For both chromate and dichromate, the number of subjects with thresholds in the three lowest concentrations was the same for water and petrolatum.

Wahlberg (1973b) - Patch testing with potassium chromate (n = 47) or potassium dichromate (n = 43) was conducted with three carriers - pH 12 buffer, distilled water and petrolatum similarly to Wahlberg (1973a). For potassium chromate, the mean threshold for petrolatum was slightly larger than that for water, with alkaline buffer giving the lowest threshold. With dichromate, petrolatum gave a mean threshold between distilled water and buffer. The percentage with a lower threshold with petrolatum or with water was 23% and 44% respectively.

Liden and Lundberg (1979) – The penetration of Cr(VI), as potassium dichromate, through intact human skin was studied in thin-sections of punch biopsies from volunteers (n = 3-10) to whose back, patches were applied. The patches contained either 0.5% (5,000 ppm) of Cr (VI) in 6-8 mg of petrolatum (approximately 35 μg of Cr(VI)), or 0.5% Cr(VI) in 10 μL of water

(approximately 50 μg Cr(VI)). Biopsies were taken after removal of the patches at, 5, 24 and 72 hr after application. Regardless of the carrier material in which the Cr(VI) was contained, the Cr(VI) penetrated into the lowest level of dermis available from the biopsies. However, the penetration from the petrolatum was 2-7 times greater than from the water solution. Both the extent of penetration and the mass of Cr(VI) retained in the skin at 5 hr following the aqueous exposure remained unchanged at 72 hr. The kinetics of penetration from the petrolatum were not examined. This suggests that steady state was achieved by 5 hr. Although this observation does not predict the rate of elimination from the skin after 5 hr of exposure compared to the rates of elimination that would occur after longer exposure periods, it suggests the possibility that a 5 hr exposure could be sufficient to deliver a dose of Cr(VI) to the target cells in the dermis sufficient to elicit the an allergic contact dermatitis response.. The kinetics of an ACD response over periods shorter than 24-48 hr do not seem to have been investigated or reported elsewhere.

Gammelgaard et al.(1992) - The absorption and passage of "chromate" through excised skin was studied using petrolatum or "aqueous solution" on a filter. Application was occluded on the excised skin for 170 hr. The Cr was dispersed in the petrolatum as solid crystals. Recovery of Cr on the distal side of the skin layer was about 300 times greater for application of the aqueous solution than for application of the petrolatum. However, the mass of Cr retained in the skin surface and upper layers of the stratum corneum with the aqueous solution was only about twice that for the petrolatum. Thus, although permeation of Cr(VI) through the skin was much more effective for aqueous solution, the two carriers were roughly comparable in mobilizing the Cr(VI) into the skin. The authors conclude that "...only [*i.e., even*] very small amounts of chromium are able to elicit an allergic reaction, as the petrolatum patch test vehicle usually results in positive patch test reactions in chromium allergic patients."

Wass and Wahlberg (1991) - In response to reports of ACD in workers handling metal parts coated with a very thin (<1 μm) layer of Cr(VI) as protection against oxidation, patch testing with coated metal discs taped directly to the skin was conducted with Cr-sensitive subjects (n = 5). The release of Cr(VI) from the discs was characterized for each batch from which the test discs were drawn by a standard extraction procedure into synthetic sweat. A large inter-batch variability in release potential was noted. The discs were capable of eliciting ACD in a dose-response fashion relative to their Cr(VI) release potential. The authors note that the wide variability in release potential may explain negative results for "patch" testing of coated metal material directly on the skin in other studies (see Fregert et al., 1970; Bruynzeel et al., 1988).

Based on evaluation of these studies, the group concluded that it was not necessary that Cr(VI) be, *a priori*, in contact with the skin in aqueous solution to elicit ACD. Presumably, soluble Cr(VI) can be solubilized and mobilized by sweat. Furthermore, based on observations of solid Cr(VI) crystals in petrolatum, it appears that even solid Cr(VI) can be mobilized into the skin. The group agreed that elicitation of ACD by solid Cr(VI) in petrolatum may be analogous to elicitation of ACD from Cr(VI) in dry soil on the skin surface. The group therefore concluded that it was reasonable to consider an exposure scenario based on loading of Cr(VI) in soil on the skin without prior solubilization. The group further agreed that this could result in a risk-based approach quantified in terms of μg Cr(VI)/cm$^2$ skin surface, and, mg Cr(VI)/kg soil for a given loading of soil on the skin surface.

*Quantitative assessment of studies potentially useful for derivation of an ACD risk-based loading of Cr(VI) on skin*

The group identified three studies from which a dose-response relationship for elicitation of Cr ACD could be derived based on measurement of μg Cr(VI)/$cm^2$ skin. These are summarized briefly below.

Hansen et al. (2003) - Subjects (n = 18) known to be patch-test positive to Cr(VI) were patch tested with aqueous solutions of potassium dichromate. Although this study was conducted using solutions of Cr(VI) rather than dry or non-aqueous preparations, a known volume of material was administered in a chamber (Finn chamber) with a specific cross-sectional area attached to the skin surface. Thus, the applied solutions corresponded directly to known loadings of Cr(VI) in μg/$cm^2$. Skin reactions were read after 48 hours of exposure. There is some uncertainty in the published paper as to the diagnostic criteria used to identify ACD-positive reactions, with some indication that a more inclusive (i.e., more sensitive) criterion was used than that commonly used in patch test studies. This, however, is contradicted by other descriptions of the criterion in the paper, and the exact criterion is unclear. The minimum elicitation threshold (MET) – the smallest loading giving a positive reaction – was reported. This was converted to the proportion of the subjects responding at each loading. This reflects a consistent dose-response relationship

Wass and Wahlberg (1991) - This study in which Cr(VI) coated steel discs (7 per subject) were applied directly to the skin of five subjects for 48 hours was described previously. In this study, the available loading of Cr(VI) on the surface of each disc was determined by extraction of batch samples of each disc in a synthetic sweat solution. Thus the reported loading for each dermal application is an estimate of the Cr(VI) that could be presented to the skin surface when mobilized by sweat. This is not necessarily equivalent to the total loading of Cr(VI) on each disc. In addition, since the available loading was determined on batch samples rather than on the discs applied to the skin, the reported loading is somewhat uncertain. The dose-response data (converted to the proportion of subject responding at each level) show a consistent relationship with a clear threshold. However, the small sample size may result in overestimating the effective threshold.

Nethercott et al. (1994) - Subjects (n = 54) with a known Cr(VI) sensitivity were patch-tested with known loadings of potassium dichromate applied on the skin for 48 hours. The patches were TRUE-test patches containing a known mass of Cr(VI) incorporated into a hydrophilic gel that is spread over a known-area patch and then dried. Thus, a known loading of Cr(VI) (in terms of μg Cr(VI)/$cm^2$ skin) was applied dry. The gel could be hydrated on the skin by sweat, although this approach does not necessarily preclude solid transport into the skin as has been demonstrated with suspensions of solid Cr(VI) in petrolatum. The results of the patch-tests were read according to standard (NACDG) criteria. The response data, reported in terms of cumulative response, show a clear dose-response relationship.

The following table summarizes and compares the results of these studies based on the Cr(VI) loading at which 10% and 50% of the subjects responded with an ACD reaction. The table reflects the estimated responses based on fitting each data set to the same simplified dose-

response model (log-response) for purposes of comparison across models. This model does not necessarily give the best fit for any particular data set.

**Table 3.1 Comparison of Dose-Response Among Patch Test Studies Directly Measuring Surface Loading**

| Study | **10% Response** [a] | **50% Response** [a] |
|---|---|---|
| Hansen et al. (2003)<br>48 hr patch exposure<br>n = 18<br>$K_2Cr_2O_7$ | 0.02 μg/cm$^2$ [b,c] | 0.2 μg/cm$^2$ [b,c] |
| Nethercott et al. (1994)<br>48 hr exposure<br>n = 54<br>$K_2Cr_2O_7$ | 0.06 μg/cm$^2$ [b,d] | 0.5 μg/cm$^2$ [b,d] |
| Wass and Wahlberg (1991)<br>48 hr exposure<br>n = 5<br>"chromate" | 0.02 μg/cm$^2$ [b,e] | 0.1μg/cm$^2$ [b,e] |

**a.** This refers to cumulative response (not threshold).
**b.** Based on fitting cumulative response data to a log-response model.
**c.** Scoring of patch test reactions according to ICDRG criteria with + being the weakest response considered .
+ = "weak positive reaction – erythema, infiltration, discrete papules"
**d.** Scoring of patch test reactions included weak responses:
"erythema, infiltration, papules" (stated to be consistent with NACDG criteria)
**e.** Loading refers to available Cr(VI) solubilized from discs in synthetic sweat

Although there is some uncertainty regarding the comparability of the diagnostic scoring scale used by Hansen et al. (2003) relative to the other studies there is, nonetheless, a close agreement among the studies in terms of quantitative dose response. This provides confidence that surface loading is a consistent and reasonable metric for predicting Cr(VI) ACD. Based on these considerations, the group concluded that dose-response data based on skin surface loading of Cr(VI) in a non-aqueous medium could be used to derive a soil cleanup level. The group further concluded that, in light of the comparability among the studies, the Nethercott et al. (1994) study was the most appropriate study for quantitative dose-response modeling because of its much larger sample size.

Benchmark dose modeling was carried out on the Nethercott et al. (1994) data using the U.S.EPA's BMDS software package (ver. 1.3). The best fit was provided by the linear quantal model, which is a generalized statistical model. Other models (gamma, logistic) gave similar fits with similar model predictions. The details of these calculations are presented in Appendix C of

this report. The group agreed that it was appropriate to calculate the $BMDL_{10}$ (i.e., the lower 95% confidence limit on the dose corresponding to a 10% response) because the 10% response rate was within the lower end of the observable data, and because this is consistent with the benchmark dose approach previously conducted in support of the solution-based ACD soil cleanup guideline. The $BMDL_{10}$ was calculated to be 0.08 μg Cr(VI)/$cm^2$ skin. The $BMD_{10}$ (i.e., the dose corresponding to a 10% response) was calculated to be 0.1 μg Cr(VI)/$cm^2$ skin. This corresponds closely to the 10% response dose of 0.09 μg Cr(VI)/$cm^2$ skin reported by Nethercott et al. (1994), and used by MADEP (Zewdie, 1998). Because a 10% response is not a no-effect level, the group agreed that it was more appropriate to base a cleanup value on the BMDL rather than on the BMD.

*Uncertainty Factor (UF) Adjustments*

Of the standard categories for application of UFs in non-cancer risk assessment (sub-chronic-chronic, animal-human, LOAEL-NOAEL sensitive human populations, and database uncertainty), only the LOAEL-NOAEL and sensitive human population categories are potentially applicable to the consideration of the Nethercott et al. (1994) data. When basing risk-based standards on consideration of the administered doses only, ideally, one attempts to identify the NOAEL (no-observed-adverse-effect-level). If none of the administered doses corresponds to a NOAEL, then the dose corresponding to the lowest observed-adverse-effect level, the LOAEL, is identified, and a UF is applied to the LOAEL dose to estimate the theoretical NOAEL. The BMDL calculated from these data reflects the lower-bound estimate of the 10% response rate. As such, this is not, strictly speaking, a NOAEL. However, for several reasons, the benchmark dose (BMD) approach has generally been considered to supercede the NOAEL-LOAEL approach. In this case, the group agreed that the data do not suggest a clear threshold for response. Under such circumstances, the NOAEL does not have a clear meaning. Rather, the group specifically agreed that the BMDL would be used to identify a concentration corresponding to a minimal level of response that is consistent with the lower range of the data (i.e., the lower bound on the 10% response). The group believes that this approach is justified by the relatively mild nature of the adverse response at this dose. Based on this approach, the group does not believe that it is appropriate to apply a UF for the LOAEL-NOAEL adjustment. In the Nethercott et al. study, the subjects were all selected on the basis of an existing Cr(VI) sensitization. the group, therefore, believes that these data already reflect the sensitive human population. Although within this population, there is a range of sensitivities, this implications of this range have already been considered in the application of the BMDL approach. Based on these considerations, the group does not believe that it is appropriate to apply UF adjustments to the BMDL.

*Consideration of Soil Loading on the Skin*

In order to derive a soil concentration corresponding to the BMDL for Cr(VI) on the skin, it is necessary to assume a value for soil loading on the skin. The concentration of Cr(VI) in the soil corresponding to the BMDL is then calculated as the ratio of Cr(VI) loading on skin/soil loading on skin. This assumes that the concentration of Cr(VI) in the soil adhering to the skin surface is the same as the concentration of Cr(VI) in soil on the ground. There is no unique value for soil

loading on the skin. The group considered various possible scenarios leading to soil adherence on the skin. These can range from casual and/or indirect contact with soil and dust to occupational and recreational contact with wet soil and mud. Different scenarios differ not only in the amount of soil per surface area, but also on the amount of skin surface available for soil adherence. The group agreed that the soil adherence factor should not reflect rare or unusual exposures. In addition, the group took into account that in Nethercott et al. (1994) (as well as in the other studies considered), the Cr(VI) was in contact with the skin surface continuously for 48 hr before a determination of elicitation of an ACD response was made. This would tend to preclude large soil loadings that would tend to fall off or be removed during this extended period. The study of Lidén and Lundberg (1979) raises the possibility that much shorter exposures could be sufficient to elicit an allergic response. Such shorter periods could be consistent with retention of larger soil loadings. Therefore, assumption of 24 hr of contact may result in underestimating the appropriate soil loading, and thus overestimating the corresponding soil concentration of Cr(VI). However, given the incomplete evidence, the group agreed that it was appropriate to select a soil loading that was consistent with at least 24 hr of skin contact. The assumption of soil retention on the skin for 24 hr precludes heavy soil loading that is likely to fall off or to be washed off the skin within 24 hr.

The following documents were among those reviewed:

1. Massachusetts Department of Environmental Protection, Technical Update, Weighted Skin-soil Adherence Factors, April 2002.
2. U.S. Environmental Protection Agency, Exposure Factors Handbook, February 1999.
3. U.S. Environmental Protection Agency, Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites, Draft final, August 2001.
4. U.S. Environmental Protection Agency, Risk Assessment Guidance for Superfund, Volume I: Human Health, Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment), Interim, March 2003

The Risk Assessment Guidance for Superfund, Volume I, Part E (RAGS Part E) is the most current of the major, broad-based documents reviewed. The USEPA considers it to "update and supercede" all other USEPA dermal guidance documents. It is also being utilized as part of the NJDEP's Soil Remediation Standard development effort. Furthermore, the use of this document complies with the Governor's Executive Order Number 27 and N.J.S.A. 58:10B that require consideration of and to the greatest extent possible consistency with the USEPA standards and guidance. The NJDEP is currently planning to use the RAGS Part E soil adherence factor as part of the process for the remediation of contaminated soil in New Jersey. Furthermore, because the NJDEP's soil remediation program parallels the actions and intentions of the Superfund program, there is a logical reason for consistency in the choice of a soil loading/adherence factor between the two programs. Based on these considerations, the group agreed that RAGS Part E is the most appropriate source for a soil adherence factor. In recognition of the range of possible exposure scenarios, and the various parameters that mediate within those parameters, the RAGS Part E approach provides for the selection of either the central tendency estimate of a high end activity or the upper end of a more typical activity. Both of these, represent a reasonable maximum exposure (RME) estimate. The group agreed that given the uncertainty inherent in the range of possible soil adherence/loading values, the use of a reasonable maximum exposure

value was appropriate. The group therefore concluded that a soil adherence factor of 0.2 mg/cm$^2$ should be used. This value is surface area-weighted for a child resident up to 6 years of age wearing a short-sleeved shirt and shorts with no shoes. The recommended weighted adherence factor is based on the 95$^{th}$ percentile (upper end) adherence factor for children playing at a day care center (typical soil contact activity) or the 50$^{th}$ percentile (central tendency) adherence factor for children playing in wet soil (high end soil contact activity). This value is also protective of the adult in a residential setting because the corresponding adherence factor for an adult is given as 0.07 mg/cm$^2$. For a nonresidential exposure under a reasonable maximum exposure scenario, a soil adherence of 0.2 mg/cm$^2$ is applicable. This is surface weighted for an adult since children in the work place are considered to be atypical. The adult receptor is assumed to wear a short-sleeved shirt, long pants, and shoes. This recommended weighted adherence factor is based on the 50$^{th}$ percentile (central tendency) adherence factor for a utility worker (high end soil contact activity). The soil adherence/loading value of 0.2 mg/cm$^2$ differs from the value of 0.51 mg/cm$^2$ assumed by the MADEP based on a 1996 USEPA guidance (Zewdie, 1998).

It should be noted that the RAGS Part E approach was originally intended to address systemic (i.e., whole body) exposure. For that purpose, it is appropriate to express the soil loading/adherence as a weighted average of soil on the entire exposed skin surface. This is because the internal dose of a dermally absorbed contaminant is a function of the sum of absorption across all exposed areas. Thus, the weighted average soil loading/adherence factor reflects exposed areas of the body with little or no loading as well as areas with much greater loading. ACD, however, is not a classic systemic response. Rather, it results from the reaction of the immune system to allergens absorbed through one or more discrete areas of the skin and presented to T-cells at local lymph nodes. Thus, an ACD response can result from absorption of an allergen across a relatively small and localized area of skin. For the specified exposure scenarios, the RAGS Part E factor underestimates the soil loading/adherence on the discrete skin surfaces with the heaviest soil contact. Since these discrete surfaces may be sufficiently large to mobilize an ACD reaction, the RAGS Part E factor likely underestimates the appropriate soil loading/adherence relative to ACD potential, even for the specific exposure scenarios they are intended to address. Thus, because the RAGS Part E factor underestimates the effective local soil loading, use of this factor can result in overestimating the resulting ACD soil cleanup value. The group recognizes this uncertainty, but nonetheless, recommends the use of this value for consistency with use of the RAGS Part E factor in conjunction with soil cleanup standards based on systemic endpoints.

*Calculation of a Cr(VI) soil concentration based on Nethercott et al. (1994), and an assumed soil loading factor*

Assuming that the soil that adheres to the skin has the same Cr(VI) concentration as the soil on the ground from which it was derived, the Cr(VI) soil concentration is simply calculated as $BMDL_{10}$/soil loading. Given the values based on the prior conclusions of the group, the ratio is calculated as:

$$\frac{0.08\ \mu g\ Cr(VI)\ /cm^2\ skin}{0.2\ mg\ soil/\ cm^2\ skin} = 0.4\ \mu g\ Cr(VI)\ /mg\ soil = 400\ mg/g = 400\ ppm.$$

*Bioavailability*

This calculation implicitly assumes that the Cr(VI) in the soil will have the same availability to the skin surface as the Cr(VI) in the patches used by Nethercott et al. (1994). In the absence of site specific data, the extent to which such an assumption is valid is uncertain. Although the Cr(VI) material in the patches in the Nethercott et al. (1994) study was incorporated as soluble potassium dichromate, it is not known to what extent the mass of Cr(VI) in the patches actually entered into the skin (either by solubilization or solid transport). If less than 100% of the Cr(VI) in the patches entered the skin, this would result in overestimating the BMDL from the original Nethercott et al. (1994) data. On the other hand, the Cr(VI) in the soil may be less soluble than the pure potassium dichromate in the patches. This would result in underestimating the soil concentration of Cr(VI) corresponding to the BMDL. These considerations result in opposite effects on the soil cleanup value. In addition, it should be remembered that, based on the studies of elicitation of ACD with Cr(VI) in petrolatum, *a priori* solubilization of the Cr(VI) on the skin surface is not necessary for the ACD response. Therefore, considerations of bio-availability of Cr(VI) in the soil based on solubility may tend to underestimate its ACD potential. Based on these considerations, the group concluded that it was most appropriate to assume that Cr(VI) in the soil has the same bio-availability for ACD as the Cr(VI) in the Nethercott et al. (1994) patches. That is, 100% relative bio-availability should be assumed, and therefore, *a priori* adjustments for the bio-availability of Cr(VI) in soil are not appropriate.

*Consistency with the existing Cr (VI) ACD standard*

The approach developed here may eliminate some of the uncertainties and assumptions inherent in the previous approach based value based on exposure of the skin to Cr(VI) in solution, and expressed in terms of concentration (μg Cr(VI) /L). Nonetheless, the group agreed that a soil cleanup value based on direct contact of dry soil on the skin expressed in terms of surface loading (μg Cr(VI) /$cm^2$ skin) addresses a different scenario than the previous ACD approach. The previous ACD approach addresses exposure to Cr(VI) that has already been eluted from the soil, and is present in the environment in solution. Such a scenario will occur in the case of a puddle or wet, muddy soil. The direct contact approach developed here, specifically addresses contact with dry soil. The group believes that both approaches are valid for their specific scenarios. The group recommends that each approach be considered in terms of the specific application, the practicality of its use, and the extent to which each can provide adequate protection of public health. In the case where both approaches are applicable, both values should be calculated, and the lower value should be selected as the ACD cleanup criterion.

## Recommendations

1. The results of the Davidson et al. (2004) study of the co-carcinogenicity of UV radiation and Cr(VI) ingestion should not form the basis of a revised soil cleanup value for Cr(VI). Nonetheless, this study raises the possibility that the cancer risk posed by exposure to Cr(VI) could be larger than that currently used by the NJDEP in the derivation of its soil standards. Therefore, additional research on the oral carcinogenicity of Cr(VI) would be valuable and any

additional data should be rapidly evaluated to determine whether they provide sufficient additional evidence of oral carcinogenicity for Cr(VI).

2. The NJDEP should consider adopting a cleanup value based on the Nethercott et al. (1994) study and USEPA's current guidance on reasonable maximum soil adherence on skin as developed in this document. Based on the assessment of this group, a value of 400 ppm Cr(VI) is recommended for direct contact with soil. This value should be applied under the assumption of 100% bioavailability. The current approach for calculating an ACD-based Cr(VI) soil cleanup value based on the concentration of Cr(VI) in solution remains valid. That approach, and the approach developed here, based on direct contact with Cr(VI) in soil, should be used in parallel. In situations where both exposure scenarios are reasonable, the approach yielding the lower soil cleanup value should be employed. The methodology for COPR aqueous extraction procedures should continue to be used in its current form. However, efforts should be made to determine whether a more precise and accurate method can be derived.

3. Findings from the ongoing National Toxicology Program's chronic ingestion bioassay of Cr(VI) should be closely followed. The NJDEP's policy and soil cleanup guidance for Cr(VI) should be re-evaluated in conjunction with those findings.

4. New assessments of the ingestion carcinogenicity of Cr(VI) from California state government and elsewhere should be evaluated when they become available. NJDEP policy should be re-evaluated based on expert review of those assessments.

5. Cr(VI) should be considered to have the potential to elicit allergic contact dermatitis (ACD) with direct contact from contaminated soil without prior solubilization

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# Appendix A

## Analysis of Data from Davidson et. al. (2004) Paper

## The Data

The raw data were provided by the authors in a personal communication to Dr. Leo Korn (DSRT/NJDEP) in the form of an Excel spreadsheet. The study is described in Davidson et. al. (2004). All of the mice included in the provided data were exposed to UV. The Excel data were converted to a SAS data set. A printout of the data is attached (see Table A.2). All tumors were tested for malignancy in the two lower dose groups (0 ppm and 0.5 ppm). In the higher dose groups (2.5 ppm and 5.0 ppm) a random sample from all tumors was tested for malignancy. The number of malignant tumors will always be less than or equal to the number of tumors diagnosed.

## Data Analysis Strategies

The possible outcome measures of interest are:

1. Number of mice with tumors
2. Number of tumors per mouse.
3. Number of mice with malignancies.
4. Number of malignancies per mouse.
5. Proportions of malignant tumors per mouse.

It is of interest whether there is a relationship between magnitude of dose and these five outcomes.

Table A.1. Davidson Data

*Davidson Data*

| Mouse ID | Chromium Dose (ppm) | Number of Tumors > 2mm | Number of Tumors Diagnosed | Number of Malignant Tumors |
|---|---|---|---|---|
| 16 | 0.0 | 0 | 0 | 0 |
| 17 | 0.0 | 2 | 2 | 1 |
| 18 | 0.0 | 0 | 0 | 0 |
| 19 | 0.0 | 0 | 0 | 0 |
| 20 | 0.0 | 1 | 1 | 1 |
| 21 | 0.0 | 1 | 1 | 0 |
| 22 | 0.0 | 4 | 4 | 2 |
| 23 | 0.0 | 0 | 0 | 0 |
| 24 | 0.0 | 1 | 1 | 1 |
| 25 | 0.0 | 1 | 1 | 0 |
| 26 | 0.0 | 0 | 0 | 0 |
| 27 | 0.0 | 0 | 0 | 0 |
| 28 | 0.0 | 0 | 0 | 0 |
| 29 | 0.0 | 1 | 1 | 1 |
| 3 | 0.0 | 0 | 0 | 0 |
| 31 | 0.5 | 1 | 1 | 1 |
| 33 | 0.5 | 1 | 1 | 0 |
| 35 | 0.5 | 0 | 0 | 0 |
| 36 | 0.5 | 3 | 3 | 1 |
| 37 | 0.5 | 0 | 0 | 0 |
| 38 | 0.5 | 0 | 0 | 0 |
| 39 | 0.5 | 4 | 4 | 2 |
| 41 | 0.5 | 3 | 3 | 2 |
| 42 | 0.5 | 0 | 0 | 0 |
| 43 | 0.5 | 2 | 2 | 1 |
| 44 | 0.5 | 0 | 0 | 0 |
| 46 | 2.5 | 2 | 2 | 1 |
| 47 | 2.5 | 0 | 0 | 0 |
| 48 | 2.5 | 0 | . | |
| 49 | 2.5 | 2 | . | |
| 50 | 2.5 | 2 | 2 | 2 |
| 51 | 2.5 | 5 | 3 | 1 |
| 52 | 2.5 | 1 | . | |
| 53 | 2.5 | 0 | . | |
| 54 | 2.5 | 1 | . | |
| 55 | 2.5 | 0 | . | |

*Davidson Data*

| Mouse ID | Chromium Dose (ppm) | Number of Tumors > 2mm | Number of Tumors Diagnosed | Number of Malignant Tumors |
|---|---|---|---|---|
| 56 | 2.5 | 2 | . | . |
| 57 | 2.5 | 2 | . | . |
| 58 | 2.5 | 0 | . | . |
| 59 | 2.5 | 3 | . | . |
| 60 | 2.5 | 0 | 0 | 0 |
| 61 | 2.5 | 10 | . | . |
| 62 | 2.5 | 5 | . | . |
| 63 | 2.5 | 1 | . | . |
| 64 | 2.5 | 11 | . | . |
| 106 | 5.0 | 5 | . | . |
| 107 | 5.0 | 2 | . | . |
| 108 | 5.0 | 5 | . | . |
| 109 | 5.0 | 9 | 4 | 2 |
| 110 | 5.0 | 4 | . | . |
| 111 | 5.0 | 2 | . | . |
| 112 | 5.0 | 4 | 3 | 2 |
| 113 | 5.0 | 2 | . | . |
| 114 | 5.0 | 0 | . | . |
| 115 | 5.0 | 0 | . | . |
| 116 | 5.0 | 4 | . | . |
| 117 | 5.0 | 9 | . | . |
| 118 | 5.0 | 4 | 3 | 3 |
| 119 | 5.0 | 0 | . | . |
| 120 | 5.0 | 10 | 2 | 1 |
| 121 | 5.0 | 10 | . | . |
| 122 | 5.0 | 17 | . | . |
| 123 | 5.0 | 0 | . | . |
| 124 | 5.0 | 3 | 3 | 3 |

## Number of Mice with Tumors

Table A.2 presents the proportion of mice with tumors in each dose group.

Table A.2: Proportion of Mice with Tumors in Each Group

| Dose (ppm) | Number of Mice | Proportion of Mice with Tumors |
|---|---|---|
| 0 | 15 | 0.4666667 |
| 0.5 | 11 | 0.5454545 |
| 2.5 | 19 | 0.6842105 |
| 5 | 19 | 0.7894737 |

There appears to be a relationship between dose and proportion of mice with tumors. The statistical significance of this relationship can be ascertained by the Jonckheere-Terpstra test. This is a non-parametric test for trend. The two-sided p-value for this test is .0002. The observed trend is highly significant.

Another way to look at the relationship is through a logistic regression model, which predicts the probability of a mouse having at least one tumor as a linear function of dose. The estimated dose parameter in this model is 0.2849 (p=0.0450). There is a significant positive relationship between dose and probability of tumor. The odds ratio for a 1 ppm increase in dose is 1.33 with a 95% confidence interval of (1.006, 1.757).

## Number of Tumors per Mouse

Table A.3 presents the average number of tumors per mouse in each dose group.

Table A.3: Average Number of Tumors>2mm in Each Group

| Dose (ppm) | N | Average Number of Tumors | Std Dev | Minimum | Maximum |
|---|---|---|---|---|---|
| 0 | 15 | 0.7333333 | 1.0997835 | 0 | 4 |
| 0.5 | 11 | 1.2727273 | 1.4893562 | 0 | 4 |
| 2.5 | 19 | 2.4736842 | 3.2209112 | 0 | 11 |
| 5 | 19 | 4.7368421 | 4.4701741 | 0 | 17 |

There appears to be a relationship between dose and the average number of tumors. The statistical significance of this relationship can be ascertained by a Poisson Regression model, which predicts the expected number of tumors, by a function of dose. The estimated parameter for dose is 0.3199 ($p<0.0001$) so the observed trend is highly significant.

Graphically, the relationship can be illustrated in Figure 1. In the plot, the stars represent one or more data points and the diamonds represent the average count in each dose group. Line segments connect the average counts. The increasing trend in the average counts can be clearly seen.

## Number of Mice with Malignancies

The analysis of malignancies is more complicated due to the random sampling of tumors at higher doses. Since selection was randomized with respect to tumors rather than with respect to mice, mice with large numbers of tumors would be more likely to be sampled than mice with only a few tumors. If there is an association between the number of tumors and the probability of malignancy then the analysis might be biased. On the other hand, an examination of the data in the two highest dose groups does not show a gross over-sampling of mice with many tumors. Table A.4 breaks down the number of samples taken from mice with the specified number of tumors. From Table A.4 one can see that tumors were sampled from mice with 2 tumors and 5 tumors in dose group 2.5 and from mice with 3,4,9 and 10 tumors in dose group 5. Mice with 10 tumors and 11 tumors were not sampled in dose group 2.5. A mouse with 17 tumors and one of the mice with 10 tumors were not sampled in dose group 5

Table A.4: Number of Samples taken from Mice with Specified Number of Tumors

| Dose | # Total tumors per mouse >2mm | # Tumors per mouse diagnosed for malignancy | Number of mice |
|---|---|---|---|
| 0 | 1 | 1 | 5 |
| 0 | 2 | 2 | 1 |
| 0 | 4 | 4 | 1 |
| 0.5 | 1 | 1 | 2 |
| 0.5 | 2 | 2 | 1 |
| 0.5 | 3 | 3 | 2 |
| 0.5 | 4 | 4 | 1 |
| 2.5 | 2 | 2 | 2 |
| 2.5 | 5 | 3 | 1 |
| 5 | 3 | 3 | 1 |
| 5 | 4 | 3 | 2 |
| 5 | 9 | 4 | 1 |

| | | | |
|---|---|---|---|
| 5 | 10 | 2 | 1 |

There are several ways to count proportions. Since some mice have no tumors, they may be counted as mice with no malignancy. If the mice with no tumors are included in the counting, the proportions of mice with malignancies in each dose group are shown in Table A.5.

Table A.5: the proportions of mice (with malignancies, counting mice with no tumors)

| Dose | N | Proportion of Mice with Malignancy |
|---|---|---|
| 0 | 15 | 0.3333333 |
| 0.5 | 11 | 0.4545455 |
| 2.5 | 19 | 0.3333333 |
| 5 | 19 | 0.5555556 |

Table A.5 does not show a well-defined trend. A logistic regression model has a non significant parameter estimate for dose, (0.13, $p<0.42$). There is no evidence of a dose response relationship when looking at the data in this way.

If mice with no tumors were not counted as having zero malignancies, this could be considered an analysis conditioned on mice with tumors. In this case the proportions of mice with malignancies are given in Table A.6.

Table A.6: The proportions of mice with malignancies (omitting mice with no tumors)

| Dose | N | Proportion of Mice with Malignancy |
|---|---|---|
| 0 | 7 | 0.7142857 |
| 0.5 | 6 | 0.8333333 |
| 2.5 | 3 | 1.0000000 |
| 5 | 5 | 1.0000000 |

While there does appear to be a defined trend in the observed proportions, the sample sizes are very small and the logistic regression is not significant (dose parameter estimate=1.7, $p<0.42$).

## Number of Malignancies per Mouse

Interpreting the average number of malignancies per mouse is perilous, since it will be dependent to some extent on the number of tumors per mouse and the number of tumors sampled per mouse. Even if a dose-response is clearly evident, it is not obvious what it means. Table A.7 presents the average number of malignancies per mouse in each dose group, including mice with zero tumors.

Table A.7: Average number of malignancies per mouse

| Dose | N | Average # Malignancies | Minimum | Maximum |
|---|---|---|---|---|
| 0 | 15 | 0.4000000 | 0 | 2. |
| 0.5 | 11 | 0.6363636 | 0 | 2 |
| 2.5 | 19 | 0.8000000 | 0 | 2 |
| 5 | 19 | 2.2000000 | 1 | 3 |

This Table A.7 shows a well-defined trend. A Poisson regression model indicates that the dose parameter is significant (0.3133, p<. 001).

## Proportions of Malignant Tumors per Mouse

The proportion of malignant tumors per mouse is defined as the number of malignancies divided by the number of tumors tested. Those mice with no tumors may be counted as either undefined or as zero. Tables A.8 and A.9 present these results.

Table A.8: Mean Proportion of Malignancies with Zero Tumors Counted as Zero Proportion

| Dose | N | Mean Proportion |
|---|---|---|
| 0 | 15 | 0.2666667 |
| 0.5 | 11 | 0.2727273 |
| 2.5 | 9 | 0.2037037 |
| 5 | 19 | 0.4074074 |

Table A.9: Mean Proportion of Malignancies with Zero Tumors Not Counted

| Dose | N | Mean Proportion |
|---|---|---|
| 0 | 7 | 0.5714286 |
| 0.5 | 6 | 0.5000000 |
| 2.5 | 3 | 0.6111111 |
| 5 | 5 | 0.7333333 |

In both tables, the trends are not well defined. Note that the sample sizes are quite small in table 8. Tests of significance were not performed on the data of Tables A.8 and A.9.

## Conclusions

There is a significant relationship between dose and counts of total tumors, dose and proportion of mice with tumors, and dose and malignancy counts. The interpretation of malignancy counts is difficult due to the sampling scheme and the relationship between number of total tumors and number of malignancies.

## References

1. Davidson, T., Kluz, T., Burns, F., Rossman, T., Zhang, Q., Uddin, A., Nadas, A., Costa, *M. (2004). Exposure to chromium (VI) in the drinking water increases susceptibility to UV-induced skin tumors in hairless mice.* Toxicology and Applied Pharmacology (in press).

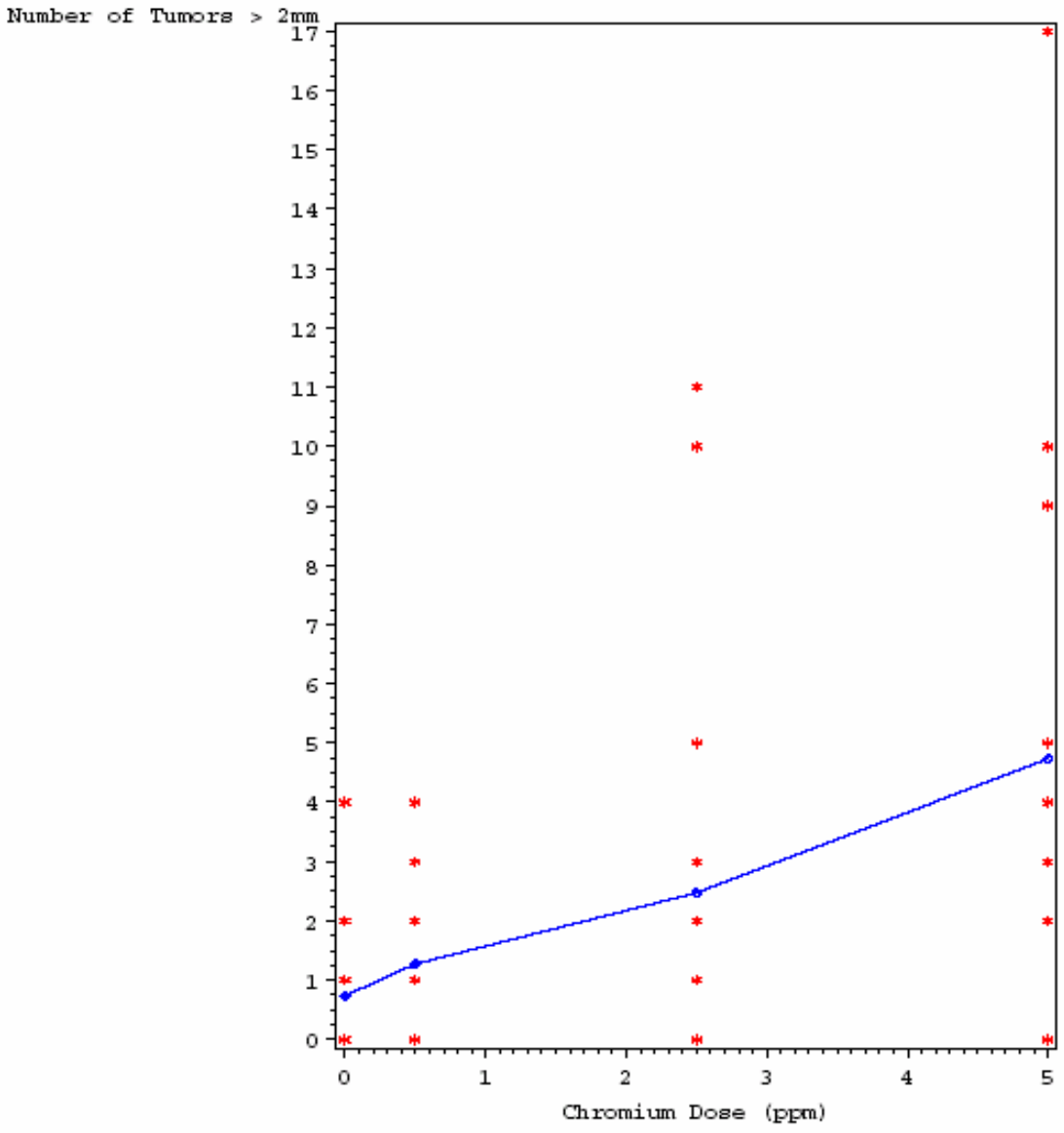


**Figure A.1: Number of Tumors Greater than 2mm**

## Appendix B

## Background Information on the Physics and Biology of UV Radiation with Reference to the Exposures in Davidson et al. (2004)

**DEFINITIONS AND CONVERSION FACTORS**

| | |
|---|---|
| Action Spectrum | An action spectrum is a range of wavelengths in which biological effectiveness can be defined. |
| Biological Effectiveness - | The biological effectiveness is a measure of the effectiveness of radiation at different wavelengths (within a defined range or action spectrum) in carrying out a specific reproducible photobiological process. |
| Irradiance - | The unit of radiant power per unit area (Watt/cm$^2$) is the irradiance. |
| MED - | Minimal erythema dose. |
| Radiant Exposure (Dose) - | The unit of radiant energy per unit area (joules/ cm$^2$ ) is the radiant exposure. |
| Relative Biological Effectiveness - | The relative biological effectiveness is an experimentally determined ratio of an absorbed dose of a reference radiation required to produce an identical biological effect in a particular organism or tissue. |

Radiant Energy Units

| | erg | joule | W sec | µW sec |
|---|---|---|---|---|
| erg= | 1 | $10^{-7}$ | $10^{-7}$ | 0.1 |
| joule= | $10^7$ | 1 | 1 | $10^6$ |
| W sec= | $10^7$ | 1 | 1 | $10^6$ |
| µW sec= | 10 | $10^{-6}$ | $10^{-6}$ | 1 |

Radiant Exposure (exposure dose) Units

| | Erg/cm$^2$ | joule/cm$^2$ | W sec/cm$^2$ | µW sec/cm$^2$ |
|---|---|---|---|---|
| erg/cm$^2$= | 1 | $10^{-7}$ | $10^{-7}$ | 0.1 |
| joule/cm$^2$= | $10^7$ | 1 | 1 | $10^6$ |
| W sec/cm$^2$= | $10^7$ | 1 | 1 | $10^6$ |
| µW sec/cm$^2$ | 10 | $10^{-6}$ | $10^{-6}$ | 1 |

Irradiance (exposure dose rate) Units

| | Erg/cm$^2$ sec | joule/cm$^2$ sec | W/cm sec $^2$ | µW/cm$^2$ sec |
|---|---|---|---|---|
| erg/cm$^2$ sec = | 1 | $10^{-7}$ | $10^{-7}$ | 0.1 |
| joule/cm$^2$ sec = | $10^7$ | 1 | 1 | $10^6$ |

| | | | | |
|---|---|---|---|---|
| W /cm$^2$ = | $10^7$ | 1 | 1 | $10^6$ |
| μW/cm$^2$= | 10 | $10^{-6}$ | $10^{-6}$ | 1 |

Ultraviolet radiation is at shorter wavelengths than the visible spectrum (400 to 700nm). In physics applications UV is divided into three components (NASA, 2004):

UVA - 315 to 400 nm (Long wave)
UVB - 280 to 315 nm (GE does not make these)
UVC - less than 280 nm

Environmental photobiologists normally define wavelength regions slightly differently as:
UVA - 320 to 400 nm
UVB - 290 to 320 nm
UVC 200 to 290 nm (Diffey, 1991)

The division between UVB and UVC is chosen at 290 nm because UV radiation (UVR) at shorter wavelengths is unlikely to be present in terrestrial sunlight except at high altitudes (Henderson 1977, as cited by Diffey, 1991).

## Physics of Ultraviolet light:

### Sunlight

Most of the light that hits the earth comes from our sun which emits radiation with wavelengths as short as 100 nanometers (nm = millimicron = mμ). Oxygen in the upper atmosphere absorbs most of the radiation shorter than ~ 200 nm. This process produces ozone, which absorbs strongly with a maximum at 253 nm, but a weak tail extends to approximately 330 nm. This edge of the ozone absorption band determines the cut-off of ultraviolet (UV) that reaches the earth. Except at high altitude, very little light < 295 nm reaches earth.

Light is scattered by the atmosphere and by particulates, which can both scatter and absorb radiation (light). Light interaction with air molecules causes Raleigh scattering which is a function of wavelength: shorter wavelengths, such as UV being scattered more. As much as two thirds of the UV at 310 nm is scattered.

Ozone (O3) is formed by dissociation of oxygen by short wavelength UVR (lambda <242 nm) at altitudes of 25 to 100 km. Absorption of UVR at wavelengths up to 320 nm converts the O3 back to O2 and O (Chapman 1930, as cited by Diffey, 1991). Dissociation of O3 is responsible for preventing wavelengths less than about 290 nm from reaching the Earth's surface.

The spectral irradiance of UVR on the Earth's surface is modified by temporal, geographical, and meteorological factors such that the UV spectral irradiance falls by a factor of two or three as the wavelengths decrease from 400 to 320 nm at solar altitudes higher than 20 degrees. They drop rapidly by three orders of magnitude or more from 320 to 290 nm by the absorption of stratospheric ozone (Diffey, 1991).

The energy in about a 3-minute sunlight exposure (UVA, primarily 365 nm) would be:

Dosage Energy = UV Intensity X Time
= 2.5 mW/cm2 X 200 sec
= 500 mJ/cm2
Where:

mW = milliwatts
mJ = millijoules

## UV Lamps

Hill and Hill (2000) reported the following spectral distributions for the Westinghouse lamp used by Davidson et al. (2004).

Westinghouse polychromatic FS20: 0.0065 % UVC, 42.3% UVB, 37.3 % UVA, and 23.8 % visible.

The FS-20 lamp emits an energy spectrum with a high influence in the 280 - 360 nm UVB region peaking at 313 nm (as cited in Peus et al., 2000 and Mitchell et al., 2002).

Davidson et al. (2004) reported that less than 1% of the UV light from the FS-20 lamps was in the UVC range, while 85% was in the UVB spectral range (320 - 400 nm) and the visible spectrum. Hill and Hill (2000) independently reported the FS-20 bulb emitting 0.0065% in the UVC spectral.

General Electric Lighting Company via e-mail. Technical specialist Donna L. Quesenberry (GE Consumer & Industrial), provided the following information:

The only lamps GE makes in the UV range are germicidal (UVC 100-280 nm) and the blacklight (white glass-blue light)/blacklight blue (blue glass-blue light) (315-400nm, UVA). GE does not make any UVB lamps which are sometimes used for medical purposes or tanning beds.

Some wavelengths (180-220) produce ozone, some (220-300) are bactericidal, some (280-320) erythemal (redden human skin), others (320-400) cause secondary luminance (blacklight).

Spectral Distribution curves are available in the GE Lighting Application Bulletin which is available in e-doc (keyword blacklight or UVA).

Two faxed pages contained SPB UV and BL/BLB UV Maintenance curves (Percent UV emitted versus Lamp Life in hours of usage) and BLB and BL Spectral Power curves comparing Irradiance expressed as W/cm2/nm versus Wavelength in nm. These curves for the BL lamp showed maximal peaks at ~375 (range 350 to 400), and visible light peaks at ~410 (very minimal), a middle value peak at ~440, and a smaller peak at 550 nm.

## Biology of Ultraviolet light:

Diffey (1991) discusses molecular and cellular ultraviolet photobiology, absorption characteristics of important biomolecules, action spectra, photoproducts, inactivation of microorganisms, and repair mechanisms. Observable biological effects in man due to UVR are limited to the skin and eyes because of the low penetrating properties of UVR in human tissues. Penetration is less than 1 mm in skin (Bruls et al., 1984; as cited by Diffey, 1991) and UVR is absorbed by ocular tissues, mainly the cornea and the lens, before reaching the retina.

Acute reactions of UVR on the skin are sunburn, tanning, and vitamin D production. Photo-aging and skin cancer are considered chronic reactions produced by prolonged or repeated UVR exposures.

Sunburn, or erythema, is an acute injury following excessive exposure to sunlight. Redness of the skin results from an increased blood content of the skin by dilatation of the superficial blood vessels in the dermis, mainly the subpapillary venules. Half an hour of midday summer sunshine in the UK on the unacclimatized skin of Caucasian subjects is normally sufficient to elicit a subsequent mild reddening of the skin. Erythema reaches a maximum about 8 to 12 hours later and fades within 1 to 2 days (Olson et al., 1996; Farr et al., 1988; as cited by Diffey, 1991). Repeated exposures to sunlight for longer periods progressively shortens the time before appearance of erythema, lengthens the persistence, and increases its intensity. High exposures may result in edema, pain, blistering, and, after a few days, peeling.

The minimal erythema dose or MED at a given wavelength in a group of fair-skinned individuals is distributed lognormally. In 254 normal subjects in North East England the MED at 300 nm was determined to be 34 mJ/cm$^2$ with a 95% confidence interval of 14-84 mJ /cm$^2$ (Diffey, 1991). Above 300 nm the effectiveness drops rapidly, falling to an efficiency at 320 nm of about 1% of that at 300 nm. The erythema action spectrum up to 400 nm has been determined, although the rate of change of effectiveness is much less from 330 to 400 nm, than from 300 to 330 nm. ) Figure B.1 shows an action spectrum accepted by the Commission Internationale de l'Eclairage (CIE) and the International Electrotechnical Committee (IEC) and has been shown to predict accurately the erythemal effectiveness of several polychromatic light sources differing greatly in spectral composition (Urbach 1987, as cited by Diffey, 1991). Learn et. al., (1993) reported that for an equal amount of energy delivered, radiation from the unfiltered lamps was more potent in causing the erythemal response than filtered lamps that removed the UVC spectral component of that lamp. Specifically, on a power versus response basis 3.2 % of the power for UVC was responsible for an average of 13.9 % (11.1 and 16.7%) of the erythemal response.

Although UVA is much less erythmogenic than UVB, broadly speaking by a factor of 1000, the much higher UVA present in sunlight means in summertime UVA radiation contributes about 15 to 20% to the sunburn reaction.

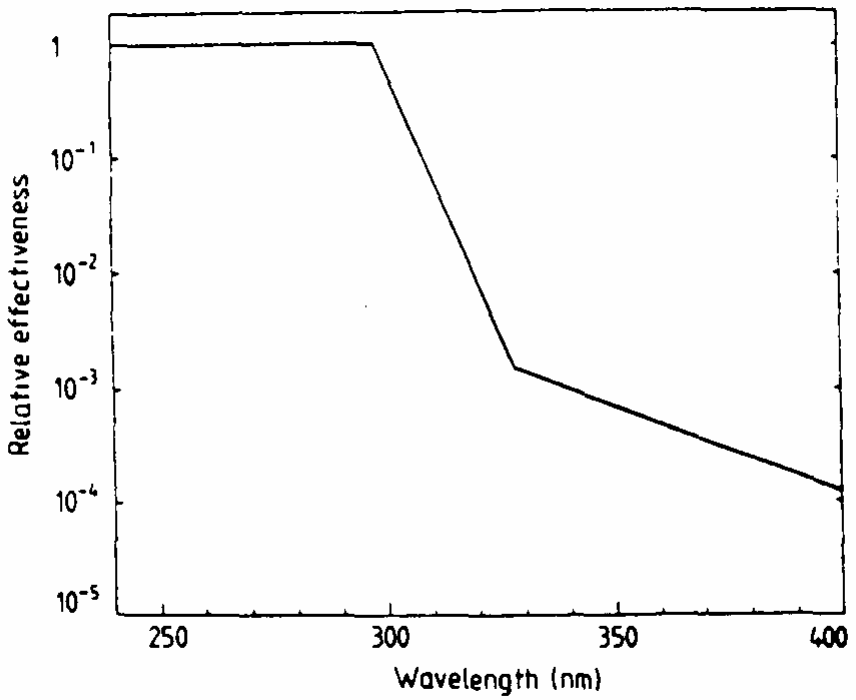


**Figure B.1: The CIE Reference Erythema Action Spectrum [McKinlay and Diffey (1987)**

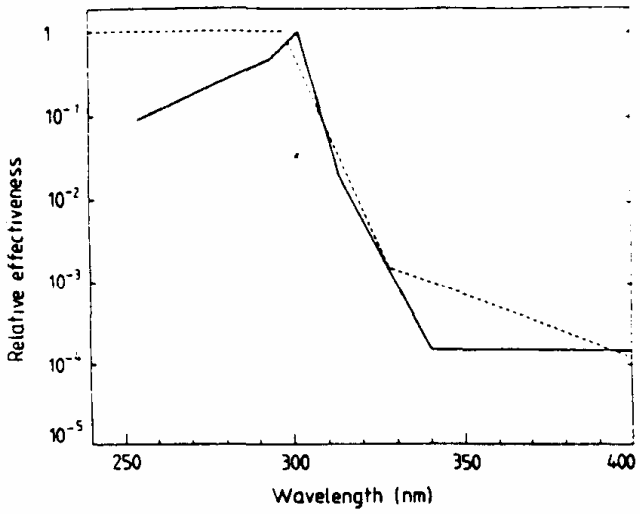


**Figure B.2: The absorption spectrum of nucleic acids and the action spectrum for the inactivation of *E. coli.* cells [reproduced from Harm (1980)].**

Figure B.2 compares the CIE Reference Erythema Action Spectrum to the action spectrum for UV photocarcinogenesis. Note that the action spectra for photocarcinogenesis is at a maximum at about 302 nm and drops by a factor of 10 at approximately 254 nm, whereas, the erythema action spectra is maximal from about 297 to below 254 nm. At wavelengths greater than 290 nm there is reasonable agreement between the curves. Thus, while UVC is generally more effective than UVB in producing erythema, it is much less effective in production of tumors. An explanation for this difference is suggested by Figure B.3. It appears that while UVC radiation is readily absorbed by nucleic acids, the extent of damage due to the large amount of energy transfer produces irreversible damage leading to cell death rather than to viable cells with inheritable mutations. Thus, the curves for nucleic acid absorption and cell inactivation closely

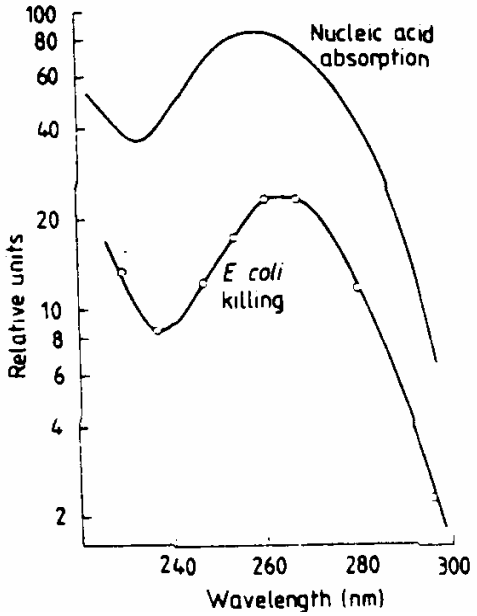


**Figure B.3: The absorption spectrum of nucleic acids and the action spectrum for the inactivation of *E. coli cells (reproduced from Harm (1980))***

parallel each other.

With respect to the UV exposures in the Davidson et al. (2004) study, the UVC radiation appears to have contributed considerably less than 1% to the total UVR output of the Westinghouse lamps and noe of the ouitput of the GE lamps. Thus, some minor fraction of the total UV radiation was of a UVC with wavelength that is not available in the natural sunlight reaching the ground surface every day in New Jersey. However, the action spectra of UVC at these wavelengths is only about 1/10 the effectiveness for causing photocarcinogenesis as for causing erythema. Therefore, given that the Westignhouse lamps produced UVR containing less than 1% UVC, and that UVC is less than 10% as effective as UVB in the prodcution of skin tumors, , it does not seem likely that the UVC radiation received by the mice in this study made a significant contribution to the observed tumor production compared to the other wavelengths of UV radiation they received

## References:


Davidson, T., Kluz, T., Burns, F., Rossman, T., Zhang, Q., Uddin, A., Nadas, A., and M. Costa. 2004. Exposure to Chromium (VI) in the Drinking Water Increases Susceptibility to UV-Induced Skin Tumors in Hairless Mice. Tox. Appl. Pharmacol. 196(3):431-437.

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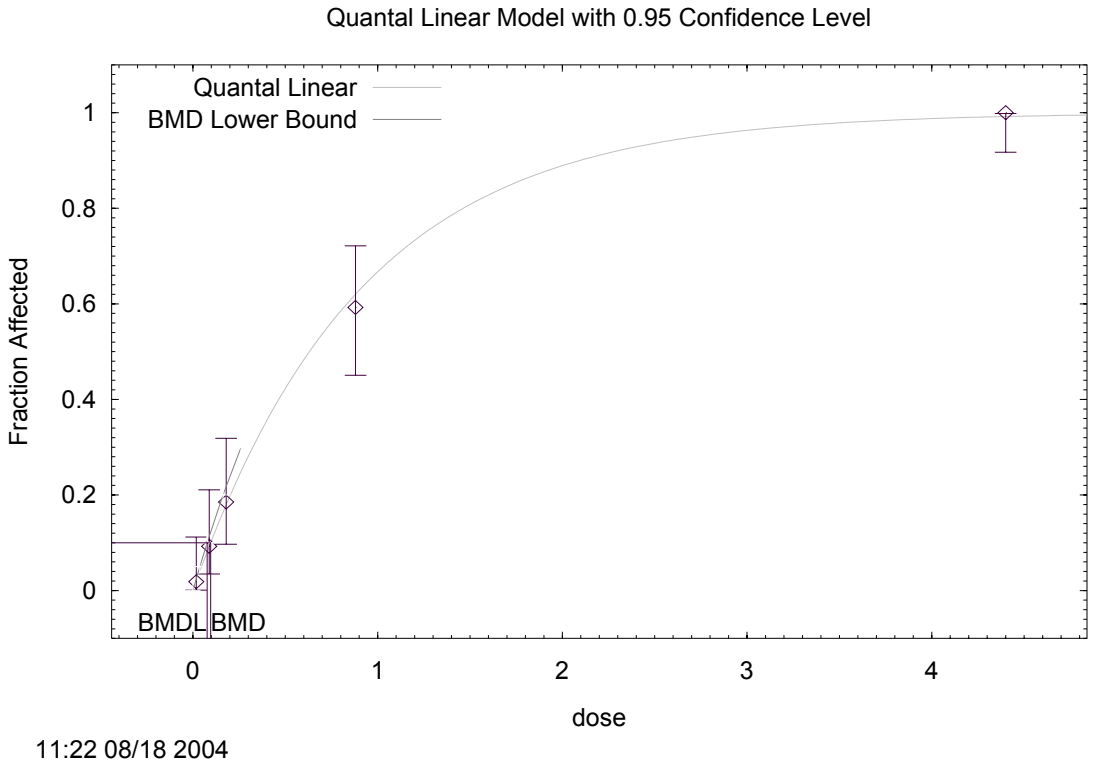
Mitchell, D. L., Meador, J., Paniker, L., Gasparutto, D., Jeffrey, W. H., and J. Cadet. 2002. Development and Application of a Novel Immunoassay for Measuring Oxidative DNA Damage in the Environment. Photochem. Photobiol. 75(3):257-265.

NASA. 2004. Datad Product: Erythemal UV Exposure. National Aeronautics and Space Administration. Goddard Space Flight Center. Revised July 20, 2004. Http://toms.gsfc.nasa.gov/ery_uv/euv.html.
Peus, D., Vasa, R. A., Meves, A., Beyerie A., and M. R. Pittelkow. 2000. UVB-Induced Epidermal Growth Factor Receptor Phosphorylation is Critical for Downstream Signaling and Keratinocyte Survival. Photochem. Photobiol. 72(1):135-140.

Urbach, F. 1982. Photocarcinogenesis. The Science of Photomedicine. Ed. J. D. Regan and J. A. Parrish (New York, Plenum) pp. 261-292.

# Appendix C

## Benchmark Dose Calculations for Nethercott et al. (1994)



```
=========================================================================
            Quantal Linear Model Revision: 2.2 Date: 2000/03/17 22:27:16
            Input Data File: U:\CR WORKGROUP\NETHERCOTT.(d)
            Gnuplot Plotting File:  U:\CR WORKGROUP\NETHERCOTT.plt
                                                        Wed Aug 18 11:22:36 2004
=========================================================================

BMDS MODEL RUN
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

  The form of the probability function is:

  P[response] = background + (1-background)*[1-EXP(-slope*dose)]

  Dependent variable = COLUMN3
  Independent variable = COLUMN1

  Total number of observations = 5
  Total number of records with missing values = 0
  Maximum number of iterations = 250
  Relative Function Convergence has been set to: 1e-008
  Parameter Convergence has been set to: 1e-008

            Default Initial (and Specified) Parameter Values
              Background =         0.5
                  Slope =     0.910758
                  Power =           1   Specified

        Asymptotic Correlation Matrix of Parameter Estimates

        ( *** The model parameter(s)  -Background    -Power
            have been estimated at a boundary point, or have been specified by the user,
            and do not appear in the correlation matrix )

             Slope

   Slope          1

                  Parameter Estimates

     Variable        Estimate          Std. Err.
   Background              0             NA
      Slope          1.10098          0.147508

NA - Indicates that this parameter has hit a bound
    implied by some inequality constraint and thus
    has no standard error.

                  Analysis of Deviance Table

     Model      Log(likelihood)  Deviance  Test DF     P-value
   Full model        -84.012
  Fitted model       -84.5343      1.04465      4          0.903
```

| | | | | |
|---|---|---|---|---|
| Reduced model | -179.001 | 189.977 | 4 | <.0001 |

AIC: 171.069

Goodness of Fit

| Dose | Est._Prob. | Expected | Scaled Observed | Size | Residual |
|---|---|---|---|---|---|
| 0.0180 | 0.0196 | 1.060 | 1 | 54 | -0.05849 |
| 0.0880 | 0.0923 | 4.986 | 5 | 54 | 0.006389 |
| 0.1800 | 0.1798 | 9.708 | 10 | 54 | 0.1035 |
| 0.8800 | 0.6205 | 33.506 | 32 | 54 | -0.4224 |
| 4.4000 | 0.9921 | 53.575 | 54 | 54 | 0.6546 |

Chi-square = 0.62 DF = 4 P-value = 0.9607

Benchmark Dose Computation

Specified effect = 0.1

Risk Type = Added risk

Confidence level = 0.95

BMD = 0.0956969

BMDL = 0.0770345

# CHAPTER 4
# ANALYTICAL CHEMISTRY SUBGROUP

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# New Jersey Chromium Workgroup Report

## CHAPTER 4

## Analytical Chemistry Subgroup

### Charges Being Addressed

1. Certified Method

The Site Remediation and Waste Management Program has been accepting analytical results for hexavalent chromium using a non-NJDEP certified analytical method for Cr(VI) digestion. There is an USEPA-certified method available (Method 3060A). Should the Department mandate use of the USEPA method for hexavalent chromium determinations? What should the Department do about data obtained by the non-certified method the Site Remediation and Waste Management Program has been using for site decisions?

2. Data Review and Acceptance

What should the Department policy be on analytical data where the associated quality assurance protocols are outside method limits?

3. Additional Analytical Methods

USEPA Method 6800 "Elemental and Speciated Isotope Dilution Mass Spectrometry" is approved and included in SW846 for the analysis of speciated metals, including chromium. The Office of Quality Assurance (OQA) does not currently offer certification for USEPA Method 6800. Should the OQA offer certification for USEPA Method 6800? If so, what should be the extent of its potential applications?

4. Method Deficiencies

There is a question that the methods for the regulatory-approved methods of preparation and analysis of hexavalent chromium (USEPA Methods 3060A, 7196a and 7199) underestimate its in-situ concentration in certain types of soil. What are the circumstances where the low bias in hexavalent chromium measurements exist? Are there any conditions under which high bias (resulting from oxidation of Cr(III) to Cr(VI)) in sample preparation and/or measurement occurs?

5. Quality Assurance Tools

The Department has proposed a collaboration with USEPA, National Institute of Standards and Technology (NIST) and the Environmental and Occupational Health Sciences Institute (EOHSI) to develop a reference material of defined Cr(VI) concentration using a source material from Hudson County, New Jersey that can be used to assess the efficacy of future Cr(VI) measurements. Should such a reference material be developed?

## 6. Other Measurement Options

Is it possible to develop a commercially available, NJDEP-certifiable method to replace the current method (Method 3060A)? If not, should speciation of hexavalent chromium continue to be performed should only total chromium be measured? Are there any known biases to the measurement of total chromium in soil that would prevent its use in establishing chromium remediation standards?

**Summary**

- The Department has been using methods which have not been certified by the New Jersey Environmental Laboratory Certification Program to prepare non-aqueous samples for Cr(VI) measurements. The Department has been using both USEPA Method 3060A (USEPA 1995a) and NJDEP Modified Method 3060 (NJDEP, 1992). The Department's Site Remediation and Waste Management Program has recommended that only USEPA Method 3060A be used. The Subgroup concurs with the Site Remediation and Waste Management Program's recommendation to use only USEPA Method 3060A to prepare samples for the analysis of Cr(VI), and the Department should make plans to implement this policy for all new sampling endeavors. For those sites for which Department approved oversight documents exists, the Department shall notify the Responsible Parties and/or their representatives of the changes in analytical methodology prior to the next sampling activity at that site. Any corresponding oversight document shall be revised by the Responsible Party and/or its representatives to reflect the methodology change.

- Quality Assurance/Quality Control (QA/QC) data from past Cr(VI) analyses have shown that variations in sample matrices can result in biased results. The biased results can be attributed to both sample matrices and the specific analytical method used to test the sample. Because of these biases it is important that the QA/QC of methods be closely evaluated, most specifically the "Spike Recoveries." The Subgroup recommends that only Cr(VI) analytical results that have met the "Spike Recoveries" required in the analytical methods be used without qualification. As part of this recommendation, a Departmental Workgroup should be immediately established to define the data usability policy to be followed in the remediation decision processes. The Departmental Workgroup will consist of staff representing the Site Remediation and Waste Management Program (SRWMP), the Division of Science, Research and Technology, and the Office of Quality Assurance. The usability of data associated with spike recoveries outside criteria shall be determined on a case-by-case basis in concert with the recommended data usability procedure generated by the workgroup, except for samples where decisions are made for <u>unconditional</u> "No Further Action", in which case qualified data may not be used.

- The Subgroup recommends that samples be analyzed for Cr(VI) using a tiered approach that includes USEPA Method 7196A, USEPA Method 7199 and USEPA Method 6800 (Figures 4.1-4.5 at the end of this chapter). If the spike recovery obtained from USEPA Method 7196A is found acceptable, the analytical results from the associated samples are also acceptable. If the spike recovery is found outside limits, the NJDEP case team should

require a new sample digestate be reanalyzed using USEPA Method 7196A, as per the method requirements. If USEPA Method 7196A was again used and the spike recovery remains unacceptable, the NJDEP case team shall determine the usability of the data on a case-by-case basis using the data usability procedure described in this chapter. Further action may include using the data or requiring additional analysis using a different analytical method. If USEPA Method 7199 is used and the spike recovery obtained is found acceptable, the analytical results from the associated samples are also acceptable. If USEPA Method 7199 was used and the spike recovery is outside limits, remains unacceptable, the NJDEP case team should require a new sample digestate be reanalyzed using USEPA Method 7199, as per the method requirements. If the spike recovery remains outside limits, it is recommended that the NJDEP case team shall determine the usability of the data on a case-by-case basis using the data usability procedure described in this chapter. Further action may include using the data or requiring additional analysis using a different analytical method. Alternatively, a choice to begin the analytical process by using either USEPA Method 7199 or USEPA Method 6800 is an option. If the quality control requirements obtained from USEPA Method 6800 are found acceptable, the analytical results from the associated samples are also acceptable. If the quality control requirements are not fulfilled, new sample digestates must be reanalyzed using USEPA Method 6800, as per the method requirements. If the quality control requirements remain unmet, results may be qualified or rejected and usability shall be addressed by the NJDEP case team using the data usability procedure described in this chapter. Any decisions requiring additional analyses for Cr(VI) when corresponding matrix spike recoveries are outside method specified criteria will be made by the NJDEP case team, using the Department's data usability policy and on whether or not the data will be used in the issuance of an unconditional "No Further Action" or "Final Remediation Action" declaration.

- The Subgroup recommends that all samples analyzed for Cr(VI) also be analyzed for total chromium. The sample selected for the matrix spike shall also be analyzed for Eh and pH.

- The Department will arrange and participate in the development of speciated reference materials to be used when analyzing for Cr(VI) in non-aqueous sample matrices.

- The Department will fund a series of research projects to address key remaining questions and uncertainties. These projects will focus on areas where no existing information and/or data is available.

## Responses to Charges

### 1. Certified Method

*Should the Department mandate use of the USEPA Method 3060A for hexavalent chromium determinations?*

The Department should require the use of USEPA Method 3060A (USEPA, 1995a) for the digestion of non-aqueous matrices when samples are to be analyzed for Cr(VI). This policy should begin to be implemented immediately for all chromate ore processing residue (COPR) and non-aqueous matrices. For those sites for which Department approved oversight documents already exist (such as sampling plans and Quality Assurance Project Plans), the Department shall notify the Responsible Parties and/or their representatives of the changes in analytical methodology prior to the next sampling activity at that site. Any corresponding oversight document shall be revised by the responsible party and/or its representatives to reflect the methodology change. USEPA Method 3060A uses an alkaline digestion solution (0.28 M $Na_2CO_3$/0.5 M NaOH) at elevated temperatures for a proscribed period of time, and it is designed to dissolve both water soluble and water insoluble Cr(VI) compounds. USEPA Method 3060A provides the digestion step necessary when quantifying Cr(VI) in both COPR and non-COPRA sample matrices using USEPA Methods 7196A, 7199 and/or 6800.

USEPA Method 3060A is intended to minimize changes in the indigenous amounts of Cr(III) and Cr(VI) due to oxidation or reduction. In an oxidizing matrix Cr(III) converts to Cr(VI), and in a reducing matrix Cr(VI) converts to Cr(III). USEPA Method 3060A is effective for extracting Cr(VI) in COPR wastes (USEPA 1996b). However, applications of USEPA Method 3060A to soils and sediments containing matrix components that promote either oxidizing and/or reducing conditions may result in inaccurate data due to the interconversion of indigenous and spiked Cr(III) and Cr(VI) during the digestion (Vitale et al., 1994). The causes of such method performance issues are addressed in greater detail in the "Method Deficiencies" section below.

*What should the Department do about data obtained by the non-certified method the Site Remediation and Waste Management Program has been using for site decisions?*

The Department has used USEPA Method 3060, NJDEP Modified Method 3060 and USEPA Method 3060A when testing for Cr(VI). USEPA Method 3060 was withdrawn from the SW846 methods compendium for solid and hazardous waste in the late 1980s because of data documenting the failure of the method to accurately quantify Cr(VI) in samples containing a reducing condition. The Department needed to continue to analyze for Cr(VI), in the early 1990s the NJDEP developed a new method, designated NJDEP Modified Method 3060 to digest non-aqueous samples for subsequent Cr(VI) analysis.

In 1994 and 1995 the SW846 Inorganic Methods Workgroup met to review the NJDEP Modified Method 3060 in response to a proposal to include the method in the SW846 methods compendium. NJDEP Modified Method 3060 was brought to the SW846 Methods Workgroup by Rock Vitale, Environmental Standards, Inc. In 1996 the SW846 Inorganic Methods Workgroup approved the use of NJDEP Modified Method 3060 only after changes were made by

the Workgroup to the method's QA Section. These changes included the redigestion and reanalysis of the samples when Spike Recoveries are outside method limits.

In 1996 the Workgroup approved the newly revised method and designated it USEPA Method 3060A, for the Digestion of Non-Aqueous Samples for Cr(VI). The Department has continued to use NJDEP Modified Method 3060 rather than USEPA Method 3060A to respond to concerns surrounding long term data consistency. This policy was followed as the chemistry in NJDEP Modified Method 3060 differs subtly from USEPA Method 3060. NJDEP Modified Method 3060 lacks the addition of magnesium salt during the digestion which was a step that was designed to curtail the possible oxidation of Cr(III) to Cr(VI). NJDEP Modified Method 3060 also required shorter holding times which was designed to reduce the possibility of Cr(VI) reduction that could occur during the neutralization step/pH adjustment. It is unknown what affect the differences between Methods 3060 and 3060A may have on the measured amounts of Cr(VI).

It is the recommendation of the Subgroup that decisions made using data previously obtained shall remain. The data was obtained using the digestion methodology acceptable at the time (USEPA Method 3060 and NJDEP Modified Method 3060). Overall, the Subgroup considers that the decisions made in the past were based on the most reliable data available at the time. It is also the Subgroup's recommendation that if the Department elects to revisit previous decisions, new samples will be collected using the proposed list of analytical methods given in this report.

Additionally, analytical data obtained from the NJDEP Modified Method 3060 and USEPA Method 7196A that have yet to be validated shall be validated in accordance with the procedures discussed in the data validation documents developed by the Department (Appendices 6A and 6B). The data usability group will also consider modifications to the existing validation documents if warranted.

## 2. Data Review and Acceptance

*What should the Department policy be on analytical data where associated quality assurance protocols are outside method limits?*

The Analytical Chemistry Subgroup has developed a data decision tree to support a tiered approach for Cr(VI) analyses (see Figures 4.1-4.5 at the end of this chapter). A summary of the approach follows below.

Samples analyzed for Cr(VI) are first digested using USEPA Method 3060A. The digestate may be analyzed for Cr(VI) using either USEPA Method 7196A, 7199 or 6800. For an analytical result to found acceptable without qualification, the associated Quality Assurance (QA) results must meet the requirements of the selected analytical method. For Departmental purposes, QA results shall be focused on Spike Recovery data.

Method 3060A requires that the Cr(VI) matrix spike recovery meet the acceptance criteria within a range. The range of spike recovery must be no less than 75% and no greater than 125% of the

known spike. The method also requires redigestion and reanalysis when the matrix spike recovery fails to meet this criteria. This range of spike recovery is also applicable to two of the three analytical methods – USEPA Methods 7196A and 7199. USEPA Method 6800 has other quality control requirements that must be met for the resulting data to be accepted by the Department. Data usability, therefore, would follow the following sequence:

If USEPA Method 7196A is selected, the Spike Recovery data must be not be less than 75% or greater than 125%. If the Spike Recovery data fails to fall within this range, then a new digestate of the sample must be prepared and re-analyzed using USEPA Method 7196A, as per the method requirement. If the spike recovery data is again either less than 75% or greater than 125%, then the sample results will be qualified or rejected pursuant with the data validation Standard Operating Procedure (Appendix 6b). If it is determined that non-qualified/non-rejected data are required, then the NJDEP case team should require a new digestate of the sample be prepared and analyzed using either USEPA Method 7199 or 6800. If USEPA Method 7199 is selected, the spike recovery data for a sample must be not less than 75% or greater than 125 %. If the spike recovery data fails to fall within this range, the NJDEP case team should require a new digestate of the sample be prepared and re-analyzed using USEPA Method 7199, as per the method requirement. If the spike recovery data is again either less than 75% or greater than 125% then the sample results will be qualified or rejected. If it is determined that non-qualified/non-rejected data are required, then the NJDEP case team should require a new digestate of the sample be prepared and analyzed using either USEPA Method 6800. When USEPA Method 6800 is selected, the quality control requirements associated with this method must be met. If the quality control requirements are still not met, then the sample results will be qualified or rejected. Data usability will be determined using the data usability policy to be developed by the Department.

Flow charts indicating the sequence of how the analytical methods to be used under the conditions of the acceptable and unacceptable matrix spike recoveries appear in Figures 4.1-4.5 at the end of this chapter. There may be instances where, even after redigestion and re-analysis, the percent recovery of a matrix spike fails to meet acceptance criteria. While data may be qualified or rejected, it is possible that data may be used or additional Cr(VI) analyses may not be required. The Department policy on how these data are to be handled shall be defined in the data usability policy to be developed by the Department.

A major component in the field of data validation (of environmental sample data) is how noncompliant QA results are handled. The USEPA has functional guidelines published to address how data are to be reviewed. In the guidelines, data outside method published criteria may be qualified, rejected, or in some instances, deemed acceptable. Acceptance criteria for QA parameters are frequently expanded from the method specified criteria and it is the expanded criteria that are used to make data validation decisions. For instance, in the USEPA Statement of Work (USEPA, 2002), the method-specified criteria for the matrix spike recovery is greater than or equal to 75% and less than or equal to 125%. In the USEPA contract laboratory program guidelines (USEPA, 2002), it is stated that if the matrix spike recovery is 30-75% and the sample results are above the minimum detection limit, then the results are qualified. Additionally, if the matrix spike recovery is 125%, non-detect results are not qualified but useable.

The SRWMP has data validation protocols in place to handle situations where QA results do not meet criteria for numerous compounds represented by the routine analyses performed for the program (Appendices 6A and 6B). Both the USEPA and the Department's Office of Quality Assurance have approved the data validation protocols for use. The validation process is based on spike recovery data and the concentration of the matrix spike relative to the concentration of the sample. As a result of the validation, it may be determined that the data are qualified or rejected due to unacceptable matrix spike recoveries. However, data qualified or rejected due to matrix spike criteria outside method specified levels does not necessarily render the same associated sample result unusable even though the actual amounts of Cr(VI) in the samples could have increased uncertainty. Other factors such as site-specific concerns and additional analytical results are frequently considered before reanalysis of a sample is required. Professional judgement is required when interpreting the findings brought forth from the data validation and deciding how best to proceed with a remediation. Examples where professional judgement is used are as follows:

Example 1: Samples are analyzed by USEPA Method 7196A. The Cr(VI) matrix spike recovery is 60%. The Cr(VI) results from samples associated with the matrix spike are all above the applicable remediation standard. Samples were redigested and re-analyzed as per method requirements with the same end results. The area of concern represented by the samples would require remediation. There would be no need to reanalyze samples by another method.

Example 2: Samples are analyzed by USEPA Method 7196A. The Cr(VI) matrix spike recovery is 30%. The Cr(VI) results from samples associated with the matrix spike are slightly below the applicable remediation standard. Samples were redigested and re-analyzed as per method requirements with the same end results. Total chromium was the only other analysis performed on the samples. Total chromium results were slightly below the remediation standard. The samples would be redigested and re-analyzed by USEPA Methods 7199 and/or 6800.

In summary, decisions concerning the use of qualified or rejected data shall be handled consistently using the protocol specified in the proposed data usability policy. Redigestion and re-analysis may or may not be required. In some instances, qualified sample data obtained from USEPA Method 7196A may be all that is needed to make a remedial decision, except in instances where unconditional "No Further Action" decisions are being requested. In other instances, it may be imperative to know what the effects of the matrix are on the sample results and USEPA Method 6800 may be selected.

It is the opinion of the Subgroup that USEPA Method 6800 can generate reliable data where the sample matrix is either highly reducing or oxidizing. USEPA Method 6800 uses speciated isotope dilution mass spectrometric techniques and the method has shown that it is capable of identifying and correcting for chromium species conversion (Kingston et al, 1998). However, not all the literature reviewed during the Subgroup's activities support this opinion. For instance, a recent paper questioned the efficacy and scope of application of this methodology to completely correct for conversion of Cr(VI) to Cr(III) in highly reducing soil conditions (Tirez et al, 2003). But overall, the literature reviewed during the Subgroup's activities supported the use of USEPA Method 6800 to address the conversion of Cr(VI) between the collection and analysis of a sample.

The Subgroup recommends that the Department should establish a more formal policy describing data usability. It is acknowledged that no such policy currently exists for any contaminant. Such a policy will provide the procedures and standards needed to determine when data can be used that has not met the "Spike Recoveries" required in the analytical methodology. However, this policy is intended only for data that is not used to make Unconditional No Further Action decisions. The Department has included a process for addressing its emerging Quality Assurance (QA) issues in the FY05/06 Departmental Quality Management Plan (QMP). The process includes submittal of suggested issues to the Department Quality Assurance Officer (DQAO), review of the submitted issues by the DQAO, submittal of issues needing attention to the Department's Senior Staff for approval to establish a temporary workgroup, and selection of the workgroup members by the Senior Staff and the DQAO. The Subgroup recommends that the Department use this process immediately to address the updating of its current data usability policies relating to COPR Cr(VI) analytical results.

Because of the complexities surrounding the Cr(VI) analyses and subsequent data usability issues, it is imperative that laboratories performing Cr(VI) analyses should maintain an open line of communication with the Department and/or responsible parties. In those instances where samples are to be re-digested and re-analyzed, the Department may be contacted to determine if accurate Cr(VI) measurements from the samples in question are needed. As part of the remedial process, the Department (i.e. technical coordinators, case managers) shall evaluate the available data incorporating the criteria set forth in the data usability protocol to determine if further testing is necessary. There may be situations where, based on the analytical results of other samples and/or other parameters, remedial decisions can be made without having Cr(VI) results that have passed the spike recoveries for a given recommended analytical method. As a result, the Department may decide that there is no need for a laboratory to proceed with further analytical testing. The exception is in cases where unconditional decisions are being requested, in which cases no qualified or rejected data shall be used to make these determinations.

The Subgroup also recommends that careful attention be given to the definition of a Sample Delivery Group (SDG). That is, what constitutes those samples that are grouped together for subsequent analysis. USEPA Methods 3060A, 7196A and 7199 all call for one sample from the SDG to be spiked with a known amount of Cr(VI); the results for that sample are used to evaluate the efficacy of data for the entire SDG. Since studies have shown that spike recoveries vary with the nature of the sample matrix, only samples with similar matrices shall be included in any one SDG.

## 3. Additional Analytical Methods

*Should the Office of Quality Assurance offer certification for USEPA Method 6800?*

USEPA Method 6800 "Elemental and Speciated Isotope Dilution Mass Spectrometry" (USEPA, 1997) is approved and included in SW846 for the analysis of speciated metals, including chromium. The Office of Quality Assurance (OQA) does not currently offer certification for USEPA Method 6800. The OQA uses N.J.A.C. 7:18, Regulations Governing the Certification of Laboratories and Environmental Measurements, to administer the State of New Jersey's

Environmental Laboratory Certification Program. N.J.A.C. 7:18 adopts-by-reference the SW846 analytical methods. Therefore, the Department has the existing authority to add USEPA Method 6800 to the list of methods offered for New Jersey Environmental Laboratory Certification. The OQA will add USEPA Method 6800 to its responsibilities effective immediately. Additionally, several academic and commercial laboratories have indicated their willingness to become certified for USEPA Method 6800.

*If so, what should be the extent of its potential applications?*

USEPA Method 6800 could be used when either USEPA Method 7196A or 7199 is used to test for Cr(VI) and the spike recovery results fall outside the method's acceptable limits. However, USEPA Method 6800 is acceptable for analyzing Cr(VI) in all instances when the regulated community chooses to forgo the use of either USEPA Method 7196A or 7199.

## 4. Method Deficiencies

Empirical data have indicated transformation of chromium species may be occurring or may have occurred in certain soil types both environmentally and during sample analysis. Cr(VI) under certain conditions can be reduced to Cr(III), resulting in less Cr(VI) than may actually be present (low bias) while Cr(III) can be oxidized to Cr(VI) resulting in more Cr(VI) than may actually be present (high bias) (James et al., 1997).

*What are the circumstances where the low bias in hexavalent chromium measurements exists?*

Over the past years, data from the analysis of COPR material has, in many cases, yielded satisfactory matrix spike recoveries. Analytical results comparing USEPA Method 7196A (the traditional colorimetric method) to USEPA Method 6800 (the speciated isotope dilution mass spectrometry method designed to correct for species transformation) indicate COPR sample concentrations of Cr(VI) can be virtually identical for many samples (Huo et al., 2000). But in those cases where the Cr(VI) matrix spikes yield percent recoveries less than the method acceptance criteria, there is a cause to be concerned, as the measured values may indicate less Cr(VI) than is present in the sample collected.

There are several possible causes for reduction of Cr(VI) to Cr(III). The chemical nature of the matrix itself could be providing the necessary conditions under which reduction of Cr(VI) in the matrix spike occurs. Researchers have stressed the necessity to characterize the soil matrix by determining Eh (oxidation-reduction potential), pH, total organic carbon, ferrous iron, and sulfide to evaluate its potential to interconvert Cr(III) and Cr(VI) (Vitale et al., 1997). If a reducing condition exists as defined by the chrome Eh-pH phase diagram (Figure 4.6 at the end of this chapter); the presence of TOC, $S^{-2}$, Fe(II) and/or acidic conditions then the potential for the sample to reduce the laboratory Cr(VI) spike or not sustain the existence of Cr(VI) in the sample's natural environment also exists (James 1997). The presence of iron in different species and organic matter has also been shown to interfere with Cr(VI) by reducing it during measurement by USEPA Method 7196A (Huo et al., 1998). Data indicates that Fe(II) and sulfides can decrease the recoveries of Cr(VI) spikes. Fe(III) has been shown to oxidize DPC (diphenylcarbizide), thus not allowing it to react with all of the Cr(VI) in the sample. The result

of this oxidation reduces the efficiency of the matrix spike recovery. Additionally, during this oxidation process, Fe(III) is reduced to Fe(II) which in turn could reduce Cr(VI).

Reduction of Cr(VI) occurs when reducing material from the matrix is allowed to react with Cr(VI) during the neutralization process. Method-induced reduction of Cr(VI) to Cr(III), either by digestion or measurement, has been documented (Huo and Kingston, 2000). It has been recommended by analysts experienced in the analysis of Cr(VI) in soils that for future Cr(VI) analyses the digestion solution should be neutralized immediately before measurement as Cr(VI) has been observed to reduce during neutralization.

The comparisons and discussions of the analytical techniques have focused thus far mostly on USEPA Methods 7196A and 6800. Much of the reduction is believed to occur due to the presence of reducing material during the digestion and/or neutralization process. USEPA Method 7199 (USEPA, 1996a) removes some potentially reductive species through use of a guard column in the front end of the instrumentation. Studies conducted by the NJDEP Laboratories (NJDEP, 1993) reported that for comparable sample analyses of Cr(VI), digests yielded higher results by Method 7199 than by Method 7196A (USEPA, 1995b), although the lowest percent recovery noted was 74% using USEPA Method 7196A while all other recoveries for both USEPA 7196A and 7199 were within the 75% to 125% acceptance criteria. USEPA Method 6800 may be able to be used to gain better information relating to species interconversion. This Subgroup recommends that laboratories experiencing unacceptable matrix spike recoveries with samples analyzed and reanalyzed by USEPA Method 7196A are to re-digest the samples by USEPA Method 3060A and re-analyze the samples by USEPA Method 7199. Laboratories should also have the option to perform Cr(VI) analyses by USEPA Method 7199 or USEPA Method 6800 from the outset. Additionally, to help determine if the matrix is reducing in nature, laboratories shall be required to perform basic testing (eH, pH, and possibly TOC, sulfides and total iron) on select samples and on all matrix spike samples.

*Are there any conditions under which high bias (resulting from oxidation of Cr(III) to Cr(VI) in sample preparation and/or measurement occurs?*

Cr(III) can be oxidized to Cr(VI). However, the extent of oxidation of Cr(III) depends on the chemical form of the Cr complex in which it exists. Cr(III) and freshly precipitated $Cr(OH)_3$ are relatively easy to oxidize, while $(Cr_2O_7)^{-2}$ and aged $Cr(OH)_3$ are resistant to oxidation. Oxidation is more likely to occur during the digestion step where conditions are thermodynamically favorable.

There are instances where, under the correct environmental conditions, that oxidation of Cr(III) may occur simultaneously with the reduction of Cr(VI) (Vitale et al., 1994). It is the Subgroup's opinion that this can be documented by using USEPA Method 6800 to track species interconversion.

## 5. Quality Assurance Tools

*The Department has proposed a collaboration with EPA, NIST and EOHSI to develop a reference material of defined Cr(VI) concentration using a source material from Hudson County,*

*New Jersey that can be used to assess the efficacy of future Cr(VI) measurements. Should such a reference material be developed?*

The Subgroup recommends that a project be completed to develop reference materials. The Department has an existing proposal (See Research Section), managed by OQA, which has been agreed to by the USEPA, the National Institute of Standards and Technology (NIST) and the Environmental and Occupational Health and Science Institute (EOHSI). It is recommended that the Department supply some of the funding needed to complete the project; NIST has funding to prepare the first chromium sample for homogenization and distribution for round-robin analyses. Activities to initiate this project should begin by June 2005.

## 6. Measurement Options

*While advanced analytical methods (such as USEPA Method 6800) exist to better analyze the concentration of this species, is it possible to develop a commercially available, NJDEP-certifiable method to replace the current digestion method (USEPA Method 3060A)?*

The Subgroup is not aware of any procedure to quantitatively remove Cr(VI) from soil matrices while maintaining indigenous Cr(III) and Cr(VI) concentrations other than USEPA Method 3060A. However, it may be possible that another method that can quantitatively remove Cr(VI) from non-aqueous samples without being subject to specie interconversion can be developed. Research on options for sample preparation as well as in-situ methods of analysis are part of a separate list of research proposals.

*If not, the question is: should speciation of hexavalent chromium continue to be performed, or is it more protective to measure total chromium only?*

Cr(VI) analyses should still be performed using the current digestion and analytical methods available. For COPR matrices, using the combination of USEPA Methods 3060A and 7199 has shown to yield accurate and reproducible results (Kingston et al., 1998). This subgroup also recommends that in addition to Cr(VI) analyses, total chromium analyses be performed simultaneously on all samples. Both methods should yield sufficient data upon which remedial decisions could be made.

*Are there any known biases to the measurement of total chromium in soil that would prevent its use in establishing Cr remediation standards?*

An option to the direct measurement of Cr(VI) is to measure total Cr by USEPA Methods 3050/6010B or USEPA SOW ILMO5.2. For most matrices, review of Performance Testing data show that Total Cr measurements have less uncertainty and better accuracy than measurements of Cr(VI). However, the Department (Site Remediation and Waste Management Programs) has observed Total Cr empirical data with both high and low biases. The Subgroup recommends that Cr(VI) measurements be continued, and that Total Cr measurements also be required on all samples requiring Cr(VI) analyses.

The Subgroup also recommends that a research project be completed to address the analytical uncertainties. Comparisons of USEPA Methods 7196A, 7199, and 6800 shall be performed to determine differences, if any, in analytical precision and accuracy. Total chromium and material left on filters would be analyzed in parallel to provide information on mass balance and species conversion.

**Research**

The Subgroup recommends that the following questions be considered through the use of research projects.

*After the digestion of soil samples containing Cr(III) and Cr(VI) using USEPA Method 3060A, which of the following three analytical methods best responds to the interconversion of Cr(III) and Cr(VI) in reducing and oxidizing soils?*

- Method 6800, Elemental and Speciated Isotope Dilution Mass Spectroscopy
- Method 7199, Determination of Hexavalent Chromium in Drinking Water Ground Water and Industrial Effluents by Ion Chromatography
- Method 7196A, Chromium (Colorimetric)

*How is the oxidation/reduction potential of chromium contaminated soil determined and are field measurements and laboratory measurements similar?*

The pH and eH of soil samples should be measured in the field and at the laboratory. The measurements must be made with calibrated instruments and the times recorded. The procedure is described in USEPA Method 3060A. These measurements should be taken for the samples used in first project listed above.

*Is there another digestion method that will remove Cr from soil without changing the indigenous content of Cr(III) and Cr(VI)?*

A detailed search of literature should be conducted to identify other possible methods. If methods are found, research should be conducted to determine if these methods are improvement over USEPA Method 3060A.

*Is there an analytical method that can determine Cr(III) and Cr(VI) in reducing and oxidizing soils without digestion?*

- Evaluation of analytical methods that can determine Cr(III) and Cr(VI) in reducing and oxidizing soils without digestion is needed. It is necessary to investigate the availability of methods that do not involve wet chemistry to address the concerns with interconversion and matrix spike recoveries. Researchers have investigated the use of a wide range of X-Ray methods for in-situ metals measurements. This research project should include use of the COPR matrix. These techniques would be able to determine worst case scenarios without first digesting the COPR waste into the

aqueous phase where reduction and/or oxidation could potentially inter-convert between the species present.

Research utilizing these methods would evaluate the ability of a solid-state analytical method to make in-situ measurement of Cr(VI) in soils and sediments.

The next step of the research project would characterize the Cr(III) and Cr(VI) ratio in COPR waste at the major waste sites in Hudson county. This information could then be used in the analysis of soils and sediments to determine Cr (VI) in soils and sediments. Additional methods that are capable of determining Cr(III) and Cr(VI) in soils without digestion should be explored and pursued.

*How can Cr(VI) measurements in non-aqueous media be improved?*

Evaluation of the efficacy of measurements of Cr(VI) in non-aqueous media such as soils and sediments would be aided by the availability of a reference material containing a known amount of Cr(VI). The development of reference material with defined species-specific Cr concentrations faces a number of technical challenges, including long-term specie stability and the potential for both the nature of the sample matrix and/or the analytical methods used for detection and quantitation to influence final measured results.

Agreement has been reached between a project team comprised of staff from the New Jersey Department of Environmental Protection, United States Department of Commerce - National Institute for Standards and Technology (NIST), United States Environmental Protection Agency, and the Environmental Occupational Health Sciences Institute – Rutgers University to develop a series of reference materials derived from different types of soils and/or sediments. The first sample in this series will be collected at a site in New Jersey, homogenized at a United States Geologic Survey facility, and aliquots distributed for an interlaboratory evaluation study to selected participating government, academic and commercial laboratories. The methods used for sample preparation and analysis of this material by each laboratory will be carefully monitored. Results will be evaluated by the project team, and the product, containing a description of the type of soil from which it was derived and containing a Cr(VI) concentration with defined limits of uncertainty, will be made available for sale by NIST.

**Recommendations**

Programmatic:

- OQA will add USEPA Method 6800 to its list of certifiable analytical methods.
- USEPA Method 3060A will be used for digestion of all future soil samples for Cr(VI) analysis.
- A tiered approach to selection of determinative methods for Cr(VI) will be used as per Figures 4.1-4.5 (at the end of this chapter).

- USEPA Method 6800 could be used when sample digests have been analyzed by either USEPA Method 7196A and/or USEPA Method 7199 and the spike recoveries are less than 75% or more than 125%. USEPA Method 6800 may also be used initially.

- The Department will develop a data usability policy to permit the use of Cr(VI) analytical data that has not met the "Spike Recoveries" given the analytical methods. The Policy will permit the use of this data when it is not used for unconditional "No Further Action" decisions. The decision to either use or not use the data will be made by the Department in consultation with Responsible Parties.

- Total chromium will be analyzed concurrently with Cr(VI) for all samples.

- Measurements of the oxidative/reductive (Eh and pH) properties of the soil matrix will be made for all samples from sites with oxidizing or reducing conditions. Measurements will be made in the field and/or on receipt at the laboratory.

- Spike recoveries must meet the requirements stated in the analytical measurements for the Cr(VI) results to be acceptable without qualification.

- The Department will arrange and participate in the development of speciated reference materials to be used when analyzing for Cr(VI) in non-aqueous sample matrices. Once available, this reference material will be analyzed with every SDG.

- Careful attention should be given to the definition of a SDG; that is, what constitutes those samples that are grouped together for subsequent analysis. The SDG will consist only of samples of a similar matrix type.

- Decisions made using data previously generated by other analytical methods shall remain. If the Department elects to revisit previous decisions, new samples shall be collected using the proposed list of analytical methods given in this report.

Research:

- Comparison of analytical methods used to detect Cr(VI) in soil samples

A research project should be designed to answer the following question:
After the digestion of soil samples containing Cr(III) and Cr(VI) using USEPA Method 3060A, which of the following three analytical methods best responds to the interconversion of Cr(III) and Cr(VI) in reducing and oxidizing soils?

Method 6800, Elemental and Speciated Isotope Dilution Mass Spectroscopy
Method 7199, Determination of Hexavalent Chromium in Drinking Water
Method 7196A, Chromium (Colorimetric)

- Evaluation of analytical methods that can determine Cr(III) and Cr(VI) in reducing and oxidizing soils without digestion is needed. It is necessary to investigate the availability of methods that do not involve wet chemistry to address the concerns with

interconversion and matrix spike recoveries. Researchers have investigated the use of a wide range of X-Ray methods for in-situ metals measurements. This research project should include use of the COPR matrix. These techniques would be able to determine worst case scenarios without first digesting the COPR waste into the aqueous phase where reduction and/or oxidation could potentially inter-convert between the species present.

Research utilizing these methods would evaluate the ability of a solid-state analytical method to make in-situ measurement of Cr(VI) in soils and sediments.

The next step of the research project would characterize the Cr(III) and Cr(VI) ratio in COPRA waste at the major waste sites in Hudson county. This information could then be used in the analysis of soils and sediments to determine Cr (VI) in soils and sediments. Additional methods that are capable of determining Cr(III) and Cr(VI) in soils without digestion should be explored and pursued.

- Examination of other digestion methods that will remove chromium from soil without changing the indigenous content of Cr(III) and Cr(VI). A detailed search of literature should be conducted to identify other possible methods. If methods are found, research should be conducted to determine if these methods are improvement over USEPA Method 3060A.

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**Figure 4.1. Procedure for analytical method selection to analyze Cr(VI)**

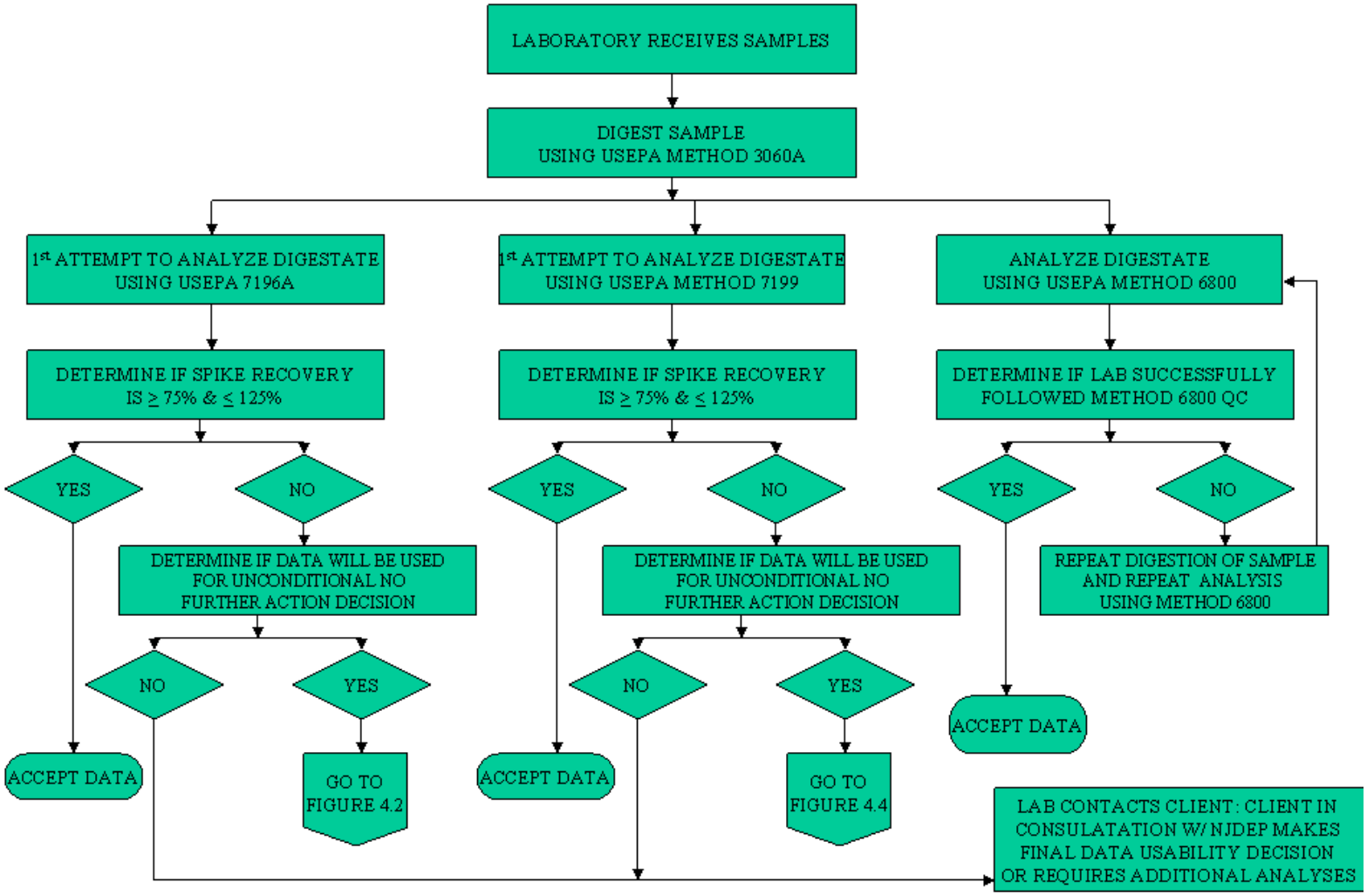


**Figure 4.2. Procedure for analytical method selection to analyze Cr(VI) when 7196A fails quality control**

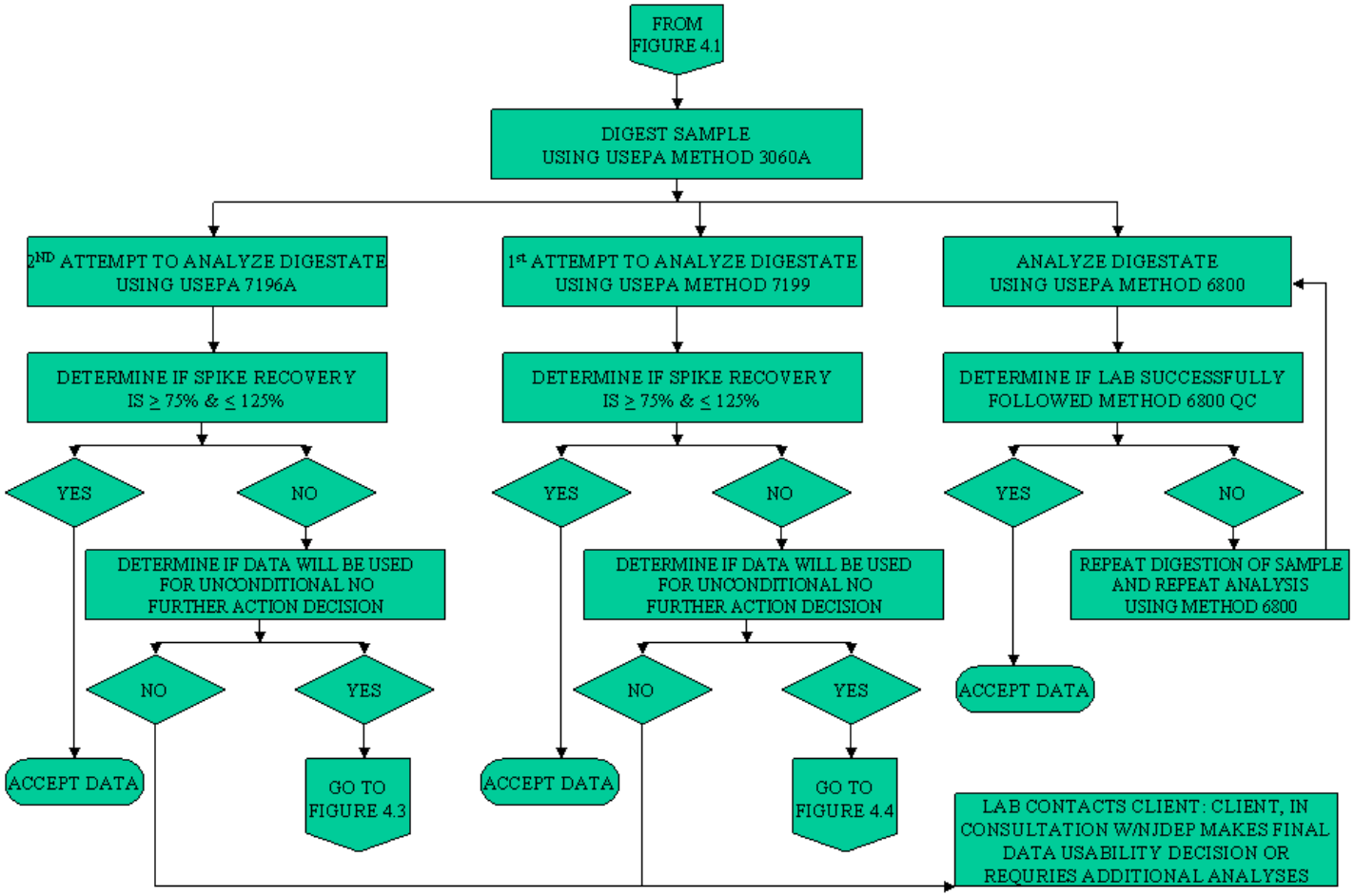


**Figure 4.3. Procedure for analytical method selection to analyze Cr(VI) when 7196A fails quality control a second time.**

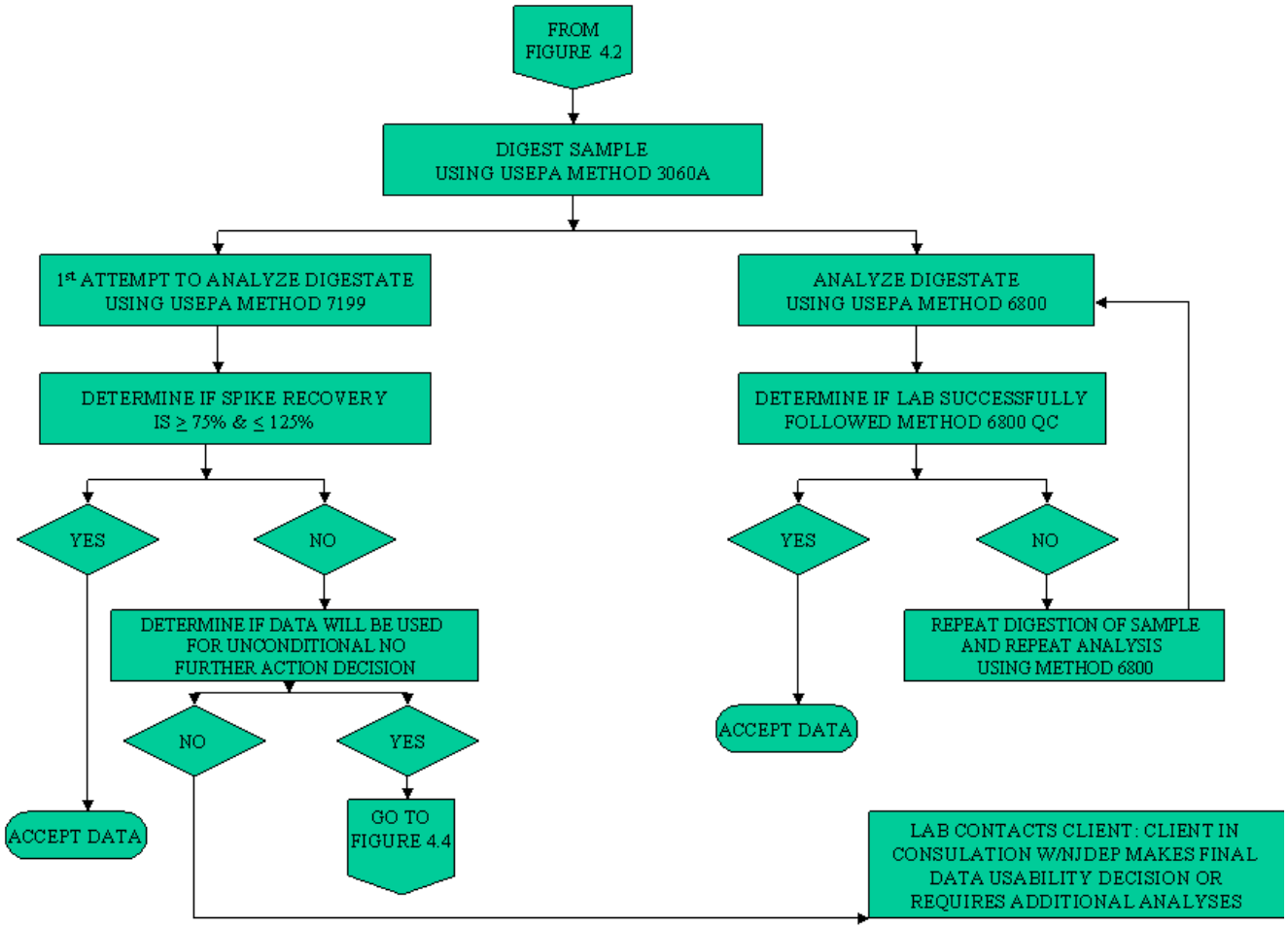


**Figure 4.4. Procedure for analytical method selection to analyze Cr(VI) when 7196A and/or 7199 fail quality control once or twice.**

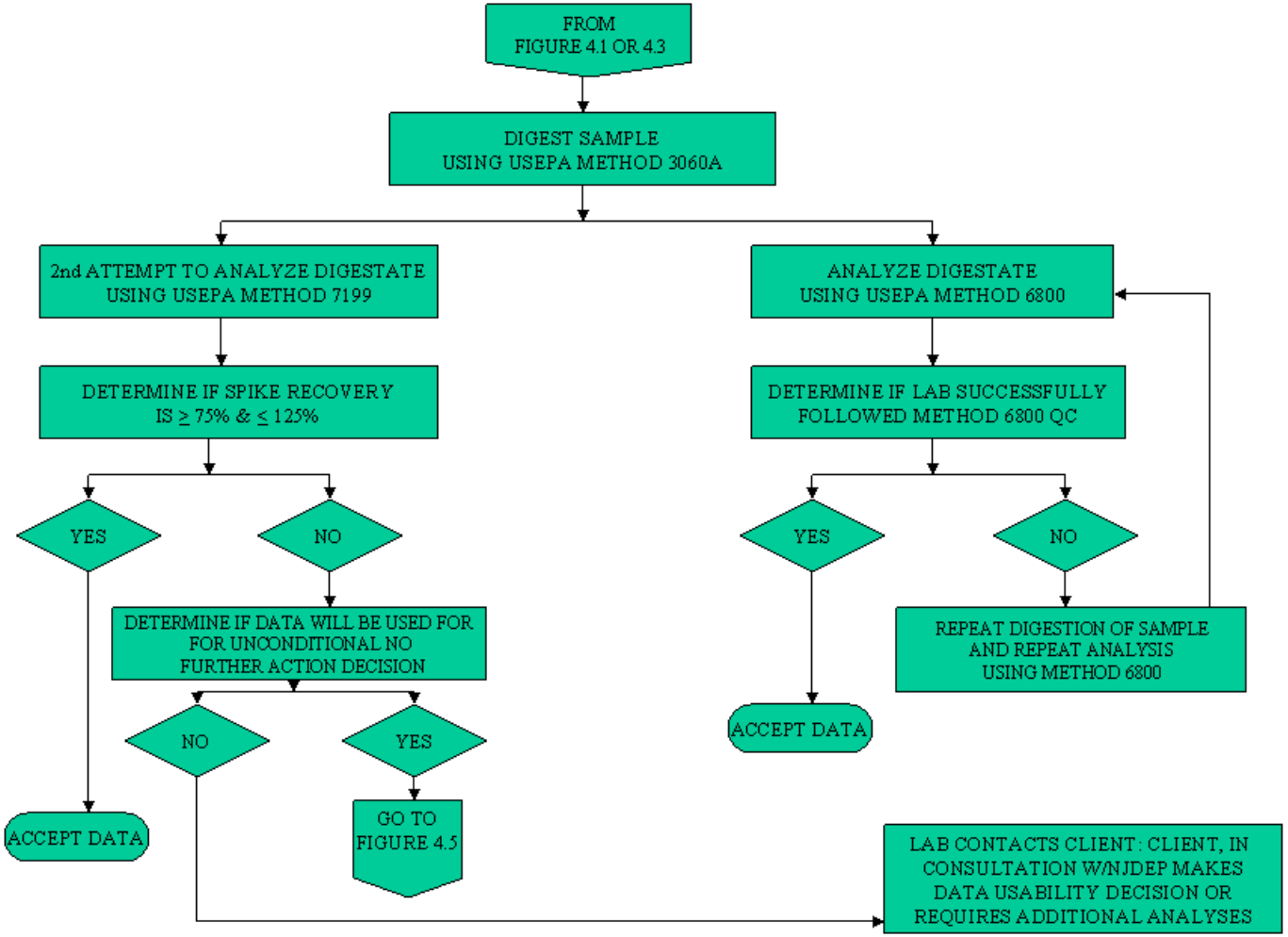
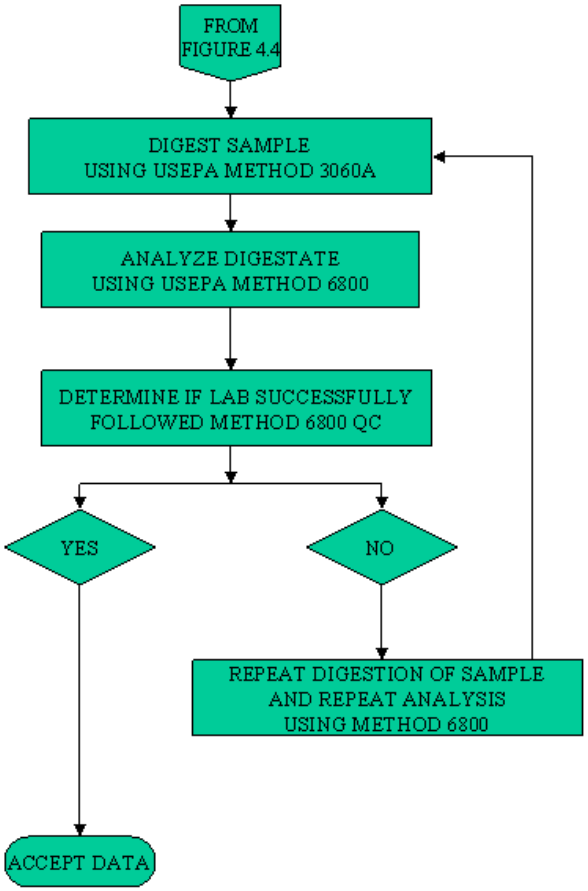


**Figure 4.5. Procedure for analytical method selection to analyze Cr(VI) when 7196, 7199 and/or 6800 fail quality control.**



## Figure 4.6 Eh/pH Phase Diagram

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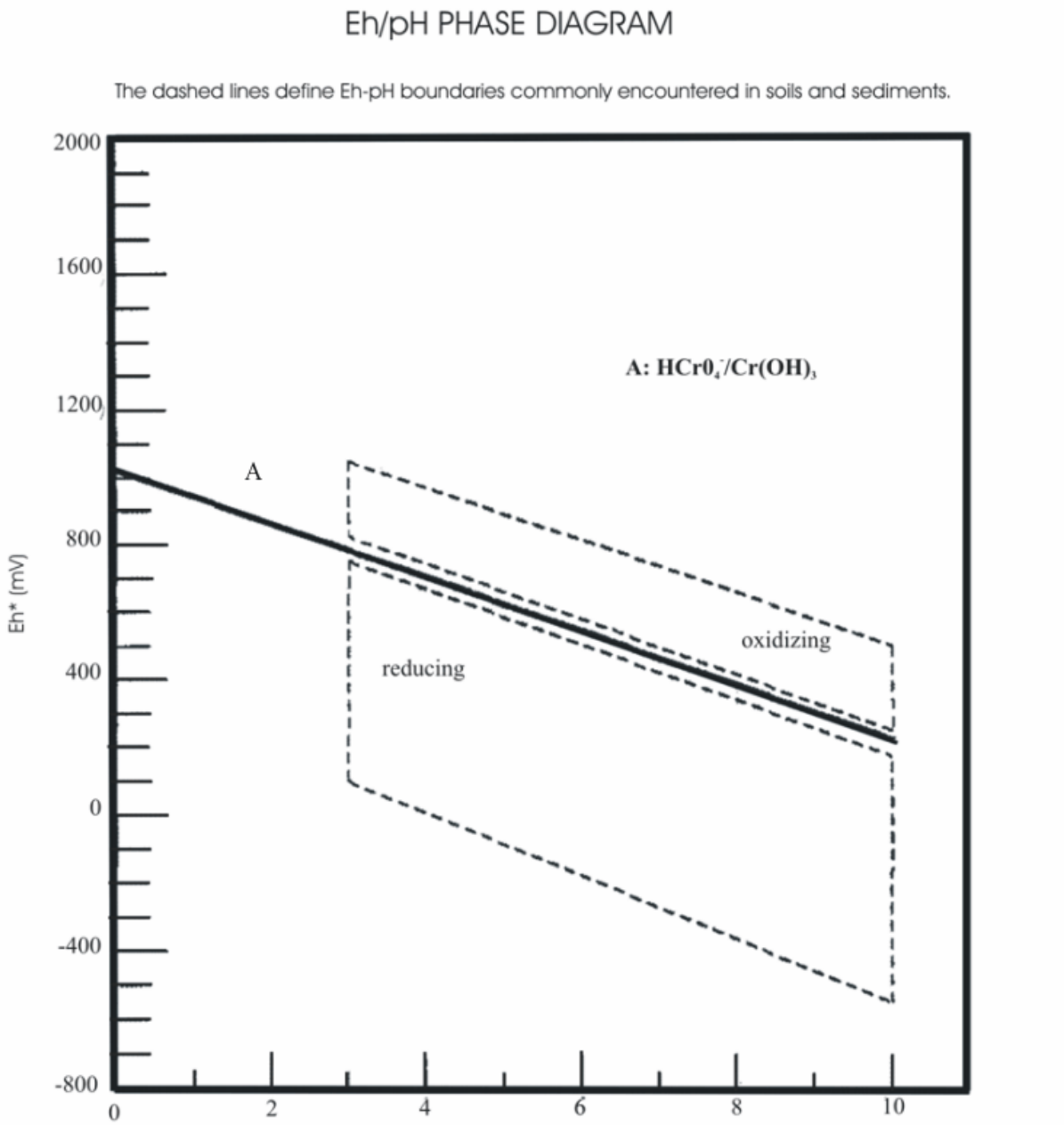


* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added is a combination platinum electrode is used.

# CHAPTER 5
# AIR TRANSPORT SUBGROUP

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# New Jersey Chromium Workgroup Report

## CHAPTER 5

## Air Transport Subgroup

### Charge Being Addressed

The protocol for development of alternative remediation standards for chromium needs to include the physical mechanism by which dust gets into the air and reaches humans via inhalation. Are the mechanisms for this transport adequately calculated?

In 1998, the Department began to use Soil Clean-up Criteria (SCC) for chromium to help guide the investigation and remediation of contaminated sites. The SCC for hexavalent chromium at nonresidential sites is currently 20 mg/kg in soil. Since that time, an effort has been underway to promulgate Soil Remediation Standards (SRS) and a draft proposal for SRS is currently available for interested party review on the Department website. The SRS for inhalation is based on some slightly different assumptions and methodologies from those used for the SCC, but the recommended value for hexavalent chromium SRS for nonresidential sites of 29 mg/kg has changed very little from the existing SCC.

The method for developing an Alternative Remediation Standard (ARS) has also changed over time. In this report, the focus will be on the ARS's that have been developed over the past six years and attempt to put them in the context of the physical mechanisms by which contaminated dust can enter the air.

### Summary

- It is essential that evaluation of ARS's and the process for selecting the one that drives the selection of the final Remedial Action be fully documented and be readily available upon request. The current review process does not require this.

- The USEPA methodology for predicting emissions has changed over the past few years, so that the impact from the truck traffic pathway and the fugitive dust pathway have drawn closer together. Therefore, future SRS's and ARS's should be calculated on the basis of impacts from both pathways.

- The NJDEP methodology for calculating ARS's has been evolving and has become much more restrictive, allowing changes in fewer parameters. It should be noted, however, that the ARS's developed to date for the inhalation pathway have not been the basis for the final Remedial Action selected.

### Response to the Charge

The charge can be addressed by answering the following questions.

1. What are the physical mechanisms by which particles enter the air?

2. What assumptions are made in the models and how do they influence the predicted air concentrations of hexavalent chromium?
3. How do particle size assumptions affect the Inhalation Remediation Standards in general?
4. How were Alternative Remediation Standards developed for the inhalation pathway?
5. Are the physical mechanisms adequately described in the development of Alternative Remediation Standards?

**Discussion**

*What are the physical mechanisms by which particles enter the air?*

There are two physical mechanisms by which contaminated dust could get into the air at contaminated sites. The predominant mechanism is from vehicle traffic on the site. A secondary mechanism is from wind suspending loose soil into the air.

Truck Traffic: This mechanism is well-described by USEPA (2003) in the Emissions Factor guidance known as AP-42.

When a vehicle travels on an unpaved road, the force of the wheels on the road surface causes pulverization of surface material. Particles are lifted and dropped from the rolling wheels, and the road surface is exposed to strong air currents in turbulent shear with the surface. The turbulent wake behind the vehicle continues to act on the road surface after the vehicle has passed. (USEPA 2003: page 13.2.2-1)

The emissions calculation provided by USEPA (2003) in this guidance include the following parameters: mean vehicle weight and other truck characteristics, silt content, and soil moisture content.

Wind-blown Dust: Particulate emissions from industrial wind erosion are described by USEPA as dust "generated by wind erosion of open aggregate storage piles and exposed areas within an industrial facility" (USEPA 1995a: Section 13.2.5-1). The model described in that document assumes a storage pile, which for COPR sites can be set to a very low height. When emissions are calculated for a pile that is disrupted once each working day, the predicted emission rate for the pile is about one twentieth of the emission rate for the 25 vehicles per day truck traffic scenario (see Table 5.1 Below).

**Table 5.1. Particulate (PM10) Emission Rate Estimates from AP-42 (USEPA, 2003* & 1995a**)**

| Truck Traffic*<br>(25 Trucks per Working Day) | Wind Blown Dust**<br>(600 square meter pile) |
|---|---|
| 0.14 grams/second | 0.0080 grams/second |

*What assumptions are made in the models and how do they influence the predicted air concentrations of hexavalent chromium?*

There are two types of models used to calculate soil clean-up levels. The first set of models predict emission rates of particulate from truck traffic and wind-blown dust as described above. The second set of models is used to describe the movement of this particulate through the air and predict air concentrations at designated points at and around the site. These predicted concentrations are then used to back-calculate to the soil concentration that would result in the 1 in a million cancer risk level for inhalation for a specific contaminant.

- The Industrial Source Complex (ISC) model (USEPA 1995b) was used to generate air concentrations for deriving the SCC for hexavalent chromium. This is a standard USEPA model which is generally preferred when doing regulatory modeling since it is easy to use and more conservative than the Fugitive Dust Model (FDM, described in USEPA 1992). The ISC model usually predicts air concentrations of a pollutant from an area source that are approximately two times greater than those predicted by the FDM for the same size area source.

- The ISC model was used to predict particulate concentrations at points on the edge of the property and in an array spread across the property. The highest predicted concentrations tend to be in the middle of the property for dust sources such as those considered at contaminated sites. The SCC is derived from the average concentration (predicted at all points in the array). This value is higher than the concentrations predicted at the property line. For example, when evaluating a two-acre site, the average unitized dispersion factor (i.e. the impact for each g/second of emissions) from truck activity for on-site workers was calculated to be 184 (ug/$m^3$)/(gram/sec), while the 24-hour dispersion factor for off-site exposure from both truck activity and wind erosion is 106 (ug/$m^3$)/(gram/sec). Thus, off-site individuals are exposed to air concentrations lower than the level associated with a one in a million increased risk of cancer when the average on-site concentration is used to develop the SCC.

- Although wet and dry deposition calculations are an option with the ISC model, no particle deposition was calculated in deriving the SCC. Instead, it was assumed that all particles stay in the air and contribute to the predicted air concentration rather than falling out and depleting the amount of contaminant in the plume that is available to be breathed. This would lead to higher predicted air concentrations that will then result in more protective clean-up criteria.

*How do particle size assumptions affect the inhalation soil remediation standards?*

Review of the methodology for developing the SCCs indicates that we were able to calculate emission estimates for Inhalable Particulate (PM-10) using the USEPA (1995a) emission factor guidance in AP-42. A smaller portion of the particulate matter emissions would be 2.5 um or less in diameter, and therefore able to penetrate to the lowest portion of the respiratory tract. Basing the SCC (and subsequent ARS) on the PM-10 fraction is consistent with general guidance from USEPA which recommends that analysis of ambient air concentrations of toxic metals be based on speciation

of PM-10 samples, since all of the PM-10 is available to the respiratory system (although PM-2.5 will penetrate the farthest), and may therefore be of toxicological significance.

The question of how fugitive dust is apportioned among the various particle size categories has been explored by a number of authors. Watson, Chow and Pace (2000) report that about 52.3% of the particulate from road and soil dust is less than 10 micrometers in diameter; of this particulate 10.7% has been found to be smaller than 2.5 micrometers in diameter; and the remaining 41.6% falls between 10 and 2.5 micrometers (sometimes referred to as coarse particulate). Another way of stating these findings is that PM2.5 mass emissions account for about 20% (i.e. 10.7% divided by 52.3%) of the PM10 mass emissions.

Kitsa, et al. (1992) found a similar particle size distribution when resuspending soil taken from a COPR site in a sealed chamber. In their experiment, the large particles (greater than 30 micrometers in diameter) accounted for 50% of the mass, while the coarse fraction was 30% and the fine (PM2.5) fraction was 7%.

Finally, the latest version of AP-42 guidance for Unpaved Roads and Industrial Wind Erosion (USEPA 2003) now provides factors that can be used to estimate fugitive dust emissions of various sizes. Using the same assumptions regarding truck traffic and pile size that were used in the derivation of the SCCs, the emission estimates shown in Table 5.2 can be calculated using this new guidance.

**Table 5.2. Particulate Emission Rate Estimates (grams/second) from Various Revisions to AP-42**

| | PM30 | PM10 | PM2.5 |
|---|---|---|---|
| Emissions from Truck Traffic (USEPA, 1995a)* | 1.54 | 0.23 | 0.061 |
| Emissions from Truck Traffic (USEPA, 1998) | 0.70 | 0.15 | 0.022 |
| Emissions from Truck Traffic (USEPA, 2003) | 0.48 | 0.14 | 0.022 |
| Emissions from Wind Blown Dust (USEPA, 1995a) | 0.015 | 0.008 | 0.003 |

* Input values initially used for silt content and vehicle speed differ from current values that are used.

In the Truck Traffic scenario (USEPA 2003), the PM10 fraction is 29% of the PM30 emission rate and the PM2.5 fraction is 5%. For the Wind Blown Dust scenario, the PM10 and PM2.5 fractions are 53% and 20%, respectively.

If the SCC's or ARS's were based on the mass of PM2.5 (instead of PM10) that is likely to get into the air due to activities at the COPR sites or from wind-blown dust, the allowable hexavalent chromium concentrations would be somewhat higher in soil. However, if it were assumed that the smaller particles had higher concentrations of hexavalent chromium than what can be observed by standard soil testing methods, then a weighted average method could be used to account for this concentration and a somewhat lower allowable soil concentration of hexavalent chromium would be

derived. How much lower depends on the degree of hexavalent chromium concentration on the particle, but one sample calculation suggests that assuming an order of magnitude increase in hexavalent chromium on the small particles would lower the allowable soil concentration (SCC or ARS) by about 25%. Compared to the general conservative nature of the ISC model (sometimes over predicting by as much as a factor of 2) and other conservative assumptions that have been made, this difference of 25% is negligible.

*How were alternative remediation standards developed for the inhalation pathway?*

In the past, calculations of ARS's have been allowed to make adjustments for site size, amount and type of vehicle traffic, and thus far have only considered dust generated from truck traffic. In some cases, when an ARS was developed for a site that is inaccessible to vehicles or otherwise unlikely to have vehicle traffic, a nominal number of trucks (e.g. 5 per day) was still assumed as a worst-case assumption. This method should overestimate the impact compared to what would be generated by wind-blown dust.

Two USEPA-approved models are available to predict concentrations of particulate in the air that will result from the emissions described above. These are the ISC and the FDM models. As a general rule, the FDM could also be used to develop an ARS and submitted to the Department for review, but the resulting ARS might not always be accepted. The ISC model is preferred by the Bureau of Air Quality Evaluation (BAQE) because it is more conservative (i.e. predicts higher concentrations) and is easier to use. When an ARS was submitted using the FDM, the BAQEv would recalculate the clean-up number using the ISC model for comparison.

While the FDM requires a particle size distribution in order to predict an ambient concentration, the ISC model does not differentiate among particle sizes in predicting particulate impacts. Rather the ISC model treats particulate matter as if it were a gaseous pollutant. The only circumstance when particle size distribution is applied by the ISC model is in calculating deposition (and, as noted elsewhere, when deposition is calculated the model does not account for plume depletion). In general it was found that the ISC resulted in ARS that were about a factor of 2 times lower than FDM, which is within the range of variability expected from dispersion models.

**Table 5.3. Comparison of Dispersion Factors and ARS using ISC and FDM and 1990 Newark Meteorological Data**

| | ISC assuming all PM10 | FDM assuming the same particle distribution |
|---|---|---|
| Dispersion Factor (ug /m3)/(g/sec) | 184 | 90 |
| ARS for Cr(VI) (mg/kg) | 28 | 57 |

The Air Transport Subgroup was able to identify 13 COPR sites for which final actions have been determined. For nine of these, an inhalation ARS was calculated, although none of these inhalation ARS actually drove the final selection of a remedy. The site-specific ARS's are reported in Table 5.4 along with other information about these sites. The table show that the Inhalation ARS range from 106 to 7,420 mg/kg. Note that the very high ARS value of 213,000 mg Cr(VI)/kg that has been reported elsewhere does not appear on this chart. It had been mistakenly attributed to site #201 (which had a NJDEP-approved ARS of 2,330 mg/kg) and may have been a typographical error.

Prior to 2001, the SCC or ARS was compared to the 95 percent Upper Confidence Limit of the overall mean concentrations (aka General Mean) found in the soil samples from the site to determine if the inhalation criteria were met. After that time, the comparison was changed to the 95 percent Upper Confidence Limit of the mean of the maximum concentrations (aka Mean of Max) found in each boring, in order to avoid diluting the sample with an exceptional amount of clean soil. Note that using the Mean of Max is more conservative (i.e. more health protective) than using the General Mean.

**Table 5.4. Draft Summary of the Remedial Analysis Employed for the No Further Action Sites after the Issuance of the Inhalation Pathway Soil Clean-up Criterion (September 1998)**

| Site Name | Site No. | Max Cr(VI) in Soil Remaining (mg/kg)[1] | 95% Upper Confidence Limit: General Mean[3] (mg/kg)[1] | 95% Upper Confidence Limit: Mean of Max's[4] (mg/kg)[1] | Inhalation ARS (mg/kg)[1] | Remedy Selected |
|---|---|---|---|---|---|---|
| Kenney Steel Treating Co. | 52 | 212 | 59.6 | | 205 | Excavation |
| West Hudson Lumber Co. | 62 | 180 | 56.3 | | 164 | Excavation |
| Bergen Barrel and Drum | 170 | 140 | 94 | | 159 | Excavation |
| Belleville Turnpike No. 1 | 195 | 47 | | | NC[2] | Excavation |
| Bellezza Construction Co. | 145 | 167 | 27.4 | | 106 | Excavation |
| Goldies Auto Parts | 47 | 220 | 33.3 | | 265 | Excavation |
| Pen Horn Creek | 40 | 477 | | 63.2 | 235 | Deed Notice |
| New Rent Trucking | 55 | 217 | | 220 | 533 | Treatment |
| N.J. Turnpike Kearny No. 1 | 56 | 204 | | 139 | 7,420 | Treatment |
| Posnak and Turkish, Inc. | 163 | 18 | | | NC[5] | Excavation |
| Clinton Cartage | 48 | 9,550 | | 2,110 | NC[6] | Cap, Deed |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | Notice, and CEA |
| N.J. Turnpike Kearny No. 2 | 201 | 2,820 | 129 | 2,330 | Cap and Deed Notice |
| Kenrich Chemical | 152 | 5 | | NC[5] | No Remedial Action Needed |

[1] Concentration terms are expressed as milligrams (mg) of hexavalent chromium (Cr(VI)) per kilogram of dry weight soil (kg).
[2] NC means not calculated because the site conditions precluded vehicle traffic.
[3] The compliance mechanism for the General Mean sites is the 95 percent upper confidence limit of the mean of all soil data collected from the site.
[4] The compliance mechanism for the Mean of the Max's sites is the 95 percent upper confidence limit of the mean of the highest value of hexavalent chromium in each soil boring (changed in 2001).
[5] NC means calculation not needed since the maximum value on site is less than the remediation criterion.
[6] NC means calculation not needed since the selected remedy was Cap, Deed Notice and CEA.

Attachments 1 and 2 describe the process of selecting a clean-up target for Sites 201 and 56, respectively. These were of special interest since they have the highest ARS developed to date for the inhalation pathway. As described in more detail in Attachment 1, Site 201 (New Jersey Turnpike Kearny No. 2) is practically inaccessible to traffic. At this site, the 95 percent Upper Confidence Limit of the Mean of the Maximums was found to be 129 mg/kg, which is about 6.5 times higher than the inhalation SCC. Although the calculated ARS was 2,330 mg/kg, simply complying with the Residential SCC of 270 mg/kg would have been adequate to show compliance with the inhalation pathway. However, the simple maximum hexavalent chromium concentration at the site was 2,820 mg/kg which is 5 times higher than the next most stringent pathway (i.e. 516 mg/kg for allergic contact dermatitis) so the responsible party opted to cap the site and accept a deed restriction rather than clean up to that level. Therefore, the inhalation ARS was not used to select the final remedy.

As described in more detail in Attachment 2, Site 56 (New Jersey Turnpike Kearny No. 1) is an unused access road, restricted to traffic by guard rails and difficult terrain. At this site, the 95 percent Upper Confidence Limit of the Mean of the Maximums was found to be 139 mg/kg (about 7 times higher than the inhalation SCC). Although the calculated ARS was 7,420 mg/kg, the ingestion pathway criterion of 240 mg/kg was used to determine the level of remediation.

*Are the physical mechanisms adequately described in the development of alternative remediation standards?*

The ARS's that have been developed thus far have not accounted for windblown dust from the sites. Since the contribution of windblown dust to overall particulate levels is very small compared to the truck-generated particulate, the ARS's have most likely been protective. However, windblown dust should be included in future SRS and ARS calculations in order to more completely described the dust generation from contaminated sites.

## Recommendations

It is recommended that future ARS calculations be limited in the number of parameters that can be varied for the inhalation pathway. The Inhalation SRS that are currently available for interested party review would allow only the silt content of the soil or the fraction of vegetative cover to be changed. We recommend that facility-generated ARS vary silt content only while the SRS are being reviewed. Limiting ARS changes to site-specific silt content is advisable for a number of reasons. One is that the silt-content is an existing parameter that can be measured and is unlikely to change, in contrast to truck traffic (which is projected) and site size (which could change if a lot is subdivided or if adjacent lots are annexed).

It is also recommended that future SRS and ARS include both traffic generated dust and wind-blown dust in the calculation. In cases where no traffic is anticipated, an ARS should be based on exposure to windblown dust at a hypothetical residence located at property fenceline (the default being 270 mg/kg at the moment).

In USEPA (2003), the soil moisture content was removed from the equation for traffic-generated dust, because "unpaved roads have a hard, generally nonporous surface that usually dries quickly after rainfall or watering, because of traffic-enhanced natural evaporation." Removing this factor results in higher estimate of particulate emissions from truck traffic. This new equation should be used in the development of the Inhalable SRS and any interim ARS.

Finally, the Subgroup found that it was very difficult to compile the history of how an ARS was developed and the final decision-making process that led to the selection of a remedy. For future ARS's submitted to the Department, all of the information found in Table 5.1 and an elucidation of the decision process should be contained in a summary document. The possibility of making this information available to all interested parties via NJEMS should be explored and pursued.

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## Attachment 1

**Site 201** is located in Kearny, New Jersey and is linear in nature . The site is approximately 75 feet wide and 1,700 feet long. An active rail line crosses the site approximately 1,000 feet north of the Belleville Turnpike. The property is owned by the New Jersey Turnpike Authority and lies along the western spur of the New Jersey Turnpike. There are no buildings/facilities present and the site is unoccupied. It is bounded by wetlands or water bodies as well as the embankment of the New Jersey Turnpike. The primary access to the site is restricted by locked gates, fencing, guard rails, and elevated soil berms.

The chromium contamination exists as five areas or pockets of fill predominantly surficial in nature with maximum concentrations occurring at depths of under 2 feet. The highest concentration is 2, 820 mg Cr(VI)/kg. Most of the site does not exhibit chromium contamination at levels above regulatory concern relative to the soils. Ground water contamination occurs in close proximity to the chromium contaminated fill. However, it does not extend vertically beyond the meadow mat which underlies the site and is estimated to be 5 feet thick. The horizontal movement also appears limited, possibly due to processes such as reduction, adsorption , etc. that result from interaction with the on site soil and organic matter.

Currently, portions of the site, including the areas with the highest chromium contamination, are paved as part of the remedial action imposed on this site. A deed notice is in place which requires inspection, monitoring, and maintenance of the engineering controls. The applicable remedial soil concentrations under a nonresidential exposure scenario are 2,330 mg Cr(VI)/kg for the inhalation pathway, 516 mg Cr(VI)/kg for the allergic contact dermatitis endpoint, and 6,100 mg Cr(VI)/kg for the ingestion pathway. The relevant ground water standard is 100 micrograms of total chromium per liter of water.

The critical regulatory value for the site soil is 516 mg Cr(VI)/kg which is based on the allergic contact dermatitis endpoint. Because there are exceedances of this value, engineering and institutional controls are required. Please note that estimates of a much larger alternative remediation standard of 213,000 mg Cr(VI)/kg have been mistakenly attributed to the site instead of the Department approved value.

While not the critical value, the inhalation pathway alternative remediation standard of 2,330 mg Cr(VI)/kg was based on the following site assumptions: There are 5 large trucks (18 wheels and weighing 17 Mg) per day for a period of 250 days a year which travel 1 kilometer over an unpaved road at a speed of 20 kilometers per hour for a total period of 25 years. Compliance is established by comparing the 95 percent upper confidence limit of the mean of the highest values in each of the boring against the value 2,330 mg Cr(VI)/kg. The 95%ile upper confidence level of the mean of the maximums was 129 mg Cr(VI)/kg which means that the inhalation pathway would not be of regulatory concern in this case since the site conditions do not exceed the alternative remediation standard of 2,330 mg Cr(VI)/kg. This calculated upper confidence limit of the mean of the maximum values of 129 mgCr(VI)/kg is also below the 270 mg Cr(VI)/kg residential limit which should protect against wind generated airborne contamination.

Regulatory concern exists for the ground water because there are exceedances of the ground water standard. These exceedances are confined within the limits of the site and appear to be stable in their location. A classification exception area has been established to indicate that the ground water is contaminated. This process will include the monitoring of sentinel wells to ensure that the conditions do not change.

## Attachment 2

**Site 56** is an unused access road along the eastern spur of the New Jersey Turnpike. The site is linear in nature with a length of 1,700 feet and a width of up to 40 feet. The site is bordered on the north by the New Jersey Turnpike, on the west by the Belleville Turnpike, and on the south and east by wetlands. There are no structures or commercial operations associated with this site. The site had been used as a staging area during the construction of the New Jersey Turnpike, but currently has no regular use other than as a potential means to inspect the piers of the elevated portion of the New Jersey Turnpike. Vehicle access to the site is restricted by guard rails and the terrain present.

The chromium contamination originally existed as three pockets of hexavalent chromium with maximum values of 1,260, 1,840, and 7,700 mg Cr(VI)/kg. Elsewhere outside these pockets, there were fairly low level concentrations (typically 50 mg Cr(VI)/kg or less). An exceedance of the chromium ground water standard was not detected.

Currently, portions of the site, including the areas with the highest chromium contamination, are paved. The remedial soil concentrations proposed by the responsible party are 7,420 mg Cr(VI)/kg for the inhalation pathway, 265 mg Cr(VI)/kg for the allergic contact dermatitis endpoint, and 240 mg Cr(VI)/kg for the ingestion pathway. While the site would qualify as a nonresidential exposure scenario, the responsible party opted to meet the more conservative residential exposure scenario, ingestion pathway criterion of 240 mg Cr(VI)/kg. The site was remediated by excavation and ex situ treatment (reduction/stabilization/ solidification). Because the remaining chromium values are equal to or below this value (maximum of 204 mg Cr(VI)/kg), engineering and institutional controls are not required.

While not the critical value, the following analysis would apply if the inhalation pathway alternative remediation standard potentially was potentially the critical value. The inhalation pathway alternative remediation standard is 7,420 mg Cr(VI)/kg and is based on the following site assumptions: There is 1 truck (6 wheels and weighing 15 Mg) per day for a period of 50 days a year which travels approximately 350 meters over an unpaved road at a speed of 32 kilometers per hour for a total period of 25 years. Compliance is established by comparing the 95 percent upper confidence limit of the mean (UCL) of the maximum value found in each of the borings against 7,420 mg Cr(VI)/kg. The calculated UCL is 220 mg Cr(VI)/kg. Because this calculated value is less than the alternative remediation standard established for the inhalation pathway, the inhalation pathway is not of regulatory concern (relative to 7,420 mg Cr(VI)/kg for this site). This calculated value also means that wind generated airborne contamination would not be an issue at this site since the relevant value of concern for that mechanism is 270 mg Cr(VI)/kg.

# CHAPTER 6
# ENVIRONMENTAL CHEMISTRY SUBGROUP

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# New Jersey Chromium Workgroup Report

## CHAPTER 6

## Chromium Environmental Chemistry Subgroup

### Summary

There are four main factors that govern the existence, fate, and transport of hexavalent chromium at COPR sites. These four factors are: 1) the nature of COPR, which determines the extent and rate of dissolution from COPR of hexavalent chromium; 2) the hydrodynamics at each site that controls the rate and extent of leaching and transport of hexavalent chromium in soil solution and groundwater; 3) the characteristics of the soil matrix at each site, such as pH and amounts of organic matter and Fe(II) that affect the rate and extent of oxidation and reduction reactions; and 4) the particle size of the various soil types at each site that affects the rate and extent of adsorption of Cr(VI).

COPR contains a number of hexavalent chromium-bearing minerals that were created in a high temperature industrial process. These minerals are otherwise not found in nature and are somewhat unstable over time. The slow dissolution kinetics of the Cr(VI)-bearing minerals in COPR makes it a continuing source of hexavalent chromium to the environment. Given the lack of adequate field or laboratory data to ascertain an appropriate chromium concentration at COPR sites to avoid unacceptable impacts to groundwater, it is necessary to use available scientific tools to predict such an impact. Such tools have been developed as part of NJDEP efforts to propose and adopt soil remediation standards. These Alternative Remediation Standard options were prepared in order to provide expedient procedures for adjusting the generic impact to groundwater clean-up standards to site specific conditions. While these options are applicable to contaminated soil and at some level of COPR-soil mixtures; they are not applicable to the COPR waste material or soil with larger amounts of COPR waste material. Therefore, the Department should consider defining COPR waste material and soil with larger amounts of COPR waste material as a continuing source of contamination to groundwater that will require remediation in accordance with Department's Technical Requirements for Site Remediation (N.J.A.C. 7:26E).

A method is need for distinguishing between continuing source material and COPR-soil mixtures with smaller amounts of COPR where the impact-to-groundwater options are appropriate. However, when circumstances warrant, the Department may allow other procedures for calculating alternative remediation standards. In cases where the groundwater is not currently impacted by overlying chromium waste material, an investigation would be required to determine why such impacts have not been observed, and to demonstrate that conditions at the site will continue to prevent groundwater impacts as long as the source material is present.

Overall, studies in the literature report a wide range of results regarding oxidation of trivalent chromium, Cr(III), to hexavalent chromium, Cr(VI). Research has shown that oxidation can occur in soils, particularly those containing manganese oxides, so it is possible that oxidation takes place in areas where soil has been mixed with the COPR material. Some studies show that

the oxidation reaction is so slow as to be insignificant, while others indicate the oxidation can occur over a period of less than a decade. After much discussion within the group, it appears that there is not a preponderance of evidence in the published literature to warrant a change in the determination of soil clean-up levels based on oxidation reactions. Nevertheless, further study is needed to effectively resolve the issue for COPR sites.

The phenomenon of chromium salts precipitating on surface soils and on structural surfaces, occurring as visible yellow/green blooms, has been documented at the COPR sites in New Jersey where Cr(VI) levels are high. Whether Cr(VI) salts deposit at levels too low to result in visible blooms but high enough to be of an inhalation risk is not known. The subgroup determined that given the complexity of the factors involved, it is difficult at this time to develop a predictive model for this transport mechanism. It is recommended that the Department continue to study the issue through New Jersey-specific research. Regarding the enrichment of Cr(VI) on small, respirable particles, the subgroup found equivocal information. Again, there is not enough data to suggest a change in the application of the generic model, but the subgroup did recommend that ARS petitions submitted for the inhalation pathway provide more detailed information on Cr(VI) concentration by particle size distribution, which can be used in the approval process by DEP.

The Environmental Chemistry subgroup reviewed and discussed these factors within the context of its charges and to make recommendations to the Department. For some aspects of the report, consensus was not possible, as the individuals serving on the work groups were polarized in their professional judgement about some of the issues. This report has attempted to outline those issues for which evidence was presented that demonstrate the theoretical possibility of a phenomenon occurring. However, recommendations have been made only for issues where definitive scientific evidence was presented. The report is intended to serve as an informational resource to the Department and as a foundation for future cleanup decisions at COPR sites in the state to reduce the environmental and public health impacts of chromium contamination. The recommendations are not intended to result in any retroactive application of any new criteria/standards.

**Charge Being Addressed**

1. Nature of COPR

The interconversion question is imbedded in the larger problem of the nature of chromite ore processing residue (COPR). The physical (micropore) structure of chromite ore processing residue may be the rate-limiting factor in the release of hexavalent chromium. What is the nature of this waste material and how does it influence what we know about chromium chemistry?

Processes that determine the fate and transport of chromium at COPR sites include: 1) continuous dissolution of chromium-containing minerals in COPR; 2) oxidation of trivalent chromium to hexavalent chromium; 3) reduction of hexavalent chromium to the trivalent form; 4) adsorption and desorption of chromium to and from soil constituents; and 5) transport of chromium to groundwater. The fate and transport of chromium at COPR sites is determined primarily by the kinetics that control these processes but modeling these processes is difficult due to the complexity of the variables. Currently, predictions about chromium behavior in this

material are imperfect. Chromium-contaminated soil has properties that are very different from COPR. The focus of this charge is on the nature of the COPR material.

COPR contains a number of hexavalent chromium bearing minerals that were created in a high temperature industrial process. These minerals are otherwise not found in nature and are somewhat unstable over time. The slow dissolution kinetics of the Cr(VI) bearing minerals in COPR makes it a continuing source of hexavalent chromium over decades. Weathering changes the physico-chemical properties of the waste by reducing particle size and increasing the available surface area making it more susceptible for chemical interactions. Treatment and containment strategies for COPR need to take into account the mineralogical characteristics of the waste material. Weathering of COPR subjects the waste to changes in pH, oxidation potential, and ion exchange, all of which may affect the rate and species of chromium being released to the environment. A criteria for distinguishing between pure COPR and COPR-soil mixtures is needed.

In Hudson County, three high-lime chromite ore processing plants operated from around 1905 to 1976 generating 2 to 3 million tons of COPR over the course of their lifetime (Burke et al., 1991). The residual material was produced as a result of extracting chromium from chromite ore. Chromite ore consists primarily of chromium (III), iron, aluminum and magnesium ions in an oxidic matrix. The chromite ore generally used in the manufacturing process contained between 45 to 50% chromic oxide ($Cr_2O_3$). In the procedure, the ore was crushed and mixed with soda ash and lime and then roasted at 1150 degrees centigrade to oxidize Cr(III) to Cr(VI). Cr(VI) was then extracted from the roast in the form of sodium chromate using a countercurrent water leaching process. The solid residue left after the water extraction is chromate ore processing residue, or COPR. This high alkaline, lime-based roast process, first developed in 1845, was the standard chromate chemical production process used the world over in the first part of the 20$^{th}$ century with only minor differences in the proportion of the mix between the production facilities. The addition of lime resulted in the generation of a highly alkaline COPR. The actual amount of chromium in any COPR is dependent on the efficiency of the chromium extraction process used.

*Nature of Chromium at COPR Sites*

Chromate chemical production plants around the world have generated millions of tons of chromite ore processing residue from the extraction of chromium from chromite ore. COPR has been used as fill in urban areas in Hudson County, New Jersey and has been disposed of in landfills in Glasgow, Scotland (Geelhoed et al., 2003). The COPR that was used as fill in Hudson County, NJ has a pH of between 11 and 12 and typically contains 3 – 7% chromium present as both Cr(III) and Cr(VI). The two oxidation states of chromium show great contrast in their chemical behavior as well as in toxicity. In the environment, Cr(VI) is present in the anionic form and is relatively soluble and therefore mobile, whereas Cr(III) is virtually immobile and is in general strongly retained in the solid phase.

Weathering of COPR exposes fresh surfaces in the mineral structure. This causes continuous leaching of chromium even decades after it was originally deposited. There is a steady, albeit slow, dissolution of hexavalent chromium from the interior of particles to soils or pore water. This dissolution and subsequent aqueous transport and/or reaction of hexavalent chromium

continues for an unknown period of time (Geelhoed et al., 1999). The actual dissolution rate of chromium from the mineral structure is not known at this time. Farmer et al. (2002) contend that "…site-specific conditions can play an important role in the speciation/fractionazation of dissolved chromium." They attribute the detections of hexavalent chromium in groundwater to the deposition of COPR waste in landfills in Scotland, which occurred from 1803 to 1968. They also found that reduction of Cr(VI) to Cr(III) occurred significantly presumably due to the presence of high levels of organic matter present at the sites.

Researchers from the Macaulay Institute and the University of Edinburgh in Scotland used a range of analytical techniques including scanning electron microscopy, x-ray powder diffraction and x-ray fluorescence spectrometry to characterize COPR material deposited at three sites in Scotland (Hillier et al., 2003). An integrated analytical and experimental approach using both solid and solution–phase techniques has enabled researchers to identify the Cr(VI) substituted minerals involved in the slow release of Cr(VI) from COPR (Geelhoed et al., 2002). Equilibrium modeling indicated that, at pHs greater than 11 (typical of the Scottish COPR sites), concentrations of Cr(VI) in solution were controlled by the high-temperature minerals Cr(VI)-substituted hydrogarnet and Cr(VI)-hydrocalumite, a layered double-hydroxide clay with chromate ions held in the interlayers. These phases dissolved below pH 11, resulting in a sharp increase in predicted Cr(VI) concentrations in solution. At pH 9.5-11, agreement between results of batch dissolution experiments (conducted over 4 and 26 days) and model predictions of Cr(VI) in solution was improved by addition of Cr(VI)-ettringite (a secondary phase precipitated when hydrocalumite dissolves) to the model. COPR chemistry is dominated by calcium aluminate phases; although pH was a significant variable in predicting release of Cr(VI) from the COPR minerals, the buffering capacity of the COPR material is large. Consequently, large pH changes in the field were considered unlikely by the researchers. The model overestimated the buffering capacity of the COPR system at lower pHs (9.5 and 10.5), compared with experimental results, which the researchers attribute to "the relatively slow dissolution kinetics of the various phases in COPR."

Gradations of material containing COPR waste material mixed with soil or mixed with other material may behave differently from either COPR alone or soil. For example, impact to groundwater models appropriate for COPR-soil mixtures may not be appropriate for pure COPR slag. Therefore, it is important that pure COPR and COPR-soil mixtures be accurately defined and differentiated. At a later date, the soil standards committee should convene a group to establish guidelines that distinguish between COPR and COPR-soil mixtures. Factors such as pH, reducing conditions, mineralogy etc. are candidate factors to use in making the distinctions.

**Charge Being addressed**

2. Transport to Groundwater:

What concentration of chromium in the soil at the chromite ore processing residue sites results in chromium levels above the drinking water standard in groundwater? Do the NJDEP clean-up standards currently under development adequately protect groundwater?

This charge was divided into two principal components based upon the two questions in the charge.

*a. What concentration of chromium in the soil at the chromite ore processing residue sites results in chromium levels above the drinking water standard in groundwater?*

Laboratory studies have confirmed field observations that hexavalent chromium (Cr(VI)) is readily leachable from chromite ore processing residue (COPR) waste material and may result in groundwater concentrations that exceed the New Jersey groundwater quality criteria.

Geelhoed et al. (2002) tested the leaching potential of COPR waste from Scotland. The total chromium concentration was approximately 40,000 mg/kg (via x-ray fluorescence), with about 30% of this in the hexavalent form (determined using x-ray absorption near-edge structure spectroscopy). In batch leaching experiments (4 or 26 days in duration and across a range of pH values), measured aqueous chromium concentrations ranged from 46,000 to 750,000 µg/L, with the highest concentration at pH 8 (liquid to solid ratios of 10:1 or 5:1). These concentrations are well above the NJDEP groundwater quality criterion of 100 µg/L for chromium, and indicate that from 0.5 to 9 percent of the total chromium was removed by the batch leaching test, or 2 to 30 percent of the hexavalent chromium. Above pH 10.5, concentrations appeared to be controlled by the solubility limit of hexavalent chromium-containing minerals (discussed below). Between pH 8 and 10.5, concentrations were higher but did not appear to reach equilibrium due to slow dissolution kinetics. Below pH 8, chromate concentrations decreased due to adsorption of the dissolved chromate on freshly precipitated aluminum and iron hydroxides. Thus, the actual mechanism controlling chromate concentrations in solution was pH dependent.

Weng et al. (1994) investigated the leachability of COPR waste from Liberty State Park in Hudson County, New Jersey using batch studies and found a smaller pH dependence on the resulting chromium concentration in the leachate. Untreated COPR contained total chromium concentrations of approximately 50,000 mg/kg using scanning electron microscopy x-ray energy dispersion analysis, or 25,000 using hydrofluoric acid digestion. Aqueous concentrations of chromium in batch leaching experiments ranged approximately from 100 to 1,500 µg/L, which are likely to be lower than field conditions because of the large volume of extractant employed (liquid to solid ratio of 200:1). However, these concentrations were again at or above the New Jersey groundwater quality criterion, and chromium removed by the batch leaching test range up to 1% of the total chromium amount. The amount of organic matter was found to influence the concentration in the leachate, in that reduction of Cr(VI) was apparent in the presence of organic matter. In a more realistic simulation of leaching processes in the field, Weng et al. (2002) conducted column leaching studies using the same Hudson County waste material. Chromium concentrations in the column eluate over the first two days of leaching (about 25 pore volumes) ranged from 1,000 – 70,000 µg/L. Again, about 1% of the total chromium was readily leachable.

James (1994) studied the leachability of COPR waste from Hudson County and suggested that the soluble chromium was controlled by dissolution of chromate salts. He tested material with both high (10,400 mg/kg) and low (1,800 mg/kg) total chromium concentrations (determined using hydrofluoric acid digestion), and found that under mild extraction conditions, about 2.5% of this amount was readily leachable hexavalent chromium. This was found to be about half the

amount of hexavalent chromium determined using the USEPA modified alkaline digestion Method 3060 (USEPA 1982).

The above studies indicate that a few percent of the total chromium in COPR waste material is in the readily leachable hexavalent form and may result in concentrations in the leachate that exceed the groundwater quality criteria for this metal. Thus, there is a concern that groundwater may become contaminated from leaching of chromium from overlying waste. However, systematic laboratory studies correlating total chromium concentrations with particular chromate concentrations in the leachate have not been reported. Such studies could be conducted; however, recent evidence from NJDEP procedures for assessing dermal exposures to chromium suggests that such a correlation may be poor (NJDEP 2004a).

Field observations at COPR sites have yielded the full range of possible outcomes pertaining to groundwater impacts from overlying chromium contamination. COPR contaminated sites can be categorized by the volume of contaminant present, the concentration and speciation of the contaminant, the distance of the contaminant to groundwater, and whether or not there are unique physical characteristics present that would impact the behavior of the discharge. These unique physical features would include the presence of a sewer line, meadow mat, high organic content soils, existing impermeable surfaces, etc.

A preliminary survey of 40 sites under the jurisdiction of Tierra Solutions, Inc., is illustrative. Seventeen of these sites have large amounts of COPR material in or at the water table and have elevated levels of hexavalent chromium in the groundwater. The remaining sites showed no elevated chromium levels in the groundwater. These sites either have low levels of chromium contamination or have high levels of chromium 2-7 feet above the water table. Most of the Honeywell (Allied-Signal) sites have large amounts of COPR deposited, often extending into the water table, and most exhibit some level of groundwater contamination. In contrast, only two of thirteen sites known as Orphan I sites exhibit groundwater contamination above the Groundwater Quality Standards. These sites have low levels of chromate waste. Half of the twenty-four July 93 Directive Chrome sites have groundwater contamination.

Some of the cases discussed above with high levels of contamination do not yet exhibit contaminated groundwater, despite the length of time COPR material has been present. Some of these cases involve only a short transport distance between the source of contamination and the water table. The lack of groundwater impact in these cases could be attributed to 1) reduction of hexavalent chromium during transport between the source and the water table, 2) high adsorption of hexavalent chromium to the unsaturated zone waste material or soil, or 3) an incomplete transport pathway because of the lack of a hydrological connection between the chromium source and the aquifer under observation.

The potential for reduction of hexavalent chromium reduction in soils has been discussed by several researchers (Bartlett and James 1988, Zayed and Terry 2003, Losi et al. 1994, Wittbrodt and Palmer 1995, Jardine et al. 1999, Kozuh et al. 2000). Reduction is thought to occur in the presence of soil organic matter and $Fe^{2+}$, and evidence for partial reduction of chromium in COPR material has been observed as well (Weng et al. 1994, James 1994). In France, limited migration potential of hexavalent chromium in groundwater contaminated by COPR material

was observed due to likely reduction by ferrous iron (Loyaux-Lawniczak et al. 2001). Several of the New Jersey chromium sites contain meadow mats that lie at or near the water table which appear to either reduce or adsorb hexavalent chromium, such that significant chromium impacts to the groundwater have yet to be observed. However, it is difficult to predict whether this mechanism will operate indefinitely. Given a continuing source of fresh hexavalent chromium leachate from continued dissolution/oxidation of the overlying waste material, the reduction capacity of the available reducing agents (the meadow mat in this case) could ultimately be exceeded. Then, breakthrough of hexavalent chromium material to the groundwater might be observed.

Renewal of reducing agents may slow the rate at which their reducing capacity is exhausted. In particular, the Fe(III) produced by reduction of Cr(VI) can be reduced again to Fe(II) by humic and fulvic acids, and be available for another cycle of reducing CR(VI). Wittbrodt and Palmer (1996) pointed out that differing rates for redox reactions (Fe(III) reduced by organic matter; Cr(VI) reduced by organic matter; Cr(VI) reduced by Fe(II)) can allow for redox cycling of iron in the system organic C-Fe-Cr. Wielinga et al. (2001) describe a role for dissimilatory iron-reducing bacteria in this process, whereby Fe(III) is reduced in microbial respiration and acts as an electron shuttle, catalyzing the reduction of Cr(VI). Depending upon the chemical environment, iron can be cycled more than once.

In cases where chromium reduction occurs during groundwater transport, the plume length may slowly increase as reducing agents in the aquifer material are consumed. Whether or not breakthrough or plume lengthening would actually occur would require quantitative knowledge of the reduction capacity of the reducing agent, whether redox cycling of iron is occurring, the total amount of hexavalent chromium that would ultimately pass through this organic material, and whether the kinetics of this reduction process would continue to be adequate as the reducing agent was depleted. While at least one investigator is looking into methods for assessing reduction capacity of naturally occurring reducing agents (Lee and Batchelor 2003), much additional research is needed before it will be possible to ascertain the ultimate impact of chromate waste sites on soil and groundwater. Thus, it is difficult to predict whether COPR sites that do not exhibit chromium-contaminated groundwater at the present time will continue to do so as hexavalent chromium continues to leach in future decades.

Turning to the issue of adsorption/desorption of hexavalent chromium, some quantitative information is available pertaining to its adsorption to soil (as opposed to COPR waste) that enables a limited assessment of its potential to impact groundwater. Although hexavalent chromium is frequently considered to be a relatively mobile contaminant, this assessment may be influenced more by the observation that it is readily released from waste material, rather than actual observed transport rates through soil. While this metal is relatively mobile relative to certain other metallic contaminants, such as lead or trivalent chromium, it is nonetheless retained by soil to a significantly greater extent than water-soluble anions such as chloride and nitrate, which generally transport readily through the soil. Soil adsorption coefficient values for hexavalent chromium reported in the USEPA Soil Screening Guidance Document range from 1 to 1,800 L/kg (USEPA 1996). NJDEP studies relating to assessing the dermal exposure pathway also suggest a wide variation in values (NJDEP 2004a). Direct measurement of soil adsorption coefficients on twelve New Jersey soils using freshly applied chromate salts yielded adsorption coefficients ranging from about 3-13 L/kg (Allen et al. 1994, NJDEP 2004b). This latter range

of adsorption coefficients, when used in the SESOIL unsaturated zone transport model (Bonazountas and Wagner 1984), indicate that the time for hexavalent chromium to transport 10 feet downward through sandy loam soil ranges from 6 to 70 years (NJDEP 2004c). However, even in cases where it might appear that hexavalent chromium is highly adsorbed to soil, there may still be a concern for potential groundwater impacts. A continuing source of fresh hexavalent chromate leachate from overlying COPR material may eventually saturate all soil adsorption sites in the soil column, at which time rapid breakthrough of chromium to the water table might be expected.

If some COPR sites show a lack of a groundwater impact because of a lack of a hydraulic connection between the waste material and the groundwater, the transport pathway is incomplete and need not be evaluated. However, the lack of such a connection should be demonstrated and consideration should be given to where infiltrating water is being routed. Another receptor may be of concern. In addition, if the site is disturbed due to construction or other activities, the lack of a hydraulic connection would have to be reconfirmed.

To summarize, various concentrations of COPR or chromium-contaminated soil have been indicated to be a threat to groundwater quality, while similar concentrations in other situations have not impacted groundwater. The minimum concentration of chromium at COPR sites that may result in an unacceptable groundwater impact is unknown at the present time and is certain to be site-specific. Furthermore, direct measurement of chromium concentrations in the groundwater indicate current conditions, but do not necessarily predict possible future impacts to groundwater. Thus, laboratory and field data are inadequate to answer the first charge regarding a definitive concentration of chromium at COPR sites that result in contamination of groundwater above the chromium Groundwater Quality Criterion.

Given the lack of adequate field or laboratory data to ascertain an appropriate chromium concentration at COPR sites to avoid unacceptable impacts to groundwater, it is necessary to use available scientific tools to predict such an impact. Such tools have been developed as part of NJDEP efforts to propose and adopt soil remediation standards. This then leads to a discussion of the second charge:

*b. Do the proposed soil clean-up standards adequately protect groundwater?*

The NJDEP has not yet proposed soil clean-up standards. However, it is planning to propose soil clean-up standards that include generic soil standards and site-specific options for protection of groundwater from leaching of contaminants from soil (NJDEP 2004d). The purpose of the Impact to Groundwater Soil Remediation Standards is to prevent the unacceptable risk to human health from the ingestion of contaminated groundwater, caused by the migration of chemicals from the unsaturated soil zone to the groundwater. While these standards and procedures may be suitable for chromium-contaminated soil, their applicability at COPR sites is limited due to the unusual nature of the source contamination.

For this reason, chromium has been removed from the list of contaminants that will be included in the proposal, and is separately discussed here. The following discussion consists of seven sections:

1) a discussion of the USEPA methodology for calculating generic impact to groundwater soil clean-up standards,
2) a discussion of why this methodology is unsuitable for COPR sites,
3) an assessment of the applicability of alternate options for calculating impact to groundwater soil cleanup standards at COPR sites,
4) the recommended approach for managing COPR material,
5) the recommended approach for managing chromium-contaminated soil,
6) distinguishing COPR material from chromium-contaminated soil, and
7) Other Alternative Remediation Standard Procedures ("Tier III Standards")

**1) USEPA Methodology for Developing Generic Impact to Groundwater Remediation Standards**

The USEPA Soil Screening Level (SSL) Guidance Document (USEPA, 1996) recommends the use of the simple partitioning equation to calculate inorganic soil cleanup standards for the Impact to Groundwater Pathway (USEPA, 1996, Equation 22):

$$IGWSRS = C_{gw}\left\{(K_d) + \frac{\theta_w + \theta_a H'}{\rho_b}\right\}DAF \qquad \text{Equation (1)}$$

where:

*IGWSRS* = Impact-to-groundwater soil remediation standard (mg/kg)
Cgw = Health Based New Jersey Groundwater Quality Criteria (mg/L)
Kd = soil-water partition coefficient (L/kg)
$\theta_w$ = water-filled soil porosity ($L_{water}/L_{soil}$)
$\theta_a$ = air-filled soil porosity ($L_{air}/L_{soil}$)
*H'* = Henry's law constant (dimensionless)
$\rho_b$ = dry soil bulk density (kg/L) = 1.5 kg/L
*DAF* = dilution-attenuation factor

For New Jersey purposes, Equation 1 is expanded to separate the target leachate concentration discussed in the USEPA document into its component parts. The target leachate concentration is the product of the groundwater criteria ($C_{gw}$), and the dilution-attenuation factor (DAF). This modification allows the New Jersey groundwater quality criterion to be directly entered as an input parameter. The DAF is calculated via Equation 2. This equation requires a value for the mixing zone depth in the aquifer, which is calculated using Equation 3. These two equations are taken from USEPA SSL Guidance Document (USEPA, 1996, Equations 37 and 45), respectively.

*Equation for calculating the dilution-attenuation factor (DAF):*

$$DAF = 1 + \frac{Kid}{IL} \qquad \text{Equation (2)}$$

Where:
$i$ = gradient (m/m)
$d$ = mixing zone depth (m), calculated below (Equation 3)
$I$ = infiltration rate (m/yr)
$L$ = length of area of concern parallel to groundwater flow (m)
$K$ = aquifer hydraulic conductivity (m/yr)

*Equation for calculating the aquifer mixing zone depth, d:*

$$d = (0.0112L^2)^{0.5} + d_a\{1 - \exp[(-LI)/(Kid_a)]\} \qquad \text{Equation (3)}$$

Where:
$d_a$ = aquifer thickness (m)

This equation assumes that contaminants in soil exist in equilibrium between the sorbed phase (on soil solids), aqueous phase (in soil moisture) and vapor phase (in the soil airspace). The equations calculate the total amount of the contaminant that may be left behind in the soil such that the aqueous phase concentration of the contaminant will not exceed a specified criterion. The criteria for New Jersey are the health-based groundwater quality criteria. Since soil water will actually be diluted once it enters the groundwater, a dilution-attenuation factor (DAF) is included in the equation to account for this process. Dilution of the contaminant due to transport through the unsaturated soil zone is not included; the chemical in soil is assumed to be immediately adjacent to the water table. Chemical degradation is also not included in this model; the calculations assume that groundwater quality must be achieved immediately after remediation.

**2) USEPA Methodology not suitable for COPR waste sites**

The USEPA simple partitioning equation assumes that contaminant concentrations in soil solution is controlled by adsorption-desorption equilibrium processes, as quantified by the soil-water partition coefficient ($K_d$). This model may useful for chromium contamination in soil. In contrast, COPR waste sites may consist of pure slag waste material, chromium-contaminated soil, or a mixture of both. COPR slag waste material is not soil and exhibits fundamentally different properties than contaminated soil. Available evidence indicates that the leachable chromium in COPR slag waste results from dissolution of hexavalent chromium-containing

minerals in the waste residue, rather than adsorption-desorption between the solid and solution phases (James, 1994; Geelhoed et al. 1999; Hillier et al. 2003; Geelhoed et al. 2002). Specific hexavalent chromium containing minerals implicated in this dissolution process are hydrocalumite, hydrogarnet, and ettringite, which appear to be formed during chromite ore processing or COPR weathering. There is also a possible presence of calcium chromate, although this has not been regularly observed (Moerman 1996).

The concentration of chromium in soil solution resulting from dissolution would be controlled by the solubility of the chromium minerals, the kinetics of the dissolution process, and the effects of slag constituents on the solubilization process. This is an entirely different mechanism from the simple partitioning equation.

The dissolution process of a mineral may be described as:

$$AB(solid) \leftrightarrow A^{+}(aq) + B^{-}(aq)$$

Where AB represents the undissolved solid mineral, and $A^+$ and $B^-$ represent the cation and anion in solution. As shown, the reaction will eventually proceed to equilibrium, and dissolution and precipitation reactions will be equal. At equilibrium, the solution phase is said to be <u>saturated</u> with the salt (mineral) of interest. This may be quantitatively expressed as:

$$K_{sp} = [A^{+}] \times [B^{-}]$$

where $K_{sp}$ is the solubility product (units dependant on the salt) and $[A^+]$ and $[B^-]$ represent the concentrations of the cation and anion at saturation.

A fundamental difference between this process and the adsorption-desorption process is that the concentrations of the constituents in solution after dissolution are independent of the concentration of the mineral in the solid phase, so long as that mineral is still present at mineral solubility equilibrium. This appears to be the case at the chromium waste sites, since solid mineral continues to be present to generate hexavalent chromium. In contrast, the simple partitioning equation (adsorption-desorption model) assumes a <u>linear relationship</u> between the sorbed phase concentration and the solution phase concentration. Thus, the two models are not compatible and the USEPA partitioning equation is not appropriate for use with COPR waste material. While the use of the $K_d$ parameter as an empirical, rather than theoretical, parameter might prove useful in assessment of hexavalent chromium leaching from COPR waste, an evaluation of this possibility has not been conducted at the present time.

For portions of a chromium waste site that consist of chromium-contaminated <u>soil</u>, or a mixture of COPR waste and soil, the simple partitioning model is theoretically applicable, since the solid phase contains components that participate in adsorption-desorption processes. However, the use of this model for inorganic contaminants is complicated by the presence of multiple oxidation states of chromium and the presence of various chromium complexes, each of which would have a different $K_d$ value. Furthermore, the $K_d$ values are dependant on soil pH. Finally, when chromium-contaminated soil is subjected to continued sources of hexavalent chromium from adjacent or overlying COPR source material, the chromium-adsorbing sites on the soil may

eventually become saturated, under which conditions the simple partitioning equation would no longer apply. Therefore, the NJDEP has decided that generic use of the simple partitioning model is not suitable for determining impact to groundwater soil cleanup standards for COPR waste sites.

*Assessment of the potential of using a generic dissolution model to determine a generic impact to groundwater soil cleanup standard at COPR waste sites*

It is of interest to explore the possibility of using a dissolution model to determine a generic impact to groundwater standard for COPR material. The solubility model indicates a constant aqueous concentration of hexavalent chromium would be observed in solution at equilibrium (so long as adequate solid phase is present) regardless of the chromium concentration in soil. This aqueous concentration will either be above or below the chromium criterion in groundwater. With this model, the leachable concentration of chromium in COPR waste does not necessarily correlate with the total concentration in the solid phase, and calculation of an acceptable soil concentration for protection of groundwater is problematic.

Laboratory studies of COPR waste material, on the other hand, indicate that leachate concentrations of hexavalent chromium are sensitive to pH, the soil-to-water ratio used, and the time of leaching or extraction. This implies that 1) pH affects concentrations of other COPR constituents in solution, which in turn, affect chromate concentrations, and 2) the dissolution reactions frequently do not proceed to equilibrium (i.e. saturation).

Relating to the pH effect, the solubility of minerals in solution is more complex than the simple model described in the previous section. Different salts containing common ions (sulfate, chromate, carbonate, calcium, etc.) will interact with each other and influence the concentration of each species in aqueous solution. The pH (concentration of hydrogen ion in solution) also affects a species solubility behavior. This is known as the common ion effect, and determining the equilibrium concentration of each species in solution requires a knowledge of all minerals (salts) present in the solid phase, and the solubility products for each. Then, the concentration of each species is calculated by assuming simultaneous equilibria of all species. This requires advanced modeling using models that calculate the various simultaneous equilibria, such as the MINTEQ model (Allison et al 1991). Such models are advanced research models not suitable for routine regulatory use.

To elaborate on the second statement (non-attainment of dissolution equilibrium), Geelhoed et al (2002). presented evidence that between pH 10 and 12, dissolution of chromate minerals in batch leaching experiments proceeded to equilibrium in 24 hours, while at lower pH values, equilibrium was not attained due to slow dissolution kinetics, even though the observed leachate concentration was higher at the lower pH values. Under field conditions, it is even less likely that chromium concentrations will reach saturation levels during storm events, or during soil moisture infiltration.

The simple dissolution model described above is therefore inadequate to describe either laboratory experiments or field observations. Given the insufficient understanding of the various factors controlling the dissolution process, an alternate generic model for calculating generic

impact to groundwater clean-up standards based on the dissolution process is not available at this time.

**3) Assessment of the use of Alternative Remediation Standard Procedures at COPR sites**

NJDEP plans to propose several procedures that allow for the calculation of site-specific alternative remediation standards for the impact to groundwater pathway. Six options have been described in the draft proposal (NJDEP 2004d). They are briefly outlined below, but most are not applicable to COPR material as they often require assumptions incorporated in the simple partitioning model discussed above. For more details on these options, see NJDEP 2004d.

*Option A. Site-Specific modification of the simple partitioning equation*

As discussed above, the simple partitioning equation was judged to be unacceptable for calculation of generic chromium impact to groundwater soil clean-up standards at COPR waste sites, and it may not be used for COPR slag waste material. However, it may appropriate for use with chromium-contaminated soil if a site-specific $K_d$ value is available. A site-specific $K_d$ value may be determined for chromium-contaminated soil using the Synthetic Precipitation Leaching test (see Option C below). Additionally, a site-specific dilution-attenuation factor (DAF) may be calculated from knowledge of the infiltration rate and/or aquifer properties.

*Option B. Immobile chemicals*

This option essentially results in a waiver for the impact to groundwater pathway for chemicals that are highly adsorbed to soil and are located a minimum of two feet above the water table. As discussed in the basis and background document, these chemicals are never expected to reach the water table. Chromium sites are not eligible for this option since hexavalent chromium is a relatively mobile contaminant (USEPA 1996).

*Option C. Synthetic Precipitation Leaching Procedure*

This procedure is a standard USEPA test method (USEPA Method 1312) that directly measures the leaching potential of contaminants from contaminated soil and waste material. The draft proposed soil standards basis and background document describes several approaches for interpreting the results of this test, including pass/fail options and options for calculating site-specific alternative remediation standards. Some of them require calculations that use the simple partitioning model and are unsuitable for use with COPR material, but may be used with chromium-contaminated soil. Other options make no assumptions regarding the nature of the leaching process and are therefore generally acceptable for use. Given the facile leaching of hexavalent chromium from COPR slag waste sites, it is likely that many of these samples will not pass the leaching test. The use of this option with chromium-contaminated soil may be more useful.

*Option D. SESOIL transport modeling when groundwater has not yet been impacted*

This option allows the use of SESOIL, a vadose zone contaminant transport model (Bonazountas and Wagner 1984), to estimate the impact to groundwater of soil contaminants. The simulation model uses soil, chemical, environmental, and meteorological inputs to determine this impact. SESOIL is unsuitable for use with COPR slag waste material because it assumes an adsorption-desorption mechanism for soil contaminants. However, it may be useful with chromium-contaminated soil if a site-specific *K*d value is available.

*Option E. Vadose Zone/Groundwater Modeling (SESOIL/AT123D)*

This option is used where groundwater has already been impacted by a contaminant. It allows a combination of vadose zone and groundwater transport modeling to demonstrate contaminant concentrations in the groundwater will achieve compliance with the groundwater quality criteria within a specified time frame. It is not appropriate for COPR waste material due to the same limitations described in Option D, but may be useful for chromium-contaminated soil.

*Option F. Consideration of Observed Groundwater Conditions*

This option essentially allows for a waiver for cases where contamination is in direct contact with the water table and no groundwater impacts are observed. This situation may occur for highly adsorbed contaminants, or in the case of COPR sites, where dissolution of the contaminant is slow enough that chromium concentrations in groundwater do not exceed 100 µg/L. To qualify for this option, the highest contaminant concentrations observed at the site must be present at the water table. Further details on the application of this option are described in the proposed soil standards impact to groundwater basis and background document.

**4) Recommended approach for managing the impact to groundwater of COPR waste material: treatment of COPR material as contaminant source**

Of the six options for calculation of Alternative Remediation standards discussed above, only Option F, and to a limited extent, Option C, are suitable for use with COPR waste material. However, as explained above, NJDEP anticipates that the results of Option C will indicate that all concentrations of chromium typically associated with COPR slag waste material are unacceptable. Furthermore, it is anticipated that Option F will never be useful when COPR material is present at the water table, because groundwater impacts in these cases will typically be above the groundwater quality criteria. Because of these issues, the leachability of hexavalent chromium from COPR material, and the inappropriateness of both the generic impact-to-groundwater simple partitioning equation, the NJDEP has decided to treat COPR waste material as a continuing source that will require remediation in accordance with the Technical Requirements for Site Remediation (N.J.A.C. 7:26E) for protection of groundwater.

By treating the COPR material as a continuing contaminant source, it falls outside the scope of the impact to groundwater soil clean-up standards, which pertain to calculation of clean-up standards for contaminated soil.

**5) Recommended approach for managing chromium-contaminated soil**

As opposed to COPR material, chromium-contaminated soil falls under the scope of the impact to groundwater soil clean-up standards, because the models and assumptions contained in the standards are appropriate. While the Department feels that the generic use of the simple partitioning equation for chromium-contaminated soil is inappropriate, all six options for calculating an Alternative Remediation Standard may be used, so long as overlying COPR material has been remediated in accordance with N.J.A.C. 7:26E requirements to prevent any further or future impacts to groundwater. The reason for this restriction is that a continuing source of fresh hexavalent chromate leachate from overlying COPR material may eventually saturate all soil adsorption sites in the soil column, at which time the simple partitioning model no longer applies and rapid breakthrough of chromium to the water table might be expected.

**6) Distinguishing COPR from chromium-contaminated soil**

Many areas at chrome waste sites consist of a mixture of chromium-contaminated soil and COPR material. The most conservative way to treat these mixtures would be to treat all material that contains any COPR residue as source material. However, this ignores the ability for waste material containing substantial amounts of soil to behave as chromium-contaminated soil, in that hexavalent chromium dissolving from COPR minerals may participate in the adsorption-desorption mechanisms on soil particles that are also present. On the other hand, material containing mostly COPR material and only small amounts of soil probably behaves similar to pure COPR waste material, in that the small amount of soil present may become saturated with the high concentrations of chromium leaching from the source material and no longer adsorb chromium. A reasonable strategy is therefore proposed where material consisting largely of COPR be treated as source material, and material that consists largely of contaminated soil can be treated using the soil clean-up standard guidelines. In the field, a mechanism for separating out these two classifications is needed. While various strategies should be investigated, it is suggested that pH measurements may be a practical means for accomplishing this task. The pH of New Jersey soils typically range from about pH 4 to pH 6.5 (Lee et al. 1996, Yin et al. 1996), while pure COPR source material typically ranges from pH 10-12. Both the COPR and soil have high buffering capacities, and it is reasonable to expect that mixtures of the two materials would exhibit pH values between 6.5 and 10. A value within this range is suggested as a decision point when classifying the tested material. Further investigation should be conducted to determine a suitable pH. Material exhibiting pH values less than this value may be treated as chromium-contaminated soil. Material with a pH above this level will be treated as source material.

It has also been observed that pure COPR material typically exhibits higher chromium concentrations than chromium-contaminated soil impacted by the source material. This suggests another potential method for classifying the waste material could involve chromium concentration criteria. However, a suitable concentration criterion is not available at the present time.

NJDEP recognizes that the mixture of COPR and soil is a particularly complex issue because it is unclear how to best identify COPR and the extent of its influence over the soil matrix. In addition to the above suggestions, a weight of evidence approach may be appropriate. Research is recommended to sort out the various options available.

**7) Other Alternative Remediation Standard Procedures ("Tier III Standards")**

As described in the Brownfield and Contaminated Site Remediation Act, the Department is required to consider site-specific adjustments to the generic soil remediation standard:

***58:10B-12f.(1)*** *A person performing a remediation of contaminated real property, in lieu of using the established minimum soil remediation standard for either residential use or nonresidential use adopted by the department pursuant to subsection c. of this section, may submit to the department a request to use an alternative residential use or nonresidential use soil remediation standard. The use of an alternative soil remediation standard shall be based upon site-specific factors which may include (1) physical site characteristics which may vary from those used by the department in the development of the soil remediation standards adopted pursuant to this section… and physical characteristics of the site, including, but not limited to, climatic conditions and topographic conditions.*

For this reason, the Alternative Remediation Standard options discussed above were prepared in order to provide expedient procedures for adjusting the generic impact to groundwater clean-up standards to site specific conditions. These options are ones that the department felt would be regularly useful, and are therefore specifically described. However, when circumstances warrant, the Department may allow other procedures for calculating alternative remediation standards. These procedures will be reviewed on a site-specific basis, and will require substantially more time for review than the predefined alternative remediation standards discussed above. The field data collected may be considerably greater than that normally acquired during site investigation. Additionally, the proposed approach may involve alternative or more advanced models than those proposed by the NJDEP. In other words, effort required for these "Tier III" procedures will be substantial greater than a routine investigation of the site, and approval of such procedures shall require adequate support from the published scientific literature. NJDEP wishes to emphasize, that for reasons discussed above, the determination of current groundwater conditions at a particular site is not adequate to elucidate potential future groundwater impacts at the site. In cases where the groundwater is not currently impacted by overlying chromium waste material, an advanced investigation would be required to determine why such impacts have not been observed, and to demonstrate that conditions at the site will continue to prevent groundwater impacts as long as the source material is present.

**Charge Being Addressed**

3. Interconversion

What is the capacity of trivalent chromium to convert to hexavalent chromium in the soil of the chromate ore processing residue sites? Do the current remediation standards adequately account for this interconversion? If not, recommend some options the Department should pursue to address any discrepancy or inadequacy, including research.

The general conclusion from all of the literature reviewed so far is that the factors controlling oxidation of Cr(III) to Cr(VI) are numerous but relatively defined. Determining the dominant

variable at a specific site is more complex, in particular because sites containing COPR vary in the proportions of COPR material to soil.

Fantoni et al. (2002) studied the oxidation of Cr(III) to Cr(IV) released from serpentinized ultramafic rock (ophiolites) in Italy. These researchers speculate that the release of chromium from these Cr-rich rocks to groundwater "requires oxidation of Cr(III) to Cr(VI)"; manganese oxides, hydrogen peroxide, gaseous oxygen and Fe(III) oxyhydroxides are considered likely electron acceptors. The pH of the groundwater in the area was reported to be 7.6. Likewise, Oze et al. (2004) observed that, although ultramafic rocks collected from New Caledonia, Oregon and California contain Cr(III) exclusively, Cr(VI) was identified in the soil solutions. They attribute this to some oxidation of Cr(III) in Cr-spinels by high-valent Mn oxides. Thus, both studies state that some oxidation of the natural Cr(III) is occurring in these systems. Cooper (2002) reports that oxidation of Cr(III) to Cr(VI) due to Mn(III/IV) oxides caused chromium toxicity in Zimbabwean ultramafic soils (pH about 6). The toxicity/oxidation in formerly wetted Fe-Mn concretionary subsoils occurred after 8 years of air-dry storage. Toxicity due to oxidation also occurred in well-aerated soils treated with $KMnO_4$. This researcher cites work by Silvester et al. (1995) indicating that oxidation is possible only in the aqueous phase. Cooper (2002) indicates that labile Cr(III) that can be oxidized is likely to be present in clay-rich ultramafic soils, and that oxidation "is probably continuous in concretionary subsoils subject to wetting-drying cycles."

Most researchers agree that Cr(III) oxidation can occur in various media if the appropriate manganese oxides are present and if other conditions are also favorable. Not only pH, but oxygen, sunlight, organic matter, and Fe-oxides may affect chromium redox reactions, as may the phase containing Cr(III). James (2002) points out that "aged, less soluble, and more crystalline forms of Cr(III) (e.g. $Cr_2O_3$) are much less prone to oxidation." Eary & Rai (1987) show that oxidation to Cr(VI) is rapid in the presence of manganese oxides at pH 3-4.7. Fendorf and Zasoski (1992) studied oxidation of Cr(III) by $\delta$-$MnO_2$ over a range of concentrations and at pHs from 3 to 5. Although thermodynamics indicated that higher pH and concentrations should favor the reaction, they found that this was not the case, stating "while increases in both pH and ionic strength increased surface charge, these two variables had opposing effects on the oxidation process." Fendorf et al. (1992) found oxidation by Mn-oxides decreased with increasing pH (>4) due to formation of a $Cr(OH)_3$ precipitate on $MnO_2$ surfaces. Using manganite ($\gamma$-MnOOH) as a reactant, Johnson and Xyla (1991) showed that the oxidation rate for Cr(III) was faster than those determined for other Mn-oxides, and that the reaction was "largely independent of pH and ionic strength…" Kozuh et al. (2000) observed oxidation of Cr(III) in soils low in organic-matter content and rich in Mn (VI) oxide. Work by Zhang (2000) found that, in low pH solutions, presence of some organic acids inhibited oxidation induced by light and Fe (III) because of competition from the organic acids with Cr(III) for $^{\cdot}OH$ radicals. In a study of Cr(III) oxidation by Mn-oxides in the presence of organic ligands (oxylate, citrate, HEDTA) at pH 4 and 10, Tzou et al. (2002) show that although "freshly hydrolyzed Cr(III) could be oxidized by $MnO_x$ at high pH, organic ligands may impede the redox reactions…" , but oxylate "showed low inhibition of Cr(III) oxidation." Saleh et al. (1989) reported slower Cr(III) oxidation rates in sediments where conditions were reversed from anaerobic to aerobic, and slow oxidation in one sample of lake water (pH 7.2). It is clear that, on the basis of the studies cited above, the roles of pH, dissolved and atmospheric oxygen, hydrogen peroxide ($H_2O_2$), organic acids, sunlight, and iron oxyhydroxides in Cr(III) oxidation are complex. There are relatively few studies that investigate

oxidation of Cr(III) in waste materials, particularly those at the alkaline pHs of COPR materials, but several of these are relevant to the subject of Cr(III) oxidation.

Chuan and Liu (1996) observed that oxidation of Cr(III) species from tannery sludge amendments (high in organic matter) was slower than when pure Cr(III) species are added to soil. Pillay et al. (2003) cited a previous study (Schroeder and Lee, 1975) where oxidation was rapid in alkaline conditions; these relate to their study of oxidation of Cr(III)-bearing slag from stainless steel production. Pillay et al. (2003) found, for ground aged and weathered slags in powder, balls, and pressed pellets, that oxidation proceeded faster in weathered slag samples, and also in powdered samples rather than balls. Smaller particle size also promoted oxidation. A control experiment under $N_2$, similar to that of James (1994), indicated that "the oxidation reaction proceeds due to the presence of atmospheric oxygen." Furthermore, increasing the level of calcium present enhanced oxidation, as did the presence of atmospheric moisture. Pillay et al. (2003) conclude that, for weathered (decrepitated) slag, more surface area is exposed over time, thus allowing further oxidation, and that "a small fraction of the residual trivalent chromium in alkaline slag is amenable to atmospheric oxidation." It is not clear whether Pillay et al. (2003) measured Mn in the slag materials, so it is not known to what extent, if any, Mn oxides may have been involved in the oxidation attributed to atmospheric oxidation.

James (1994) conducted laboratory studies using COPR soils under various conditions. Interestingly, he found that at pH 8 to 10, neither oxidation nor reduction occurred when soluble Cr(VI) was added to a high-Cr(VI) soil and to a low-Cr(VI) soil. Additional factors such as Mn(II) and lactic acid were significant reductants, however--the former at high pH. Geelhoed et al. (1999) point out that at low pH (below pH 5) and low Cr(III) concentration, oxidation is fairly rapid, but that at pH above 5, Cr(III) precipitates on the Mn-oxide surface, thus restricting the reaction. They also point out that oxidation of Cr(III) by oxygen is "extremely slow" (Geelhoed et al. 1996 - citing Van der Weijden and Reith 1982). James (1994) interpreted results of experiments involving COPR and COPR by-products conducted under air and $N_2$ to indicate that oxidation of Cr(III) by oxygen does not explain Cr(VI) precipitates, or blooms, that occur on surficial materials and basement walls at and near some COPR sites. Additional experiments by James (1994) indicated some oxidation of Cr(III) added to soils containing low concentrations of Cr(VI), but oxidation of Cr(III) was not apparent in soils with high concentrations of Cr(VI).

Rock et al. (2001) show that, on soils contaminated with COPR, a $H_2O_2$ leaching solution produced higher concentrations of Cr(VI) than did a solution containing $NaNO_3$ within a 24-hr period. No decrease in Cr(VI) attributable to reduction was noted after $H_2O_2$ disappeared from the leachate. Rock et al. (2001) point out that, thermodynamically, oxidation of Cr(III) by $H_2O_2$ is favorable, although the increase in Cr(VI) in leachate does not prove oxidation. They also suggest that a Cr(VI) peroxide complex may have formed. No reduction of Cr(VI) by $H_2O_2$, which is thermodynamically possible, was observed. Hydrogen peroxide ($H_2O_2$) has been postulated to form naturally in water as a result of sunlight-induced reactions, and has been measured in both surface-water and ground-water samples exposed to light (Thurman, 1985). Further, Zhang (2000) reported light- and Fe (III)-induced oxidation of Cr(III) in simulated atmospheric waters containing Mn(II) and organic acids. There are no available data from COPR sites to indicate whether or not such reactions take place or are of environmental significance.

*Reduction of Hexavalent to Trivalent Chromium*

While the charge specifically refers to the oxidation of trivalent chromium to hexavalent chromium, it implicitly includes the reduction of hexavalent chromium to trivalent chromium as well. Hexavalent chromium in soils is reduced by Fe(II) (Buerge and Hug, 1997 and 1999; Seaman, et al., 1999; Fendorf et al., 1997). The Fe(II) may derive from reduction of Fe(III) in hydroxide phases, and this reaction may involve organic matter (Wittbrodt and Palmer, 1996). The experiments of Wittbrodt and Palmer (1996) indicate that Fe(III) may be rapidly reduced by soil humic acid, and the Fe(II) then reduces Cr(VI) or that a ferric chromate complex is reduced by humic acids. They point out that reduction of Cr(VI) is slower at higher pH (their experiments were at pH 2, 4, and 6). Fendorf and Li (1996) determined Cr(VI) reduction rates in solutions containing Fe(II) over a pH range of 6.0-8.0. They found that Fe(II) is an "effective reductant," and they indicate that oxygen would limit Cr(VI) reduction only at pH values >8. Henderson (1994) also points out that reduction of Cr(VI) is slow in ground water at "near-neutral pH values." Reduction of Cr(VI) can take place after adsorption has occurred—Deng and Stone (1996), using experimental solutions with suspended solids, indicate that adsorption is an important condition for the reduction reaction to take place. Eary and Rai (1988) conducted laboratory studies showing that, in experimental solutions, reduction of Cr(VI) to Cr(III) is favored in the presence of Fe(II) salts over a pH range of 2.0-12.0. Solubility of precipitated $Cr_xFe_{1-x})(OH)_3$ limited Cr(III) concentrations in the pH range of 5.0-11.0. Anderson et al. (1994) observed that Cr(VI) reduction in sandy aquifer sediments occurred in the presence of Fe(II)-bearing minerals and increased with decreasing pH. Further, the results of these batch studies suggest that organic compounds, even in small amounts, may influence the availability of Fe(II) by reducing Fe(III). They propose that organic matter, in and of itself, did not reduce the Cr(VI), but that organic matter affects reduction by making more Fe(II) available for reaction. Other researchers have shown that the presence of organic matter increases Cr(VI) reduction (Bartlett & James, 1988; Bartlett & Kimble, 1976); Losi et al., 1994). Wittbrodt and Palmer (1995) report that reduction rates of Cr(VI) in the presence of organic matter is strongly pH dependent, increasing with decreasing pH. Additionally, some bacteria have been shown to reduce Cr(VI) to Cr(III). Guha (2004) observed this microbiologically-mediated reduction by *Shewanella alga* in a laboratory study. In this study, it was noted that reduction rates decreased significantly in the presence of manganese oxide.

*Competing Redox Reactions at COPR Sites*

A recent study (Böhm & Fischer 2004) presents the proposition: "The actual Cr(VI) concentration in aerated topsoils is determined by two contrary processes: the Cr(III)-oxidation by Mn oxides and the reduction of Cr(VI) by soil organic matter. It depends on the temporary predominance of one of these reactions…" Bartlett (1991) also states that as site conditions vary, oxidation or reduction will dominate. James (2002) presents a visual model of the relationship between organic matter and manganese (Mn[III,IV] [hydro]oxides) on chromium oxidation, depicted in Figure 6.1. In effect, this seesaw depiction describes the phenomenon described by Böhm & Fischer (2004). The James' papers indicate that pH is a "master variable" for both oxidation and reduction reactions. The point of this illustration is to show that many

variables control the interconversion of the chromium species and that a change in any of them can alter which reaction dominates.

Recognizing that the initial interconversion charge is specific to the COPR sites, the phenomenon of the oxidation of trivalent to hexavalent chromium should be evaluated using the conditions found at COPR sites. The pH regimes found at these sites may vary somewhat, depending upon the proportions of the highly alkaline COPR material to the soils with which it may be mixed. The amount (or presence/absence) of organic matter and Mn-Fe oxides also will vary depending upon the amount and type of soil present in soil/COPR mixtures. If, for example, manganese oxides (Mn(III,IV)) are absent at sites dominated by COPR material, this would preclude the oxidation of Cr(III) to Cr(VI) by this mechanism. Nevertheless, as shown by Pillay et al (2003), atmospheric oxygen can oxidize small amounts of Cr(III) in alkaline slags, and the smaller the particle (with larger surface area) the more likely this reaction will occur. It would appear that, if COPR is subject to vehicular traffic or other disturbances at some sites, that fresh surfaces could be exposed, and that oxidation would occur to a greater extent under such conditions than at sites where COPR is not disturbed and has little contact with the atmosphere. Although the amount of Cr(III) in COPR that could be oxidized over several years may represent a small percentage of the total Cr(III), the mass of Cr(III) present at a site may be sufficiently large that even small percentages oxidized to Cr(VI) could represent a significant environmental hazard. Using data reported in the literature as a guide, an estimate of the mass of Cr(VI) that might be generated at New Jersey sites might be made. Further work is needed to investigate the potential for the oxidation of Cr(III) and the reduction of Cr(VI) in COPR and COPR-soil mixtures. Such investigations will help in determining whether cleanup standards need to be adjusted.

For reduction of Cr(VI) to occur there must be available reductants—organic matter is an important reactant. Researchers studying COPR sites in Scotland conclude that organic matter is capable of reducing Cr(VI) in COPR to Cr(III) (Geelhoed et al., 1999). If materials at COPR sites contain little or no organic matter, however, then there is less likelihood that reduction will take place, as the presence of Fe(III) hydroxides, without something to reduce the iron to Fe(II), apparently is not a sufficient condition. Nevertheless, at sites where COPR is mixed with less alkaline soils containing organic matter and iron hydroxides (or Fe(II)-bearing minerals), reduction of Cr(VI) is likely to occur. Thus, at some COPR sites, conditions may be such that Cr(VI) is reduced to a relatively insoluble Cr(III) solid.

**Charge Being Addressed**

4. Concentration Effect

Enrichment of concentrated hexavalent chromium has been observed on soils and in structures at the sites. Soluble hexavalent chromium dissolves in groundwater and can move throughout the soil column. The chromium becomes concentrated as the water evaporates. Rainfall events and movement of groundwater levels can change the location of these concentrated evaporative fronts. Can the concentration of chromium in the enrichment areas be anticipated and modeled?

Is there a concentration in the soil that protects against elevated levels of hexavalent chromium from being deposited in this way?

**Summary**

The phenomenon of enrichment of hexavalent chromium [Cr(VI)] on structures and at the land surface has been documented at the COPR sites in New Jersey. Capillary action is responsible for the movement of the soluble Cr(VI) upward and horizontally. Capillary action is a surface tension phenomena that causes the retention of moisture in the pores of a soil above the water table. Capillary action causes water to move from saturated soils to drier soil against the force of gravity, much like how plants transport liquid from the roots. The height of capillary rise is a function of the pore size and pore size distribution in the soil, which is related to the grain size distribution and density of the soil. In silt loam soils, common at many COPR sites, this rise can reach eight to nine feet above the water table. Theoretically, a rise of up to 15 feet is possible in a loam or silty clay loam soil (Knuteson et al, 1989). In sandy soils, which have larger pore sizes between soil particles, the pull is less, perhaps reaching 1.5 to 2 feet above the water table. Concentration differentials of Cr(VI) have been observed only in areas where the Cr(VI) is very high already. That is, at sites having high concentrations of Cr(VI) in the soil due to the presence of COPR slag, one would expect to see visible blooms in the form of chromium salt precipitates occurring at the land surface and on basement walls and other porous structures. However, there has been no demonstrated chromium enrichment in the form of visible blooms at sites where the Cr(VI) concentrations are lower. Because the blooms can be transient, their formation and disappearance may have gone unnoticed, or the factors involved in bloom formation may not be completely understood. Given the complexity of the factors involved, it is determined that it is difficult at this time to develop a predictive model for this transport mechanism.

The presence of Cr(VI) on small, respirable particles on unpaved surfaces warrants further investigation because such particles can be re-suspended by vehicles and by wind. This phenomenon is described in more detail in Chapter 5 of this report. The generic cleanup numbers are based on conservative estimates of a hypothetical site. Currently, the development of alternative remediation standards (ARS) is allowable by law. These standards can be developed by responsible parties to more accurately model the distribution of chromium on particles specific to their sites. However, the actual numbers generated by this process have been difficult to replicate. It is often mentioned in the literature that chromium adsorbs more to smaller particles than to coarser particles. This mechanism is expected to occur at COPR sites and should be accounted for in the development of both generic standards (which it is) and alternative remediation standards (which is unclear).

This charge was divided into two principal components in order to address the issues associated with the overall phenomenon of the potential enrichment of chromium on small particles and through evaporative increases of concentration on soil surfaces and on structures over time.

*Evaporative Enrichment (leading to the precipitation of chromium salts, as "blooms")*

For the purposes of this report, evaporative enrichment is defined as the transport of hexavalent chromium dissolved in groundwater or soil solution to surfaces where evaporation can concentrate the solution and possibly cause crystals of hexavalent chromium-bearing minerals to

precipitate. Surface enrichment may, but often may not be, discernable by yellow or yellow-green chromium "blooms", or crystallization of hexavalent chromium salts on the surface of walls or on the waste itself. The phenomenon may occur at the ground surface, on basement floors and walls, and possibly at other locations where soil solution or groundwater seeps to surfaces where evaporation can take place. Chromium salts dissolve in the water and is transported with water until a surface is reached. During dry periods, the water recedes, but the chromium salts remain precipitated on the surface of a concrete basement or surface soil or any other surface where evaporation of water and precipitation of salts can occur.

The evaporative enrichment phenomenon can occur by unsaturated transport of salts by infiltration and percolation, followed by evaporation of water from a surface. This phenomenon is of concern because hexavalent chromium may eventually be transported to a location where it can expose humans to inhalation risks, either by reaching the land surface or by seeping through walls or floors. Such evaporative blooms have been observed in basements of homes built on land where COPR was used as fill and in areas where hexavalent chromium concentrations are quite elevated. It is not known to what extent the phenomenon exists at lower soil chromium concentrations, or if there is a threshold concentration under which it does not occur.

While evaporation may be the most important factor in the appearance of blooms, there are other factors, particularly in soil, that are pertinent, including the type and nature of the material present, the number of available adsorption sites, the pH, the zero-point charge, the redox status, and the presence of organic reductants.

Two processes are of interest: 1) capillary transport of chromium upward from the subsurface to the soil surface; and 2) transport of dissolved chromium through soil and into structures.

*1) Capillary Transport of Chromium Upward from the Subsurface to the Soil Surface*

Evaporation helps to draw the soil solution upward toward the ground surface by increasing the suction pressure within the soil solution that clings to the solid grains in the porous medium Cr(VI) blooms occur by this mechanism when the depth to the water table is low and less than the thickness of the capillary zone. Data show that blooms become visible on land surfaces where gross contamination of Cr(VI) is dominated by the presence of pure COPR waste. In New Jersey, the net direction of bulk water flow in soil is downward. However, such infiltration downward through the soil column with subsequent groundwater recharge may be inhibited at times in zones where the capillary zone reaches the soil surface.

Visible blooms in areas of significant surface enrichment are typically associated with high hexavalent chromium concentrations. Initially observed in areas known to be disposal sites for pure waste, this surface enrichment on the waste was transient and appeared related to periods of dryness following precipitation events, but it has not been observed at all COPR sites. While these latter sites without visible blooms contain elevated soil chromium levels, the levels are not typically as high as those recorded at the sites where large amounts of pure waste have been deposited. Salts observed at COPR slag and adjacent sites have been confirmed as chromate. These evaporite-like deposits are transient, being readily dissolved by rainfall. When surveyed, elevated chromium concentrations in runoff, groundwater, and river sediments have been

detected proximate to these sites. Field data have confirmed the presence of chromate but have not fully characterized its distribution within the soil profile. The chromate blooms observed at many of the COPR sites occur when hexavalent chromium salts precipitate on the surface of poorly drained soils where shallow groundwater and a capillary fringe permit upward movement and evaporation of soil water containing these soluble chromate salts (James, 1994). This phenomenon has been observed on the ground surface directly above COPR, and on basement walls directly adjacent to COPR deposits (IT Corp., 1992 and 1995). The chromate blooms have not been observed at every site where COPR is found at the surface. Nor have blooms been seen across the entirety of those COPR sites where blooms have been occasionally observed. The blooms can appear during dry periods, when evaporation of soil water occurs at the soil surface, and the blooms can disappear when rainwater dissolves the salts again (James, 1994). Despite the recurrent nature of the blooms in some locations, some of the specific conditions required to create such blooms remain to be identified. Also, field measurements are needed to learn whether the absence of a visible bloom is sufficient to rule out evaporative enrichment. Thus, knowledge of Cr(VI) levels in soils might not be sufficient to predict blooms at COPR sites, except at highly contaminated sites where visible blooms have been recorded regularly. A variety of physical and chemical conditions contribute to bloom formation, such as total Cr(VI) and water soluble Cr(VI) concentrations, pH, and wetting/drying cycles.

*2) Solute Transport of Chromium through Soil and into Structures*

The presence of Cr(VI) inside buildings resulting from unsaturated or saturated transport can lead to human exposure. Water can be a vehicle to transport soluble Cr(VI) into interior living or working spaces. In this scenario, water contaminated with Cr(VI) moves through concrete slabs or cinder block indoors and deposits the soluble chromium through the evaporation of the water. Over time, the deposited Cr(VI) becomes incorporated into basement dust and is suspended by various activities.

During remedial investigations at COPR sites, the presence of chromate salts on the interior wall surfaces was observed as green or yellow precipitates. This led to a conscious effort to visually inspect all interior and exterior building surfaces (and sample when appropriate) constructed on or near COPR sites for the presence of more blooms or for conditions that would favor the development of blooms. After inspection of structures at numerous sites, it was determined that the occurrence of visible chromate salts on interior wall surfaces was associated with very high hexavalent chromium concentrations in surrounding soil in direct contact with the structures. Blooms were not observed in areas where these conditions were not met. Analytical tests were not completed, so it is not known whether Cr(VI) salt deposits were present at concentrations that would not cause a visible bloom. The most probable mechanism was determined to be hexavalent chromium contaminated water seeping horizontally or "wicking" upward through the concrete or cinder block or mortar joints. Evaporation promoted the seepage through the concrete. Subsequent evaporation and crystallization then resulted in the observed salt formation. Review of a subset of the Hudson County Chromium Sites (those of Tierra Solutions, Inc.) illustrates the observations (Brown and Caldwell, 1999, 2001a, and 2001b). Of the 40 sites being addressed by Tierra, four sites (Sites 41, 47, 58, and 209) exhibit chromate salt formation on interior walls. Interim remedial measures have been taken at these sites, which include the use of epoxy coverings to isolate salts from human contact, as well as mandated routine

inspection and testing. The experience has been that, extant physical damage to the epoxy coverings, these measures have been protective. However, despite years of inspection, new areas of chromate salt formation have not been observed and the known areas show neither significant migration nor expansion nor any change in location of chromate salt formation. This indicates certain stability in the occurrence of these visible salt formations that perhaps equilibrium is reached over time.

Examination of the cause of the chromate salt formations suggests an association with nearby high hexavalent chromium concentrations. Peak soil boring Cr(VI) concentrations of 6,940; 8,200; 1,620 (with 4,130 below); and 5,300 mg/kg were found at sites where evaporite salts were observed in basements. While elevated, these concentrations do not necessarily represent the maximum seen during the remedial investigations. Clearly, a source of chromate salts at significant concentration is one factor that can be used to predict salt deposition in basements, but it seems proximity to the contamination is also important. On a general level, the expected reductive and adsorptive capacity of the soil may affect the horizontal distance from the source where this phenomenon can occur, explaining the absence of the phenomenon in areas where chromium concentrations are not elevated. However, it does suggest that additional factors may be involved in the observed infrequency of the salt formation.

Weng et al. (2002) have explored the possibility of developing a predictive model to estimate the potential for hexavalent chromium to form salts on interior walls of residential structures. They determined that the factors are too complicated to model. The number of variables involved and the uncertainty surrounding them precluded the development of an adequate transport model for these researchers. Therefore it is recommended that the current SRWMP empirical approach to evaluate this potential concern during the remediation of each site is the most practical approach at this time and should be continued in conjunction with any model that may eventually be developed.

*Particle Enrichment*

For the purposes of this report, particle enrichment has been defined as the preferential adsorption of hexavalent chromium on smaller particle sizes such as clay-sized particles. This can occur at the surface of the soil, which is of concern here, or at depth through the soil column, which is a factor in chromium transport to groundwater. The issue of concern here is that vehicular activity on unpaved surfaces of COPR sites will result in the suspension of airborne particulates (small particles with sorbed hexavalent chromium) from the surface of the soil. If the chromium is associated with the surface particles, it will also be associated with the airborne particulates suspended from that surface.

The phenomenon when it occurs on the land surface is important because the inhalation risk-based soil clean-up criterion for chromium is determined by modeling the risk from respirable particles less than 10 microns in size. There are two types of models used to calculate soil cleanup levels. The first model predicts emission rates of particulates from truck traffic and wind-blown dust. The second is used to describe the movement of this particulate through the air and predict air concentrations at designated points at and around the site. These predicted concentrations are then used to back-calculate to the soil concentration that would result in the

one in a million cancer risk level for a specific contaminant, Cr(VI), and is compared against the soil chromium concentration in bulk soil samples collected at the top 0-6 inches. Thus, there is concern that the current methodology by which bulk sampling techniques are compared to the inhalation risk level may underestimate the risk because the sampling method does not distinguish among the different sized particles. Adsorption and other mechanisms that distribute mass on particle surfaces raise concerns that small particles may contain more chromium per mass of particles than the coarser soil particles. Techniques for separating the smaller particles are not fully developed for routine uses.

Surface area per unit mass of soil is greatest for the smallest-sized soil particles. For instance, a cobblestone could have a surface area of one square meter. If the cobble is repeatedly struck with a sledgehammer, it could be broken into possibly 100,000 individual particles while still containing the same mass of the intact cobble. Collectively these smaller particles would have a greater surface area than the initial one square meter of the intact cobble. Therefore, the surface area per unit mass is inordinately greater for the pulverized rock than for the intact cobblestone. Adsorption of contaminants onto these particles is a surface phenomenon in which a chemical species adheres to the soil interface. The larger the surface area the higher the opportunity for adsorption. The clay-sized fraction represents a significant component of soils for adsorption because they are found in layers throughout the soil column and their small size provides abundant surface area for adsorption of chromium (or other contaminant).

The smaller the soil particle or sediment grain, the larger is its surface area relative to its volume. The surface area of a gram of fine colloidal clay is about a thousand times that of a gram of medium sand. Thus, the capacity for adsorption is much greater for small soil particles than it is for large particles (Brady, 1974 and 1996). Adriano (1986), in summarizing studies of trace elements and their relation to particle-size fractions and soil horizons, reports that Korte et al. (1976) show a strong correlation between the capacity of soils for cations, the amount of clay, and the surface area. The correlation for anions is stronger for free iron hydroxides than it is for clays or surface area; nevertheless, soils of clay or silty clay texture, with a percentage of clay over 50%, and surface areas of more than 50 $cm^2/g$, are shown to have a high capacity for oxyanions such as dichromate ($Cr_2O_7^{2-}$). The correlation of oxyanions with iron hydroxides is expected, as the anions are most likely to be adsorbed to positively charged surfaces such as iron hydroxides (with a zero point of charge of about 8.5). Oxyanions such as chromate have less affinity for clays, which generally have negatively charged surfaces except when highly protonated at low pH. Iron is contained in significant concentrations in COPR sites, and amounts of $Fe_2O_3$ have been measured at 51% of total soil sample at these sites (Gafafer, 1955 as reported by Kitsa et al. 1992).

Adriano (1986) describes the work of Connor et al. (1957) who found that concentrations of chromium and other trace elements were higher in B or C horizons (which typically contain illuviated small particles) than in A horizons, and that the clay fraction contained most of the trace elements. Because almost all, if not all, of the sites in Hudson County represent disturbed soils, illuviation and concentration of material in B and C horizons is difficult to define. The soils at and near COPR sites in Hudson County undoubtedly have been disturbed. However, natural soils or sediments did exist at these locations before the disturbance for construction and use of COPR as fill. The clays and iron and aluminum oxyhydroxides continue to be present in

the soils, and typically retain the bulk of the trace metals, especially in areas where COPR is mixed with the original soils. The clay-size particles reported by Connor et al. (1957) happened to be in B and C horizons (which is where one would expect them to accumulate in undisturbed soils). Many trace elements, including chromium, tend to be adsorbed preferentially to small soil particles whether those particles are in well-defined soil horizons or whether the horizons have been disturbed.

Laboratory and field studies have demonstrated that adsorption of chromium occurs in soil and that it occurs more on smaller particles than on coarse particles. However, particle size is not the only factor influencing the adsorption and therefore the enrichment of chromium. Adsorption is strongly controlled by pH, the type of material, number of available adsorption sites, redox status, presence of organic reductants, and other environmental factors that control the fate and transport of hexavalent chromium (USEPA 1999, Farmer, et al. 2002, Weng, et al 2002, Weng, et al. 1994, Loyaux-Lawniczak et al. 2001, Pettine, et al. 2002, Grove and Stollenwerk 1985, Gaberell, et al. 2003, Anderson, et al. 1994, Deng and Stone 1996, Wittbrodt and Palmer 1995, Wittbrodt and Palmer 1996, Buerge and Hug 1997, Buerge and Hug 1998, Buerge and Hug 1999, Seaman, et al. 1999, Henderson 1994, Jardine, et al. 1999, Kozuh, et al. 2000, Lee and Batchelor 2003, Davis and Olsen 1995, Brigatti, et al. 2000, Tokunaga, et al. 2001, and Palmer and Puls 1994).

Anderson et al. (1994) found that reduction of hexavalent chromium increased as the amount of fine particles increased, which was attributed to the increase in the surface area of the fines. The relationship between adsorption of and reduction of chromium is a complex and interrelated process that is not fully understood though many studies report that the same factors controlling adsorption of chromium also control reduction. Based on Deng and Stone's 1996 work, where they indicate that adsorption is an important condition for the reduction reaction to take place, it may be that less adsorption at higher pH has an effect on the reduction rate. While there are no studies directly measuring this relationship, the data are suggestive. It seems that in COPR-affected soils with pH less than about 8.5, adsorption of Cr(VI) can occur. At pH levels above 8.5 (especially at COPR sites where the pH of contaminated soils is greater than and the pH of the pure waste ranges from 10 to 12), adsorption may be less significant. It would appear that at the pH and Eh conditions of soils at COPR sites, hexavalent chromium reduction and adsorption may occur and that the two processes may be related. Ramos, et al. (1994) concluded that the adsorption of hexavalent chromium onto activated carbon was greatly dependent on pH and, in fact, was diminished about 17 times by increasing the pH from 6 to 10. Because of the wide range of soil characteristics and various forms by which metals can be added to soil, evaluating the extent of metal retention by a soil is site/soil/waste specific. Changes in the soil environment over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes also may enhance chromium mobility and reduce chromium adsorption.

Adsorption mechanisms specific to COPR material or COPR-soil mixtures would have a significant impact on hexavalent chromium levels on all sizes of particles (especially at COPR sites where the contaminated soils are greater than pH 7 and the pure waste is 10 to 12). The influence of other factors may in part explain discrepancies between adsorption predicted on a surface area only basis and the reported data that are specifically COPR related. In the case of

pure COPR materials, if Cr(VI) is distributed throughout the COPR slag, it is possible that concentrations in various particle sizes of slag may not be substantially different. But in contaminated soils, where Cr(VI) leached from slag may have adsorbed to soil particles, the smaller particles could be expected to contain higher concentrations of Cr(VI) than large particles because of the smaller particles' larger specific surface area.

Not only does pH play a role in determining the charge distributions on solid surfaces to which chromium species can adsorb, it is a critical determinant of the chromium species that are present in an aqueous medium. Cr (VI), dominant under oxidizing conditions, is protonated at pH less than 7, existing as $HCrO_4^-$. At higher pH, Cr (VI) is present as $CrO_4^{2-}$. The Cr (VI) species do not generally form complexes with inorganic or organic ligands. Reducing conditions favor formation of Cr (III) compounds, which can be present as cations (successively $Cr^{3+}$, $CrOH^{2+}$, $Cr(OH)_2^+$) up to about pH 8.4. The neutral species $Cr(OH)_3^0$ is then dominant to about pH 10, and the anion $Cr(OH)_4^-$ dominates at higher pH (Calder, 1988). Because Cr (III) species are cationic over a large pH range whereas Cr (VI) species are anionic, differences have been noted in adsorption behavior for Cr (III) and Cr (V) to clays and iron hydroxides with their differing surface charges. Zayed and Terry (2003) postulate that the adsorption of Cr(III) to soil clay minerals increases with increasing pH. When the pH increases to levels above 8.5, adsorption of Cr(VI) is not observed. They cite the work of Griffing et al. (1977) who state that Cr(III) is adsorbed 30-300 fold more strongly to soil clay minerals than Cr(VI). Richard and Bourg (1991) reported a similar pattern.

Adsorption of Cr (VI), in particular, has some relevance to understanding the leachability and mobility of Cr (VI) derived from COPR wastes. Leaching experiments conducted by Weng et al. (2002), attempted to characterize the Cr(VI) leaching process in soils enriched with COPR. The leaching experiments were performed on crushed samples, with particles less than 1 mm, and having an average size of 250 microns. Weng et al. (2002) concluded that chromate can be readily leached from the surface of the COPR-soil particles and that the amount leached increased with increases in temperature. Results from this study therefore imply that release of Cr(VI) is important in these areas and that transport downward to groundwater is a significant pathway of concern (see section on Impact to Groundwater for a more detailed discussion of Cr(VI) mobility). Preferential adsorption of Cr (VI) on small particles has been shown to occur at low to slightly alkaline pH. At higher pH, the Cr(VI) tends to be soluble and would tend to follow soil water rather than to sorb to particles, regardless of the particle size. At COPR sites, it is proposed that there is a steady dissolution of hexavalent chromium from the slag to surrounding soil. Adsorption may also occur to some extent. To date, there has been no evidence presented in the literature showing that the adsorption of hexavalent chromium at sites dominated by COPR waste is a significant issue. However, adsorption may occur to varying extents as sites where COPR is present in smaller amounts, mixed with soils of less alkaline pH.

Cowherd et al. 1985 adopted the bulk soil concentration as the best available concentration estimate for the suspended particles, while acknowledging that concentrations on the finest particles may be enriched:

*"Contaminants in particulate form may be present either as discrete solid particles or adsorbed onto soil or other surface aggregate materials. This depends on the physical and chemical*

*interaction between the contaminant species and the surface aggregate. For adsorbed contaminants, there is usually an enrichment of contamination in the finer particle sizes because of larger surface-to-volume ratio. However, in the absence of data on the contamination level of $PM_{10}$ particles in the surface material, it will be assumed that the level of contamination … in the respirable particulate emissions matches that measured in the bulk surface material."*

Falerios, et al. (1992) provided mean ratios of respirable hexavalent chromium and total suspended particulate hexavalent chromium. The respirable fraction was defined as less than 10 micron and the total suspended particulate fraction was defined as less than 75 micron. The average concentrations for these sites show that the ratio of respirable particle Cr to total suspended particle Cr is 0.6.

A report describing chrome fractionation studies was submitted by PPG Industries to the Department in 1995 as part of the Remedial Investigation phase of a site in Hudson County (ICF Kaiser Engineers, 1993). The final report addresses NJDEP concerns about whether hexavalent chromium concentrations differed between the bulk samples and the fractions. While the authors report that "…bulk hexavalent chromium concentrations are conservative when used to estimate the hexavalent chromium concentrations in less than 75 micron and less than 10 micron size fractions," a statistical evaluation of the data by a NJDEP statistician (Korn, 2004, personal communication) indicates that this statement may not be complete. The authors cite this report as justification to discontinue soil fractionation and particle size analysis for hexavalent chromium. However, the data seem to be equivocal, at best. In the report, the argument is made that even though there is no evidence that the bulk Cr(VI) concentration is greater than Cr(VI) on smaller fractions, the concentrations are equivalent. This kind of testing has low power, so it should not be considered as strong evidence of equivalence. In summary, the report does not present evidence that Cr(VI) concentrations in bulk soil samples is higher or equal to Cr(VI) concentrations on smaller particles.

One of the few academic studies that have directly measured chromium levels on soils by particle size at New Jersey chromium sites was conducted by Kitsa et al. (1992). In this study, enrichment of chromium and other metals on particles between 10 and 30 microns was observed. Chromium concentrations on particles less than $PM_{2.5}$ and greater than $PM_{30}$ were lower. Particles less than $PM_{10}$ (10 microns) are considered to represent the thoracic fraction, and particles less than $PM_{2.5}$ (2.5 microns) are considered to represent the respirable fraction. Particles less than $PM_{30}$ (30 microns) represent the inspirable fraction. The $PM_{2.5}$ particles inhaled beyond the nasal passageways are not rejected. Rather, these particles are able to reach the lung. Therefore, the exposure to humans through these respirable particles is of particular interest. In experiments using a resuspension chamber and x-ray fluorescence analysis, the investigators report some interesting results. While chromium levels in areas of visible blooms showed increasing chromium concentrations with decreasing particle size (to $PM_{2.5}$), soils from contaminated sites but not in visible bloom areas and soils from background sites demonstrated an opposite trend. That is, enrichment of chromium on small particles seemed to occur when chromium levels were very high (above 11,000 ppm in bloom areas) but was not observed when total chromium levels were lower. Mean total chromium concentrations of 12,885; 8,591; and 7,941 mg/kg were measured on particle size fractions of between 10 and 30 microns, between 2.5 and 10 microns, and less than 2.5 microns, respectively using x-ray fluorescence analysis of

filters obtained from resuspension chamber experiments. Data taken from the study tables showing samples collected in 1991 are shown in Figure 6.2. It would appear that in a soil system inundated with chromium, adsorption sites on the smaller particles become filled with chromium; whereas in less contaminated soils, a more homogeneous distribution among particle sizes occurs. The researchers conclude that: "Thus it appears that exposure to high concentrations of contaminated dust occurs primarily during resuspension conditions at sites with visible hexavalent chromium crystals." Interestingly, the percentage of hexavalent chromium decreased with particle size: hexavalent chromium was 60%, 50% and 20% of the total extractable chromium found in the $PM_{30}$, $PM_{10}$ and $PM_{2.5}$ size fractions, respectively. If the particles of all sizes are composed of chromium bearing minerals, it might be expected that concentrations would be much the same from one size class to another. Examples of non-uniform concentrations could include fine, unattached crystals of evaporite from chromate solutions or chromium distributed somewhat uniformly over the surface area of the particles. Enrichment factors were calculated as part of the study. They show that the enrichment in total chromium at COPR sites are high when compared to rural soil. However, the enrichment factors are lowest for $PM_{2.5}$ particles (65) than for the $PM_{10}$ particles (352) or for the $PM_{30}$ particles (452). One of the conclusions of the report is: "Thus, it appears that exposure to high concentrations of contaminated dust occurs primarily during resuspension conditions at sites with visible hexavalent chromium crystals." Later, they add, "…hexavalent chromium in crystal or 'bloom'-laden soil is bioavailable in size fractions that are of concern for deposition in the respiratory system."

Application of how the results from the Kitsa et al. (1992) study is used in calculating the air dust exposure model is discussed further in the Air Transport section of this report (Chapter 5).

Assuming that there is a consistent enrichment of smaller particles in relation to the bulk soil concentration, and assuming that the enrichment is significant, how might the generic soil clean-up criteria for this pathway change? This question was posed to the air transport group. Using those assumptions, a weighted average method could be used to account for the higher concentration, and would result in a somewhat lower allowable concentration of Cr(VI) in soil. How much lower depends on the degree of Cr(VI) concentration on the particles. One sample calculation suggests that an order of magnitude increase in Cr(VI) on the small particles (PM 2.5) would lower the allowable soil concentration by about 25%, bringing the generic number from the proposed 20 ppm to about 15 ppm. Although this difference is not large, particularly given the conservative nature of the models and the conservative toxicity data employed to calculate the standards, the issue remains significant. The Department should continue investigating, through studies and through ARS petitions, the possibility that smaller particles contain higher concentrations of Cr(VI) than bulk soil concentrations and, if appropriate, consider developing an enrichment model to account for the difference.

The literature combined with empirical data submitted to the Department by responsible parties specifically from COPR sites in the state show no consistent enrichment of hexavalent chromium on smaller particle sizes nor do they show consistent equal concentrations of chromium on bulk and fractionated samples. While some level of enrichment may occur, the factor has not been quantified to date.

**Recommendations**

1. Nature of COPR

Research:

- The Department should consider developing a research project using x-ray based technologies and scanning electron microscopy to better characterize the mineralogy of COPR at the New Jersey COPR sites. It has not been established definitively that the COPR sites in New Jersey are identical to those in Scotland, where some detailed mineralogical studies have been conducted. A small project to better investigate the nature of the minerals present at New Jersey COPR sites would enhance the Department's understanding of the fate and transport of chromium at these sites.

2. Transport to Groundwater

Programmatic:

- Recommend that the Department consider defining COPR waste material and soil with larger amounts of COPR waste material as a continuing source of contamination to groundwater that will require remediation in accordance with the Department's Technical Requirements for Site Remediation (N.J.A.C. 7:26E).

Research:

- Criteria for separating COPR waste from chromium-contaminated soil.

- Exploration of the applicability of the Synthetic Precipitation Leaching Procedure at COPR waste sites.

- Investigation of the reduction capacity of meadow mats at COPR waste sites.

- Investigation of the reduction capacity of aquifer material at COPR waste sites.

- Investigation of chromium adsorption-desorption process on chromium-contaminated soil (not COPR material) in the vicinity of the waste sites. While chromium adsorption-desorption studies have been conducted on NJ soils, the soils were not from COPR sites. It is important to perform similar studies using soils in or near COPR waste sites.

- Recommend that the Department consider defining COPR waste material and soil with larger amounts of COPR waste material as a continuing source of contamination to groundwater that will require remediation in accordance with the Department's Technical Requirements for Site Remediation (N.J.A.C. 7:26E).

- The Department should begin work immediately to differentiate pure COPR slag waste from COPR-soil mixtures. Such differentiation can be based on chemical characteristics such as pH and mineralogy.

3. Interconversion

Research:

Because the conditions at COPR sites are variable, oxidation of trivalent chromium to the hexavalent form may occur only sparingly, but at some sites the mass generated over time may become environmentally significant. If the pH of soils at some sites is sufficiently low and the soils contain suitable reductants, Cr(VI) in COPR may be reduced. It is believed that proposed clean-up standards for chromium will be protective of human health; however it is recommended that oxidation rates of Cr(III) in COPR be further investigated to determine under what circumstances, if any, the production of Cr(VI) becomes environmentally significant. The determination of Cr(III)-bearing phases in COPR, such as brownmillerite, would be useful, as these may undergo oxidation at a rate that differs from that of chromite.

4. Concentration Effect

Programmatic:

- The Department should continue to monitor structures at COPR sites for the appearance of salts. It is especially important to maintain observations in areas where barriers have been installed to ensure that the salts are not regenerating. Where appropriate, evaluations should include analytical testing in addition to visible assessments.

- The Department should continue to address in a conservative way the inhalation exposure route for hexavalent chromium by recommending the use of its generic model (as described in Chapter 5).

- The approval of an alternative remediation standard should be contingent upon the responsible party conducting site-specific studies in accordance with departmental guidelines. Submissions that do not follow the guidelines should be rejected. Those that do should undergo a rigorous review with a transparent and formal approval process. Any alternative remediation standard developed to address the inhalation exposure route needs to be formally incorporated in to the case records and made available for replication. As described, the sampling and analytical capabilities for determining Cr(VI) concentration on very small particles ($PM_{2.5}$) are not fully developed or available commercially. These methods are still being developed. But there are steps that can be taken to ensure that alternative remediation standards are developed accurately:

    - when a responsible party seeks to develop an alternative remediation standard for inhalation, a complete analysis of Cr(VI) by particle size should be developed, submitted and formally approved by the Department. Such an analysis should

include experiments in a resuspension chamber and use analytical methods consistent with those described in Chapter 3 of this report.

- when investigating and describing a site in relation to the inhalation exposure route, the responsible party should include analysis of the following when determining the presence of particles at the site:
    - wind direction relative to the location of any air samplers and relative to vehicular activity. Samples should be collected downwind of vehicle traffic.
    - time of day of sample collection. Samples should be collected during the normal 8-hour work day.
    - soil sample averaging.

**Research**

- The Department should consolidate information from its site remediation files on investigations where residential structures are near COPR or COPR-soil mixtures have been studied. Existing data describing the occurrence of Cr(VI) salt formation in basements or other structures is available in the case files. A report consolidating the investigations should be written, published and made publicly available. In instances where data are not available, the Department should initiate studies to collect it. The information should include both analytical as well as visible evaluations of the structures.

- To address the question of whether or not vadose zone transport can cause blooms at low soil chromium concentrations, it is recommended that a study be conducted to investigate the potential occurrence of surface enrichment due to capillary transport of hexavalent chromium. Theoretically, enrichment on surfaces can occur at any Cr(VI) concentration, but it is now known definitively whether or not there is a threshold concentration. Specifically, COPR material and COPR-soil mixtures containing various Cr(VI) concentrations should be studied for potential evaporative enrichment via capillary action toward the goal of determining whether there is a threshold concentration in soil where evaporative enrichment via capillary action does or does not occur. It is especially important to evaluate the possibility of capillary transport at sites so that the Department is better able to evaluate the effectiveness of remedial strategies.

- Offsite migration and delineation of chromium contaminated groundwater from COPR sites should account for the vertical and spatial variability of urban soils. Construction activities (compaction, filling and scraping) may cause changes in the soil profile. These disturbances can influence water movement and retention. The dissolved chromium may migrate offsite and concentrate on surface soils, concrete foundations or any other surface that may be susceptible to capillary action. Currently, delineations are conducted at sites for Cr(VI) until levels reach the drinking water standard of 100 µg/L. It would be useful to investigate the transport of Cr(VI) in groundwater where levels are below this number in order to better understand the ultimate fate and transport of dissolved Cr(VI) in groundwater.

- Information in the published literature (Kitsa et al., 1992 and Falerios et al., 1992) and site data (PPG) present limited data on enrichment of Cr(VI) on smaller soil particles. The

mineralogy of the small soil particles is not known. Research is recommended to clarify whether particle size enrichment is or is not of concern due to the limited data available to address this issue. Systematic, specific research is needed to definitely determine levels of hexavalent chromium on smaller particle in bloom areas, chromium-contaminated areas, and background areas. The mineralogy of small particles in chromium-contaminated areas needs to be determined. The design of the study should be determined by an appropriate group of people from the Department and unbiased external researchers with expertise in this research area. The study should include sample sites from several COPR sites in New Jersey. The Kitsa et al. (1992) study is the only one that approaches this need, but it is dated and limited. The work by Falerios et al. (1992) does not demonstrate that that more chromium is present on the smaller particles. The data are equivocal. Therefore, it appears that further investigation of this matter, as a human health issue, is warranted. A larger and more current investigation than the two described here could illuminate the issue for the state and better inform the soil standard setting process. At the very least, measurements of Cr(VI) on small soil and bloom particles, as well as the routine measurements on bulk samples, could be considered as an important step in assessing human health risks from COPR. Mineralogical characterizations should be completed on samples used in experiments. It might be helpful to compare the concentrations resulting from such a study with those collected from a deep soil core for variation. Several sites plus a control site would need to be included in the study.

- Development of routine methods for particle size analysis for particle size ranges less than PM 10 should be supported.

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State of New Jersey

Department of Environmental Protection

DONALD T. DIFRANCESCO
*Acting Governor*

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Commissioner

**DIVISION OF PUBLICLY FUNDED SITE REMEDIATION**

**STANDARD OPERATING PROCEDURE**

**TITLE:** Standard Operating Procedure (SOP) for the Completion of the Hexavalent Chromium Data Validation Report Forms and the Preparation of the Final Data Validation Report.

**REVISION NO.:** 1 **ISSUE DATE:** **SOP NO.:** 5.A.09

**APPROVED:**

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**PURPOSE/SCOPE:** This document is the Standard Operating Procedure (SOP) for the completion of the data validation report forms utilized in the data evaluation and validation of Hexavalent Chromium analyzed in accordance with NJDEP Modified USEPA SW-846 preparation/reagents 3060 and 7196A and the preparation of the Final Data Validation Report required by DPFSR.

**ORIGINATING ORGANIZATIONAL UNIT(S): BEMQA**

**OTHER ORGANIZATIONAL UNIT(S) AFFECTED: ALL DPFSR and DRPSR**

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## I. PURPOSE AND SCOPE

This document is the Standard Operating Procedure (SOP) for the completion of the data validation report forms utilized in the data evaluation and validation of Hexavalent Chromium analyzed in accordance with NJDEP Modified USEPA SW-846 Methods 3060 and 7196A and the preparation of the Final Data Validation Report required by DPFSR.

## II. AUTHORITY

This document was prepared under the authority of the Assistant Director, DPFSR-HSS and Bureau Chief, BEMQA. The revision, maintenance and use of this document is a work output under the NJDEP Quality Assurance Program Plan. The Quality Assurance Program Plan was prepared by the NJDEP Office of Quality Assurance and in part, by DPFSR-HSS-BEMQA.

## III. REFERENCE

This document was prepared based on materials contained in the following documents:

A. NJDEP, Division of Publicly Funded Site Remediation, Hazardous Site Science Element, Standard Operating Procedure for Analytical Data Validation of Hexavalent Chromium, SOP No. 5.A.10, October 2001.

B. NJDEP Modified USEPA SW-846, Methods 3060 and 7196A.

## IV. RESPONSIBILITY

The Assistant Director, HSS is responsible for the final review and approval of this document. The Chief of BEMQA is responsible for the annual review of this document. The Section Chief of QAS is responsible for the preparation of any revisions to this document as well as maintaining QAS staff compliance with this document.

## V. POLICY

The actions contained in this document are the policy of DPFSR-HSS-BEMQA and are derived on the basis of requirements contained in the referenced NJDEP Modified USEPA SW-846 Methods 3060 and 7196A.

## VI. PROCEDURE

## A. Introduction

This section of the SOP consists of two distinct parts. The first part details the procedures utilized in the preparation of the final data validation report and the required format for the submittal of the data validation report. The second part details the procedures utilized in the completion of the Hexavalent Chromium Data Validation Report Forms that are to be utilized during the evaluation and data validation of Hexavalent Chromium analytical data generated using NJDEP Modified Methods 3060 and 7195A USEPA SW-846 protocol.

## B. Data Validation Report

1. OVERVIEW OF REQUIREMENTS

Upon completion of sample data validation for a given batch of samples, an original and one copy of a three part data validation report must be submitted to NJDEP-DPFSR. Specifically, the report consists of:

a. *Cover Letter* - addressed to an assigned NJDEP representative, this letter highlights the samples and fractions reviewed and any major deficiencies or QA problems encountered during data validation. Any sample rejections must be identified here. Additional information about the cover letter is presented in Section VI.B.2 of this SOP.

b. *Target Analyte Summary Hitlist* - provides data end-user a summary of the results of the samples reviewed, the data validation qualifiers added, and the final data validation decisions on acceptance, qualification, or rejection of the result. A detailed explanation of this deliverable is presented in Section VI.B.3 of this SOP.

c. *Data Validation Report Forms* - deliverable used during the data validation process to assess the technical merit of the laboratory's performance. These forms allow the data end-user to easily locate detailed quality assurance information related to any specific sample within the sample set. Detailed instructions for completing these forms and a complete set of blank forms are presented in Section VI.C. of this SOP.

2. COVER LETTER

a. The cover letter highlights the samples that were reviewed and all major quality

assurance deficiencies or problems that were encountered during data validation. The report must include the following:

1) Names of all reviewers conducting the data validation.

2) Listing of all samples reviewed. The samples are to be listed by the field ID number and the associated laboratory ID number and matrix. The data reviewer shall choose either ID and utilize that ID on the detailed data validation report forms.

3) All trip blanks, field blanks and QC samples must be identified.

4) The pages of the cover letter must be numbered.

5) The cover letter must be securely bound along the left margin. Stapling is not permitted. The Target Analyte Summary and the accompanying data validation report forms shall be bound with the cover letter to form the complete data validation report.

6) Letter Quality print is required. Compression of the print and/or dot matrix print is not acceptable.

7) The cover letter must be delivered on 8.5 inch x 11 inch paper.

b. Format of Cover Letter

1) A complete cover letter will consist of three (3) sections, a section on pertinent sample information, a general comments section and a data quality and recommendations section.

2) The structure of each section should be in a narrative format and provide explanation as to why any sample(s) is rejected. All qualifications and rejections whether by fraction or sample are to be listed and explained. The identification numbers for any sample rejected or qualified must be provided.

3) The cover letter is to be broken down in the following manner.

a) Sample Information - This section is to include laboratory and field identification numbers and sample matrix.

b) General Comments- This section is to include information on the completeness and quality of the data deliverable package general requirements.

c) Data Quality and Recommendation - This section is to include information on the quality of the data that was validated and overall recommendations.

## 3. TARGET ANALYTE SUMMARY (HITLIST)

a. The Target Analyte Summary (Hitlist) provides the data end user with the concentration of Hexavalent Chromium in all of the samples reviewed.

b. For each sample reviewed, the final data validation decision on the acceptance, qualification or rejection of the results with the appropriate footnote(s) is provided.

c. General Requirements

1) Deviations from the provided Target Analyte Summary (Hitlist) format are not acceptable.

2) Letter quality print is required. Compression of the print and/or dot matrix print is not acceptable.

3) The Hitlist must be delivered on 8.5 inch x 11 inch paper.

4) The pages of the Hitlist must be numbered. Page number format shall be as follows: page of .

5) The Hitlist must be securely bound along the left margin. Stapling is not permitted. The Hitlist, the accompanying footnotes and the data validation report forms shall be bound with the cover letter to form the complete data validation report.

6) Trip and field blanks associated with a given group of field samples are to be listed on the Hitlist first, followed by the associated field samples.

7) The column headings shall include: Site name, SDG and NJDEP job numbers, laboratory name, sampling date, sampling matrix and fraction are to be provided at the top of every page.

8) The column headings are to be provided at the top of every page in the hitlist.

9) The footnotes and footnote numbers are based on the NJDEP-DPFSR current list of footnotes. The list of NJDEP-DPFSR footnotes **can be revised** or renumbered.

10) Sample field identification numbers or laboratory identification numbers are listed on the left hand side of the paper in the first column. The concentration units for the results are to be listed next to the fraction name.

11) The analyte name is listed at the left margin below the field or laboratory identification number in column two.

12) The results for the associated preparation/reagent blank are listed in column three. The letter U is required if the analyte was not detected above the MDL in the preparation/reagent blank. If the preparation/reagent blank is associated with soil samples, the preparation/reagent blank must be reported in mg/kg.

13) The laboratory reported concentration is listed in column four.

14) The data reviewer's reported concentration is to be listed in the fifth column.

    a) If the reviewer agrees with the number reported by the laboratory, it still must be listed.

    b) If the concentration reported by the laboratory is incorrect, it must be corrected in this column.

    c) If the concentration reported by the laboratory is rejected, a line consisting of three hyphens is to be inserted in the column.

    d) If the sample is a field or trip blank associated with soil samples, the trip or field blank must be reported in mg/kg.

15) The quality assurance decision is to be listed in the sixth column. This consists of single word descriptors with more detailed explanation using footnotes in column seven. The descriptors are required only if the analyte reported by the laboratory requires a quality assurance action. If the analyte result reported by the laboratory is acceptable, this column is left blank for that analyte. The following descriptors must be used in the

sixth column.

a) negate - used when the presence of a given analyte in a sample can be attributed to laboratory/field introduced contamination.

b) qualify - used when the results of a given analyte in a sample do not meet all QA/QC criteria but are not severe enough to warrant data rejection.

c) reject - used when the results of a given analyte in a sample do not meet all QA/QC criteria so that the qualitative presence and/or quantitation of that analyte in the sample cannot be determined with any degree of confidence.

16) Footnote numbers are to be listed in the seventh column. A given analyte can have more than one footnote. If an analyte is rejected, all footnotes describing the rejection are required. If an analyte is negated, only the footnote that describes the negation is required.

d. Footnotes for Target Analyte Summary (Hitlist)

Listed below are the footnotes and footnote numbers that shall be used on the Hitlist. These footnotes can be revised or renumbered.

1) The value reported is less than or equal to 3x the value in the preparation/reagent blank. It is the policy of NJDEP-DPFSR to negate the reported value due to probable foreign contamination unrelated to the actual sample. The end-user, however, is alerted that a reportable quantity of the analyte was detected.

2) The value reported is greater than three (3) times but less than ten (10) times the value in the preparation/reagent blank and is considered "real". However, the reported value must be quantitatively qualified "J" due to the preparation/reagent blank contamination. The "B" qualifier alerts the end-user to the presence of this analyte in the preparation/reagent blank.

3) The value reported is less than or equal to three (3) times the value in the trip/field blank. It is the policy of NJDEP-DPFSR to negate the reported value as due to probable foreign contamination unrelated to the

actual sample. The end-user, however, is alerted that a reportable quantity of the analyte was detected.

4) The value reported is greater than three (3) times but less than ten (10) times the value in the trip/field blanks and is considered "real". However, the reported value must be quantitatively qualified "J" due to trip/field blank contamination.

5) The concentration reported by the laboratory is incorrectly calculated.

6) The laboratory failed to report the presence of the analyte in the sample.

7) The reported Hexavalent Chromium value was qualified because the Calibration Check Standard was not within the recovery range (90-110 percent).

8) In the Duplicate Sample Analysis, Hexavalent Chromium fell outside the control limits of ± 20 percent or ± 2ppm. Therefore, the result was qualified.

9) This analyte was rejected because the laboratory performed the Duplicate Analysis on a field blank.

10) The reported value was qualified because the PVS recovery was greater than 115 percent.

11) The reported value was qualified because the PVS recovery was less than 85 percent.

12) The non-detected value was qualified (UJ) because the PVS recovery was less than 85 percent. The possibility of a false negative exists.

13) The reported analyte was qualified because the associated Calibration Blank result was greater than the MDL.

14) The laboratory made a transcription error. No hits were found in the raw data.

15) This analyte is rejected because the laboratory exceeded the holding time for digestion and analysis.

16) The laboratory subtracted the preparation/reagent blank from the sample

result. The Reviewer's calculation puts the preparation/reagent blank back into the result.

17) The photocopy is unreadable. Therefore, the QA reviewer cannot read the laboratory's reported concentration result.

18) The reported value was qualified because the predigestion spike recovery was less than 75 percent.

19) The reported value was qualified because the predigestion spike recovery was greater than 125 percent.

20) The non-detected value was qualified (UJ) because the redigestion spike recovery was less than 75 percent. The possibility of a false negative exists.

21) The reported result was rejected because the laboratory did not record the pH value(s) of the sample in a laboratory notebook.

## C. Hexavalent Chromium Data Validation Report Forms

These are the instructions for the completion of the Hexavalent Chromium Data Validation Report Forms. Throughout the document, various decisions are required to be made by answering questions. Instructions on answering the questions are not provided. These are provided in the SOP No. 5.A.10 for the Quality Assurance Data Validation of Hexavalent Chromium.

A limited number of QA actions are provided on the forms. The SOP No. 5.A.10 DPFSR details all the QA actions to be utilized in the data validation process.

**HEXAVALENT CHROMIUM FORM 1** - Data Deliverable Requirements

This form needs only to be filled out once per deliverable batch. The ten items reflect the overall quality of the deliverable package and NJDEP requirements. The reviewer shall fill in the site name, location, laboratory name, reviewer name, the date when the review was started, job code, site manager, Bureau and what methodology was used. The following items, lettered A through J must be completed by the reviewer by indicating a yes or no

answer for each item. For "no" responses, space is provided at the lower portion of the form to describe any deviations from requirements.

**HEXAVALENT CHROMIUM FORM 2** - Holding Times for Hexavalent Chromium

This form must be filled out for every sample reviewed. The reviewer shall choose which sample ID he/she will use throughout the validation by circling the appropriate ID in the first column. In the next column, the reviewer will enter the sample matrix. The date of sample collection is specified on the chain of custody form. The analysis date for Hexavalent Chromium is taken either from the digestion logs or the raw data. If the holding time for analysis was exceeded, the reviewer must report the number of days the holding time was exceeded by in the holding time exceeded column.

**HEXAVALENT CHROMIUM FORM 3** - Instrument Calibration Curve and Calibration Check Standard (CCS) for Hexavalent Chromium

This form must be completed for all samples. All field samples, field/trip blanks and field duplicates must be listed on the line provided. If the CCS is associated with all samples analyzed, the reviewer may enter the word "All". The sample ID is the same as that chosen by the reviewer in the holding time form. All questions are to be answered and, where indicated, the quality assurance action noted.

1. The reviewer indicates whether the instrument used was properly standardized.

2. The reviewer must review the raw data to verify that the CCS was analyzed at the proper frequency.

3. The reviewer must review the raw data to verify that the CCS concentration was the same throughout the analysis.

4. A listing is done for the percent recovery of Hexavalent Chromium failing to meet QC criteria.

5. Calculate the percent recovery of Hexavalent Chromium for one CCS standard and compare to the laboratory's reported result.

**HEXAVALENT CHROMIUM FORM 4** - Calibration Blank (CB) for Hexavalent Chromium

This form must be completed for all samples. All field samples, field/trip blanks and field duplicates must be listed on the line provided. If the CB is associated with all samples analyzed, the reviewer may enter the word "All". The sample ID is the same as that chosen by the reviewer in the holding time form. All questions are to be answered and, where indicated, the quality assurance action noted.

1. The reviewer verifies that a CB was analyzed before the instrument's initial calibration standards.

2. The reviewer verifies that a CB was analyzed after the CCS.

3. The reviewer verifies that the value for Hexavalent Chromium in the CB was below the MDL.

**HEXAVALENT CHROMIUM FORM 5** - Preparation/reagent Blank Summary for Hexavalent Chromium

This form must be filled out for every Preparation/reagent blank reviewed. The reviewer shall circle which matrix the Preparation/reagent blank is associated with and the concentration units. The reviewer must fill in the Preparation/ Reagent blank ID that can be found in the digestion log or the raw data. All field samples, field/trip blanks and field duplicates must be listed on the line provided. If the Preparation/reagent Blank is associated with all samples analyzed, the reviewer may enter the word "All". The sample ID is the same as that chosen by the reviewer in the holding time form. All questions are to be answered and, where indicated, the quality assurance action noted.

1. The reviewer verifies that a Preparation/reagent blank was analyzed for each matrix and at the correct frequency.

2. Under the column for concentration, report the concentration of Hexavalent Chromium if it is greater than the IDL.

3. Under the MDL column, write the word "Yes" if the concentration of Hexavalent Chromium is less than the MDL, or the word "No" if the concentration of Hexavalent Chromium is greater than the MDL.

4. Under the IDL column, write the word "Yes" if the concentration of Hexavalent Chromium is greater than the IDL, or the word "No" if the concentration of

Hexavalent Chromium is less than the IDL.

5. Under the Comments/Action column, list any decisions that must be made when the concentration of Hexavalent Chromium is above the MDL.

**HEXAVALENT CHROMIUM FORM 6** - Predigestion Spike Analysis for Non Aqueous Hexavalent Chromium Samples

General Information - Write in the sample ID used for predigestion spike analysis, enter the percent solids for the sample used for sample spike analysis.

This form must be completed for all samples. All associated non-aqueous field samples, and field duplicates must be listed on the line provided. If the Predigestion Spike Analysis is associated with all samples analyzed, the reviewer may enter the word "All". The sample ID is the same as that chosen by the reviewer in the holding time form. All questions are to be answered and, where indicated, the quality assurance action noted.

1. The reviewer must verify the frequency of the predigestion spike analysis.

2. The reviewer must verify that the laboratory did use a field sample for predigestion spike analysis.

3. The reviewer determines if the proper predigestion spike concentration was used.

4. The reviewer determines if the predigestion spike recovery for Hexavalent Chromium met QC criteria.

5. Calculate the percent spike recovery of Hexavalent Chromium in the predigestion spike analysis performed as indicated and compare to the laboratory's reported result.

**HEXAVALENT CHROMIUM FORM 7** - Post Verification Spike Sample (PVS) Analysis for Hexavalent Chromium

General Information - Write in the sample ID used for PVS, circle the appropriate matrix, fill in the percent solids (when applicable) for the sample used for PVS analysis, and circle the appropriate units.

This section contains two forms that must be completed for all samples. All associated

field samples and field duplicates must be listed on the line provided. If the PVS is associated with all samples analyzed, the reviewer may enter the word "All". The sample ID is the same as that chosen by the reviewer in the holding time form. All questions are to be answered and, where indicated, the quality assurance action noted.

1. The reviewer must verify that the proper frequency and concentration for the post verification spike sample.

2. The reviewer must verify that the laboratory did use a field sample for post verification spike sample.

3. a. The reviewer determines if the PVS recovery for Hexavalent Chromium met QC criteria.

   b. The reviewer determines that if the PVS recovery was less than 85% the laboratory reanalyzed the sample.

4. Calculate the percent recovery of Hexavalent Chromium in the PVS sample and compare to the laboratory's reported result.

**HEXAVALENT CHROMIUM FORM 8** - Duplicate Analysis for Hexavalent Chromium

This form must be completed for all samples. All field samples and field duplicates must be listed on the line provided. If the Duplicate Analysis is associated with all samples analyzed, the reviewer may enter the word "All". The sample ID is the same as that chosen by the reviewer in the holding time form. All questions are to be answered and, where indicated, the quality assurance action noted.

General Information - Write in the sample ID used for duplicate analysis, circle the appropriate matrix, fill in the percent solids, when applicable, for the sample used for duplicate analysis, and circle the appropriate units.

1. The reviewer must verify the frequency of the duplicate analysis.

2. The reviewer must verify that the laboratory did use a field sample for duplicate analysis.

3. The reviewer must verify if the RPD of Hexavalent Chromium met QC criteria.

4. Calculate the RPD for Hexavalent Chromium and compare to the laboratory's result.

**HEXAVALENT CHROMIUM FORM 9** - Laboratory Control Sample (LCS) for Hexavalent Chromium

This form must be completed for all samples. All field samples and field duplicates must be listed on the line provided. If the LCS is associated with all samples analyzed, the reviewer may enter the word "All". The sample ID is the same as that chosen by the reviewer in the holding time form. All questions are to be answered and, where indicated, the quality assurance action noted.

General Information - circle the appropriate matrix and units.

1. The reviewer must verify the frequency of the LCS analysis.

2. The reviewer will also qualify Hexavalent Chromium concentrations if the LCS did not meet the QC criteria of 80%-120%.

3. Calculate the LCS percent recovery for Hexavalent Chromium as indicated and compare to the laboratory's reported result.

**HEXAVALENT CHROMIUM FORM 10** - Sample Result Verification for Hexavalent Chromium

This form must be completed for all samples. All field samples, field/trip blanks, and field duplicates must be listed on the line provided. The sample ID is the same as that chosen by the reviewer in the holding time form. All questions are to be answered and, where indicated, the quality assurance action noted.

1. The reviewer must verify that samples reported were within the calibration range.

2. The reviewer must check for any anomalies in the raw data.

3. The reviewer must check for any computation or transcription errors.

4. The reviewer must verify that the laboratory provided the pH readings, for methods 3060 & 7196A, for all samples and the results were within method requirements.

5. The reviewer must verify that the hotplate temperatures were provided and within method requirements.

6. Calculate the percent solids for one sample as indicated and compare to the

laboratory's reported result.

7. Calculate the concentration for one non-aqueous sample for Hexavalent Chromium.

DATA DELIVERABLE REQUIREMENTS
for
HEXAVALENT CHROMIUM

Site Name_____Job Code_____

Location_____ Site Manager_____

Laboratory Name_____ Lead Division/Bureau_____

Reviewer_____
Methodology_____

Date of Review_____ SDG_____

GENERAL REQUIREMENTS: Circle YES or NO and list the deviations at the bottom:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| A. | Permanently Bound | Yes | No | G. | Methodology Review | Yes | No |
| B. | Paginated | Yes | No | H. | Uninitialed Strikeovers | Yes | No |
| C. | Title Page | Yes | No | I. | Legible Xerox | Yes | No |
| D. | Table of Contents | Yes | No | J. | Consistent Dates | Yes | No |
| E. | Chain of Custody | Yes | No | | | | |
| F. | Non-conformance Summa | Yes | No | | | | |

Describe any deviations from the requirements
_____

_____
_____

_____

_____

HOLDING TIMES

| Sample ID Field or Lab | Matrix | Date of Sample Collection | Hex Chrome Analysis Date | Holding Time Exceeded | QA Decision |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | | | | | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | | | | | |
| 6 | | | | | |
| 7 | | | | | |
| 8 | | | | | |
| 9 | | | | | |
| 10 | | | | | |
| 11 | | | | | |
| 12 | | | | | |
| 13 | | | | | |
| 14 | | | | | |
| 15 | | | | | |
| 16 | | | | | |
| 17 | | | | | |
| 18 | | | | | |
| 19 | | | | | |
| 20 | | | | | |

List any samples that exceeded the holding time, the number of days exceeded by and QA decision.

_____

_____

INSTRUMENT CALIBRATION CURVE
and
CALIBRATION CHECK STANDARD (CCS)

ASSOCIATED SAMPLES
_____

_____
_____

1. Was the instrument properly standardized? Yes No
If no, explain and list action.
_____
_____
_____
_____

2. Was the CCS analyzed at the proper frequency? Yes No
If no, explain and list action.
_____
_____
_____
_____

3. Was the same CCS concentration used throughout the analysis? Yes No
If no, list action.
_____
_____
_____
_____

__

4. Does the CCS standard meet the QC requirements of 90-110% recovery ?

Yes No

If no, list the % recovery, and action.

_____
_____
_____

_____
__

5. Show calculation for the % recovery of Hexavalent Chromium in the CCS standard.

Lab value _____

CALIBRATION BLANKS

ASSOCIATED SAMPLES
_____

_____
_____

1. Was the calibration blank analyzed before the instrument's initial calibration standards? Yes No

   If no, list action.
_____

   _____
_____

2. Was a calibration blank analyzed after the calibration check standard? Yes No

   If no, list associated samples and action.

   _____
_____

   _____
_____

3. Was the value of Hexavalent Chromium for the continuing calibration blank below the MDL? Yes No

   If no, list associated samples and qualify them.

   _____
_____

   _____
_____

PREPARATION/REAGENT BLANK SUMMARY

Preparation/Reagent Blank ID_____

Sample matrix: Soil Water

Units: mg/kg ug/L

Does the frequency of the preparation/reagent blank analysis meet method requirements?

Yes No

If no, explain and note action

_____

_____

| ANALYTE | CONCENTRATION | < MDL | >IDL | COMMENTS / ACTION |
|---|---|---|---|---|
| Hexavalent Chromium | | | | |

ASSOCIATED SAMPLES

_____

_____

_____

PREDIGESTION SPIKE ANALYSIS

Spike Analysis performed on sample _____ % Solids_____

Sample matrix: Soil Units: mg/kg

ASSOCIATED SAMPLES
_____

_____
_____

1. Was the predigestion spike analysis performed at the correct frequency?
Yes No

If no, note deviations and action
_____

_____
_____

2. Was the predigestion spike analysis performed on a field sample?
Yes No

If no, reject all associated samples._____

_____
_____

3. Was the predigestion spike analysis performed at the proper concentration?
Yes No

If no, qualify the associated samples._____

_____
__

4. Did the % recovery for hexavalent chromium meet the criteria of 75-125 % ?

Yes No
If no, list action.

_____

_____

5. Show calculation for predigestion spike recovery of Hexavalent Chromium.

Lab value

_____

POST VERIFICATION SPIKE ANALYSIS

Post Verification Spike (PVS) performed on sample _____

Sample matrix: Soil Water % Solids_____

Units: mg/kg ug/L

ASSOCIATED SAMPLES _____

_____

1. Was PVS analysis performed at the correct frequency and proper concentration? Yes No

   If no, list action. _____

   _____

2. Was PVS analysis performed on a field sample? Yes No

   If no, list action_____

   _____

3. a. Does the PVS recovery meet the criteria of 85-115%? Yes No

   If no, list action_____

   _____

   b. If the PVS recovery was less than 85%, did the laboratory reanalyze the

sample? Yes No

If no, list action_____

_____

4. Show the calculation for % recovery for PVS.

Lab value _____

DUPLICATE ANALYSIS

Duplicate Analysis performed on sample _____ %
Solids_____

Sample matrix: Soil Water

Units: mg/kg ug/L

ASSOCIATED SAMPLES
_____

_____
_____

1. Was the Duplicate analyses performed at the correct frequency? Yes No
If no, list
action._____

_____
_____

2. Was the duplicate analysis performed on a field sample? Yes No
If no, reject all associated samples.
_____
_____

_____
_____

3. Does the duplicate analysis meet the QC control limits? Yes No
If no, qualify the associated samples.
_____
_____

_____
_____

4. Show the calculation for RPD for Hexavalent Chromium.

Lab value

_____

LABORATORY CONTROL SAMPLE

Sample matrix: Soil Water

Units: mg/kg ug/L

ASSOCIATED SAMPLES

_____

_____

_____

1. Was the laboratory control sample performed at the correct frequency? Yes No

   If no, list action.

   _____

   _____

2. Does the LCS meet the QC limit of 80-120 % Yes No

   If no, list the % recovery and action.

_____

   _____

   _____

3. Show the calculation for the LCS % recovery for hexavalent chromium.

Lab Value

_____

SAMPLE RESULT VERIFICATION

ASSOCIATED SAMPLES
_____

_____
_____

1. Were all samples reported within the calibration range? Yes No

If no, list affected samples and action._____

_____
_____

2. Was the raw data free of any anomalies? Yes No

If no, list affected samples and action._____

_____
_____

3. Was the data package free of any computational or transcription errors? Yes No

If no, list affected samples and action._____

_____
_____

4. Were both 3060 & 7196A pH readings provided and within method requirements? Yes No N/A

If no, list affected samples and action._____

_____
_____

5. Were the hotplate temperatures provided and within method requirements? Yes No N/A

If no, list affected samples and action._____

_____

6. Show the calculation for % solids for one sample. N/A

Lab value _____

7. Show the calculation for a nonaqueous sample. Lab value _____

State of New Jersey

DONALD T. DIFRANCESCO
*Acting Governor*

Department of Environmental Protection

Robert C. Shinn, Jr.
Commissioner

**DIVISION OF PUBLICLY FUNDED SITE REMEDIATION**

**STANDARD OPERATING PROCEDURE**

**TITLE:** Standard Operating Procedure (SOP) for Analytical Data Validation of Hexavalent Chromium

**REVISION No.:1 _** **ISSUE DATE:** **SOP NO.: 5.A.10**

**APPROVED:** Barry Frasco — 10-26-01
Dr. Barry R. Frasco, Assistant Director (Date)
Hazardous Site Science Element

William Lowry, Bureau Chief — 10/26/01
(Date)
Bureau of Environmental Measurements and Quality Assurance

**PURPOSE/SCOPE:**

This document is the Standard Operating Procedure (SOP) for laboratory data evaluation and validation of Hexavalent Chromium analyzed in accordance with NJDEP Modified USEPA SW-846 Method 3060 and USEPA SW-846 Final Update III (June 1997) Method 7196A.

**ORIGINATING ORGANIZATIONAL UNIT (S):** **BEMQA**

**OTHER ORGANIZATIONAL UNIT (S) AFFECTED:** **ALL DPFSR & DRPSR**

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## I. PURPOSE AND SCOPE:

This document is the Standard Operating Procedure (SOP) for laboratory data evaluation and validation of Hexavalent Chromium analyzed in accordance with NJDEP modified USEPA SW-846 Methods 3060 and 7196A.

## II. AUTHORITY:

This document was prepared and revised under the authority of the Assistant Director of the DPFSR-HSS and the Bureau Chief, BEMQA. This revision, maintenance and use of this document is a work output under the NJDEP Quality Assurance Program Plan. The QA Program Plan was prepared by the NJDEP Office of Quality Assurance and in part by DPFSR-HSS-BEMQA, and was approved by the USEPA Region II.

## III. REFERENCE:

This document was prepared based on materials contained in the document entitled: USEPA Office of Solid Waste and Emergency Response Second Edition, and Final Update III (June 1997) - "Test Methods for Evaluating Solid Waste", USEPA SW-846.

## IV. RESPONSIBILITY:

The Assistant Director of DPFSR HSS is responsible for the final review and approval of this document. The Chief of BEMQA is responsible for the annual review of this document. The Section Chief of QAS is responsible for the preparation of any revision to this document as well as maintaining QAS staff compliance with this document.

## V. POLICY:

The actions contained in this document are the policy of DPFSR-HSS-BEMQA and are derived based on requirements contained in the referenced NJDEP modified USEPA SW-846 Methods 3060 and 7196A.

## VI. PROCEDURE:

### (A) Introduction

This document is designed to offer guidance in laboratory data evaluation and validation. In some aspects, it is equivalent to a Standard Operating Procedure (SOP); in other more subjective areas, only general guidance is offered due to the complexities and uniqueness of data relative to specific samples.

Those areas where specific SOPs are possible are primarily areas in which definitive performance requirements are established. These requirements are concerned with specifications that are not sample dependent; they specify performance requirements on matters that should be fully under a laboratory's control. These specific areas include laboratory preparation blanks, calibration standards, calibration check standards, and laboratory control standards. Failure to meet these performance requirements warrants that corrective action be taken by the laboratory.

At times, there may be an urgent need to use data that do not meet all QA/QC requirements. Any decision to utilize data for which non-sample specific criteria have not been met is strictly to facilitate the progress of projects requiring the availability of the data and such decisions should be clearly noted in the data validation report. Use of this data does <u>not</u> constitute acceptance of the data in terms of method compliance nor does it release the laboratory from the obligation to perform as per the analytical method. A laboratory submitting data, which are out of specification, may be required to re-run or resubmit data. The only exception to this is in the area of requirements for individual sample analysis; if the nature of the sample itself limits the attainment of specifications, appropriate allowances must be made. An overriding concern of the DPFSR-BEMQA is to prevent non-sample specific data validation requirements from adversely affecting overall data validation activities. There is ultimately no justification for noncompliance on requirements for performance relative to such areas as blanks, calibration and performance verification standards. Ideally, data validation activities should only be concerned with subjects requiring professional judgment on individual sample results.

With these concepts in mind, this document is designed to permit structured data review. To this end, the document is arranged in order, with the most objective, straightforward validation elements given first.

It will be the data reviewer's responsibility to notify the assigned NJDEP Technical Coordinator and Site/Case Manager concerning problems and shortcomings in regards to laboratory data via a Data Validation Report and a Target Analyte Summary List. If mandatory actions are required, they should be specifically noted in a Data Validation Report. This report should also be used to note overall deficiencies requiring attention as well as comments on general laboratory performance and any discernible trends in the quality of data.

### (B) <u>Data Package Deliverables</u>

Data generated using NJDEP modified USEPA SW-846, Final Update III Hexavalent Chromium methods must be delivered to NJDEP-DPFSR/DRPSR in the regulatory format as defined in the currently active Professional Laboratory Services Contract and the Technical Requirements for Site Remediation N.J.A.C. 7:26E. Data delivered in the "Reduced Regulatory Format" can only be reviewed against the requirements of this SOP and cannot be validated.

## (C) Preliminary Review

In order to use this document effectively, the reviewer should have a general overview of the data deliverable package at hand. The exact number of samples, their assigned laboratory and field identification numbers, their matrix, and concentration level, the identity of any field QC samples (blanks, duplicates, spikes, splits), sampling dates and the name of laboratory involved for the analysis are essential information. Background information on the site is helpful but at times, it is very difficult to locate. The NJDEP Technical Coordinator or the Site/Case Manager is the best sources for answers or further direction.

The chain-of-custody record provides sample descriptions and the date and time of sampling. Sampling procedures are addressed by NJDEP "Field Sampling Procedures Manual" requirements. Any discrepancies found by the reviewer must be noted on the data validation report. The non-conformance summary that is submitted by the laboratory is another source of general information. Notable problems with matrices, insufficient sample size for analysis or reanalysis, sample temperature and preservation and unusual events should be found here.

## (D) Data Validation

### 1. Sample Holding Times

#### A. Objective

The objective is to ascertain the validity of results, based on the holding time of the sample from time of collection to time of analysis. From the standpoint of laboratory performance, the time of analysis is needed to determine compliance with the NJDEP modified USEPA SW-846, Final Update III Hexavalent Chromium method.

#### B. Requirements

The following holding time requirements were established by NJDEP.

Non Aqueous Samples for Hexavalent Chromium: seven (7) days from time of sampling to analysis.

Aqueous Samples for Hexavalent Chromium: 24 hours from time of sampling to

analysis

**C. Evaluation Procedure**

Actual holding times are established by comparing the sampling dates and times on the chain of custody with the dates and times of analysis found in the laboratory data. Exceeding the holding time for a sample may result in a loss of the Hexavalent Chromium. This occurs through any number of mechanisms, such as deposition on the sample container walls or chemical activity. Therefore, from a usability standpoint, when holding time violations occur, the results which are most severely called into question are those which fall below or close to the detection limit or a cleanup level.

**D. Action**

1) For nonaqueous samples, if the holding time is greater than seven days but less than or equal to nine days, then the sample concentration is qualified and flagged the data with a "J". If the holding time exceeds nine days, then all sample results are rejected "R".

2) For aqueous samples, if the holding time is greater than 24 hours but less than or equal to 48 hours, then the sample concentration is qualified and flagged the data with a "J". If the holding time exceeds 48 hours, then all sample results are rejected "R".

**2. Instrument Calibration Curve**

**A. Objective**

The objective in establishing compliance requirements for satisfactory instrument calibration is to ensure that the instrument is capable of producing acceptable quantitative data.

**B. Requirements**

1) The instrument must be calibrated daily (once every 24 hours) or each time the instrument is set up, whichever is more frequent.

2) The instrument standardization date and time must be included in the raw data.

3) A calibration blank and at least four (4) standards in graduated amounts and in the appropriate range (0.10 to 2.0 mg/L) are recommended in establishing the analytical curve.

4) The calibration curve must have a correlation coefficient of 0.995 or greater.

**C. Evaluation Procedure**

1) By checking the raw data, verify that the instrument was calibrated at the proper frequency.

2) Verify that the correct number of standards and calibration blanks was used.

3) Verify that the date and time of sample analysis was provided.

4) Verify that the correlation coefficient for the calibration curve was greater than or equal to 0.995.

5) Verify that if the correlation coefficient was less than 0.995, the laboratory analyzed a new calibration curve.

**D. Action**

1) If there are inconsistent time(s), date(s), or instrument IDs on the raw data sheets and reporting forms, the laboratory must be contacted and all inconsistencies must be resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data in question.

2) If the instrument calibration was not performed or calibrated daily, then all associated data are rejected "R".

3) If the correct number of instrument calibration standards was not analyzed then all associated data are qualified "J".

3) If the correlation coefficient for the calibration curve was less than 0.995, then all associated data are rejected.

**3. Calibration Check Standard (CCS)**

**A. Objective**

The CCS documents satisfactory instrument performance (calibration accuracy) during each analysis run.

## B. Requirements

1) The CCS analyses must be performed at a minimum frequency of once every 10 samples during an analysis run. The CCS must be analyzed at the beginning of the run and after the last analytical sample.

2) The CCS should be at or near the mid range level of the calibration curve.

3) The same concentration for the CCS must be used throughout the sample analyses.

4) The CCS results must fall within the control limits of 90-110% of the true value.

5) The CCS must be independently prepared standard from a different source than that used for the initial calibration.

## C. Evaluation Procedure

1) Review the supporting raw data to verify that the CCS was performed at the proper frequency.

2) Verify that the CCS was independently prepared and the standard used was at or near the mid range level of the curve.

3) Verify that the same CCS concentration was used throughout the analyses.

4) Verify that the standard used for performing the calibration verification met the acceptance criteria for 90-110%.

## D. Action

1) If there are inconsistent time(s), date(s), or instrument IDs on the raw data sheets and reporting forms, the laboratory must be contacted and all inconsistencies must be resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify, or reject the data questioned.

2) If the CCS analysis was not performed, then all associated sample data are rejected “R”.

3) If the CCS analysis was not performed at the correct frequency, then all associated sample data are qualified "J".

4) If the CCS was not at or near the mid range level of the curve, then all associated sample data are qualified "J".

5) If the CCS concentration was not the same throughout the analysis, then qualify "J" all associated sample data if the concentration was within the calibration range and reject "R" all associated sample data if the concentration was not within the calibration range.

6) If the CCS analysis was performed but did not meet the % recovery requirements, use the following guidelines:

   a) If the CCS falls outside the acceptance windows but within the ranges of 80-89% or 111-120%, flag the positive hit data of associated samples as estimated (J). In the data validation report, give an indication to the data end user as to the bias of the results (i.e., if the CCS for an analyte is 115%, then it could be stated that the reported results for that analyte should be biased high.)

   b) If an analyte is not detected in a sample and the associated CCS result is greater than 110% but less than or equal to 120%, then the analytical sample determination is acceptable.

   c) If the analyte is not detected in a sample and the associated CCS result is less than 90% but greater than or equal to 80%, then the detection limit may be biased low. In the data validation report, note that the detection limit for that sample may be elevated and flag the data for these samples as estimated (UJ).

   d) If the CCS result is less than 80% or greater than 120%, this is indicative of severe analytical deficiencies and the data are rejected as unusable (R).

7) For a given CCS, the actions described in item 6) will affect the samples that are analyzed between the two acceptable CCSs that bracket the unacceptable CCS.

## 4. Calibration Blanks

### A. Objective

Calibration Blanks are analyzed in order to establish that the instrument has no contamination or drifting problems, and to ensure that the instrument is capable of producing acceptable quantitative data.

### B. Requirements

1) A Calibration Blank must be used in establishing the analytical curve.

2) The absolute value of the calibration blank should not exceed the Method Detection Limit (MDL).

3) A Calibration Blank must be analyzed before the initial instrument's calibration standards and after each CCS.

**C. Evaluation Procedure**

1) Review the supporting raw data to verify that the Calibration Blank analysis was performed and at the proper sequence.

2) Verify that the Calibration Blank absolute value was less than the MDL.

**D. Action**

1) If there are inconsistent time(s), date(s), or instrument IDs on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data in question.

2) If the absolute value of the Calibration Blank exceeds the MDL, then highly qualify "J" the data in all associated analytical samples.

3) If no Calibration Blank was run, all associated sample data are rejected "R".

**5. Preparation/Reagent Blanks and Field Blanks**

**A. Objective**

The assessment of results regarding blank analyses is for determining the existence and magnitude of contamination problems. The criteria for the evaluation of blanks apply to all blanks, including, but not limited to preparation/reagent blanks and field blanks. The responsibility for action in the case of unsuitable blank results depends upon the circumstances and the origin of the blank. If problems with any blank exist, all associated data must be carefully evaluated to determine whether there is an inherent variability in the data set or the problem is an isolated occurrence not affecting other data.

**B. Requirements**

1) The laboratory preparation/reagent blank is an in-house blank the laboratory is responsible for reporting.

2) At least one preparation/reagent blank, consisting of deionized distilled water, processed through each sample preparation and analysis procedure must be prepared and analyzed with every Sample Delivery Group (SDG), or for each batch of samples digested, whichever is more frequent. (Exception: If only soil samples were analyzed, an aqueous preparation blank is not required for the associated field blank.)

3) The minimum field blank requirement is as follows. There should be at least 1 field blank/matrix/per sampling date.

4) It should be noted that inorganic analysis for trip blanks is not required unless specifically requested by NJDEP on a site by site basis.

## C. Evaluation Procedure

1) Review the results for the preparation/reagent blank(s) (raw data, strip charts, printer tapes, bench sheets, etc.) in order to verify that results were accurately reported.

2) Verify that the proper number of preparation/reagent blanks was analyzed.

3) Verify that the proper number of field blanks was analyzed, as per the request of the data end user.

4) Verify that the sample concentration is not corrected for any preparation/reagent blank, trip blank or field blank values.

## D. Action

1) If there are inconsistent time(s), date(s), or instrument ID(s)on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies must be resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data.

2) If any samples are not associated with a preparation/reagent blank, all data from the affected samples are rejected "R". (An aqueous reagent blank for the field blank is not required if only soil samples were analyzed).

3) If no field blanks were requested for analyses or if the incorrect number were collected and analyzed, note it in the data validation report.

4) If the preparation/reagent blank or field blank results were subtracted from associated sample results, add the applicable blank results to the sample results before proceeding to steps 6) and 7) below. The laboratory must be notified of the data reporting error and a revised data report package must be submitted.

5) If the sample concentration of Hexavalent Chromium is greater than ten (10) times the preparation/reagent blank, then no qualifications are necessary.

6) When the sample concentration of Hexavalent Chromium is less than or equal to ten (10) times the preparation/reagent blank, then the following actions are to be taken.

   a) If the concentration of Hexavalent Chromium in a sample is less than or equal to three (3) times the concentration of Hexavalent Chromium in the associated preparation/reagent blank, the presence of Hexavalent Chromium in the sample is negated due to laboratory contamination, as indicated by the preparation/reagent blank. The "B" qualifier must be reported with the analytical result.

   b) If the concentration of Hexavalent Chromium in a sample is greater than three (3) times the concentration of Hexavalent Chromium in the associated preparation/reagent blank, the presence of Hexavalent Chromium in the sample is considered "real". The "B" qualifier must be reported with the analytical result. The concentration must also be reported with the "J" qualifier and is quantitatively qualified due to preparation/reagent blank contamination.

   c) If the value of Hexavalent Chromium in the preparation/reagent blank is negative, then all positive values found in a field sample will be quantitatively qualified because of the possibility of a negative drift in the instrument and may be biased low.

   d) If the value of Hexavalent Chromium in the preparation/reagent blank is negative, then all non-detected values found in a field sample are reported "UJ" because of the possibility of a negative drift in the instrument and may give rise to a false negative (ND).

7) When the sample concentration of Hexavalent Chromium is less than or equal to ten (10) times the field blank concentration, then the following actions are to be taken.

   a) If the concentration of Hexavalent Chromium in a sample is less than or equal to three (3) times the concentration of Hexavalent Chromium in the

associated field blank, then the presence of Hexavalent Chromium in the sample is negated due to introduced contamination, as indicated by the field blank.

b) If the concentration of Hexavalent Chromium in a sample is greater than three (3) times the concentration of Hexavalent Chromium in the associated field blank, then the presence of Hexavalent Chromium in the sample is considered "real". The concentration must be reported with the "J" qualifier and is quantitatively qualified due to field blank contamination.

## 6. Predigestion Spike Sample Analysis (non aqueous samples only)

### A. Objective

The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology.

### B. Requirements

1) At least one spiked sample analysis must be performed on each group of samples of a similar matrix type (e.g., sediment, soil) and concentration (e.g., low, medium) for each digestion batch of samples or for each 20 samples received, whichever is more frequent.

2) If the spike analysis is performed on the same sample that was also chosen for the duplicate sample analysis, spike calculations must be performed using the results of the original sample analysis.

3) The analyte spike must be added before sample digestion andthe spike recovery must be within the control limits of 75-125%.

4) The predigestion spike concentration should be at 0.5 mg/L.

### C. Evaluation Procedure

1) Verify that the proper number of spikes and the proper spike concentrations were used.

2) If spike analysis is performed on the same sample that was chosen for duplicate analysis, verify that the laboratory used the original sample results for calculations.

3) Spot check the raw data to verify that results were correctly calculated and reported on the spike analysis form. Predigestion spike percent recoveries (% R) are calculated as follows:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample results
SR = Sample results
SA = Spike added

4) Verify that the spike recovery fall within the control limits of 75-125%.

5) Verify that a field sample and not a field blank was used for predigestion spike analysis as per NJDEP requirements.

**D. Action**

1) If there are inconsistent time(s), date(s), or instrument IDs on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data in question.

2) If no spike analysis was performed for non aqueous samples (i.e., either soil and/or sediment samples) or if a field blank was used, then all associated sample data are rejected "R".

3) If the frequency of the spike analysis exceeded 1 in 20 samples but was within 1 in 25, qualify "J" the data from samples 21-25.

4) If the frequency of a spike analysis exceeded 1 in 25 samples, reject "R" all sample data that follow the 25th sample.

5) If the wrong spike concentration was used, then qualify "J" that analyte(s) in all associated sample data.

6) The following guidelines are recommended for use in evaluating data usability when the spike recoveries do not fall within the control limits of 75-125%.

   a) If the spike recovery is > 125% and the reported sample results are less than the MDL, this data are acceptable for use.

   b) If the spike recovery is > 125% and the reported sample levels are greater than the MDL, then qualify the data "J" and give an indication in the data validation report as to the potential high bias of the results.

c) If the spike recovery is < 75% and the reported sample levels are greater than the MDL, then qualify the data "J". In the data validation report, give an indication as to the low bias of the results.

d) If an analyte is not detected in a sample and spike recovery is less than 75%, then the detection limit may be biased low. In the data validation report, note that the detection limit reported by the laboratory for that sample may be biased low. Flag the data for the associated samples as qualified "UJ".

## 7. Post Verification Spike Sample (PVS)

### A. Objective

The PVS analysis is designed to verify that neither a reducing condition nor a chemical interference is affecting the analysis.

### B. Requirements

1) At least one PVS analysis must be performed on each group of samples of a similar matrix type (e.g., water, soil) for each batch of samples or for each 20 samples received, whichever is more frequent.

2) As per NJDEP requirements, samples identified as field or preparation/ reagent blanks cannot be used for PVS analysis.

3) If the PVS analysis is performed on the same sample that was also chosen for the duplicate sample analysis, PVS spike recovery calculations must be performed using the result of the original sample analysis.

4) The sample chosen for PVS should be spiked at 150 ug/L or twice the sample concentration, whichever is greater.

5) The PVS spike recovery must be within the control limits of 85-115%.

6) If the PVS recovery is less than 85%, then reanalyze the PVS to determine if the low spike recovery is due to a reducing agent.

7) When the sample concentration is less than the MDL, use 0 for the sample results only for the purpose of calculating the % recovery.

### C. Evaluation Procedure

1) Verify that the PVS analysis was performed at the proper frequency (1 for every 20

samples) and that the proper PVS concentration was used.

2) Verify that a field sample and not a field blank or preparation/ reagent blank was used for PVS analysis as per NJDEP requirements.

3) Spot-check the raw data to verify that PVS recovery result was correctly calculated and reported. PVS percent recoveries (% R) are calculated as follows:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where: SSR = PVS sample result
SR = Sample result
SA = Spike added

4) Verify that the PVS recovery results fall within the specified limits of 85-115%.

5) Verify that the PVS was reanalyzed if the recovery was less than 85%.

6) Verify that when the addition of a PVS to a sample extends the concentration beyond the calibration range, a dilution was performed.

## D. Action

1) If there are inconsistent time(s), date(s), or instrument IDs on reporting forms or raw data sheets, the laboratory must be contacted and all inconsistencies resolved. If the reviewer is unable to resolve any of the discrepancies, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data in question.

2) If no PVS analysis was performed for either soil and/or aqueous samples, all associated sample data are rejected "R".

3) If a field blank or preparation/ reagent blank was used for PVS analysis, then reject “R” all associated sample data.

4) If the frequency of the PVS analysis exceeded 1 in 20 samples but was within 1 in 25, qualify "J" the data from samples 21-25.

5) If the frequency of a PVS analysis exceeded 1 in 25 samples, reject "R" all sample data that follow the 25th sample.

6) If the wrong PVS concentration was used, qualify "J", Hexavalent Chromium in all associated sample data.

7) The following guidelines are recommended for use in evaluating data usability when the PVS recoveries do not fall within 85-115% limits:

a) If the PVS recovery is > 115% and the reported sample results are less than the MDL, the data are acceptable for use.

b) If the PVS recovery is > 115% and the reported sample levels are greater than the MDL, then flag data as estimated "J" and give an indication in the data validation report as to the potential high bias in the results.

c) If the PVS recovery is less than 85% the following actions are taken:

i) If no reanalysis was performed, and the reported sample levels are greater than the IDL, then the data are qualified "J". In the data validation report, give an indication as to the low bias of the results.

ii) If no reanalysis was performed, and the reported sample levels are less than the IDL then the detection limit is qualified “UJ”. In the data validation report, note that the detection limit reported by the laboratory for that sample may be biased low.

iii) If the laboratory reanalyzes the aliquot and the recovery is within 85-115% recovery limits, no action is needed.

iv) If the reanalysis is still outside the (recovery) limits, then qualify "J" all associated samples.

8) If the laboratory failed to make a dilution to any PVS that exceeded the calibration range, qualify " J" all associated samples.

## 8. Duplicate Sample Analysis

### A. Objective

The duplicate sample analysis is used to evaluate the precision of the method for Hexavalent Chromium. The data reviewer can use the results of the duplicate analysis as an indicator of the precision of the sample results.

### B. Requirements

1) One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and for each batch of samples or for each 20 samples received, whichever is more frequent.

2) As per NJDEP requirements, samples identified as field blanks or preparation/reagent blanks cannot be used for duplicate sample analysis.

3) Duplicate results must be reported on duplicate form in ug/L for aqueous samples and mg/Kg dry weight basis for solid samples.

4) A control limit of 20 % Relative Percent Different (RPD) shall be used for aqueous samples and for nonaqueous samples whose values are greater than or equal to 8 ppm.

The RPD for Hexavalent Chromium is calculated as follows:

$$RPD = \frac{S - D}{(S + D)/2} \times 100$$

Where: RPD = Relative Percent Difference
S = First sample value (original)
D = Second sample value (duplicate)

5) A control limit of $\pm$ 2 ppm shall be used:

a) If both sample values are less than 8.0 ppm;

b) If only one sample value is less than 8.0 ppm.

## C. Evaluation Procedure

1) Verify that duplicate samples were analyzed for each matrix type and at the proper frequency.

2) Spot-check the raw data to verify that the results have been correctly reported on the duplicate form.

3) Verify that a field sample was used for duplicate analysis as per NJDEP requirements.

4) Verify that the correct control limits were used.

## D. Action

1) If there are inconsistent time(s), date(s), or instrument IDs on reporting forms and

raw data sheets, the laboratory must be contacted and all inconsistencies resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data in question.

2) If no duplicate sample was analyzed for either soil and/or aqueous matrices, then all associated sample data are rejected "R".

3) If a field blank or preparation/reagent blank was used for duplicate analysis, then all associated sample data are rejected “R”.

4) If the frequency of the duplicate analysis exceeded 1 in 20 samples but was within 1 in 25, qualify "J" the data from samples 21-25.

5) If the frequency of a duplicate analysis exceeded 1 in 25 samples, reject "R" all sample data that follow the 25th sample.

5) If the duplicate sample analyses results for Hexavalent Chromium fall outside the control windows of 20% RPD or ± 2 ppm, whichever is appropriate, the results in all associated samples of the same matrix type should be flagged as estimated "J".

## 9. Laboratory Control Sample Analysis (LCS) (non aqueous samples only)

### A. Objective

The laboratory control sample analysis (LCS) is designed to serve as a monitor of the efficiency of the digestion procedure. The inability of the laboratory to successfully analyze a known QC check sample (LCS) is indicative of an analytical problem related to a digestion/sample preparation procedures and/or instrument operations. This analysis is currently an option for the laboratory.

### B. Requirements

1) One LCS must be analyzed for every SDG of non aqueous samples received or for each batch of samples digested, whichever is more frequent. Results for each Hexavalent Chromium should be reported on the LCS form.

2) The LCS must be prepared by the laboratory.

3) The LCS percent recoveries (%R) must fall within the control limits of 80% -120%.

### C. Evaluation

1) Verify that the LCS was analyzed and at the proper frequency.

2) Review the LCS form and verify that the results fall within the specified control limits.

3) Spot check the raw data (printouts, strip chart, bench sheets) to verify the reported recoveries on the LCS form.

**D. Action**

1) If there are inconsistent time(s), date(s), or instrument IDs on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data.

2) If the frequency of a LCS analysis exceeded 1 in 20 samples, qualify "J" the data from the 21st sample on.

3) If the LCS was not within control limits, qualify "J" all associated samples.

## 10. Sample Result Verification

**A. Objective**

The sample results verification process checks the correctness of the data acquisition, computation, transcription and the validity of the calibration curve construction.

**B. Requirements**

1) It is implicit within the USEPA SW-846 Final Update III document that all required data reduction, reporting and documentation be performed and presented in such a manner so as to ensure the data package is both complete as well as free of computational and/or transcription errors.

2) Percent solids determinations are required for all non-aqueous samples. Sample dry weight corrections are made using the percent solids results.

3) NJDEP modified methods 3060 & 7196A require pH adjustments for each sample and their final readings recorded in a laboratory notebook.

   a) Method 3060-pHs of all analytical solutions for non-aqueous sample must be adjusted within a range of 7.0 - 8.0.

b) Method 7196A - pHs of all analytical solutions must be adjusted within a range of 1.6 - 2.2.

4) NJDEP modified method 3060 requires that the digestion solution temperature must be monitored at 30 minutes and 60 minutes and recorded in the laboratory notebook for one sample.

## C. Evaluation Procedure

In addition to the evaluation procedures previously outlined within this document, the specific elements of the data validation process should include the following:

1) Examine the raw data for any anomalies (i.e., negative absorbance, omissions, etc.).

2) Verify that there were no computational errors in sample concentration by re-calculating the results for Hexavalent Chromium in a percentage of samples.

3) Calculations

a) For aqueous samples, calculate the Hexavalent Chromium results as follows:

Hexavalent Chromium in mg/L = A x E

Where: A = concentration from the calibration curve in mg/L.
E = Dilution (if necessary)

b) For solid samples, when concentrations are reported as mg/Kg on a dry basis use the following formula.

$$\text{mg Hexavalent Chromium/Kg sample} = \frac{A \times B \times E}{C \times D}$$

Where: A = concentration from the calibration curve in mg/L.
B = Final digested volume in liters.
C = Wet weight of sample in kilograms.
D = % Solids/100
E = Dilution (if necessary)

4) Verify that there were no transcription errors by checking the raw data versus the analytical result summary sheet.

5) a) Verify that percent solids analysis for all non-aqueous samples was

performed.

b) Verify the percent solids determinations by spot checking the laboratory results using the following formula.

$$\% \text{ Solids} = \frac{\text{Sample dry weight}}{\text{Sample wet weight}} \times 100$$

6) Verify that the laboratory has provided pH readings for methods 3060 and/or 7196A.

7) Verify that the pH reading(s) were within the specified range(s) for each sample.

8) Verify that the temperature readings were provided, and were within a temperature range of 90 – 95 degrees centigrade.

## D. Action

1) If any raw data anomalies were found, the reviewer should use judgement on how the sample data would be affected.

2) If differences are identified between the laboratory reported result and the reviewer calculated result, the following actions should be taken:

   a) If the laboratory reported result is within 10% of the reviewer calculated result and the difference could be attributed to rounding, no corrective action is required.

   b) If the laboratory reported result differs by 10% from the reviewer calculated result, but not attributable to rounding, try to determine the source(s) of error. If this cannot be determined, the laboratory should be contacted about the sample result discrepancy. If an error is confirmed, request submission of corrected data sheets from the laboratory. Summarize all actions taken in the Data Validation Report.

3) Transcription errors that affect the data shall be noted in Data Validation Report. Also, the laboratory shall be contacted and the submission of corrected data sheets shall be requested.

4) If the % Solids data were not provided then note the deficiency in the data validation report. The results are qualified and possibly biased low.

5) If the pH readings are not provided, then contact the laboratory. The data are conditionally rejected pending satisfactory verification of the pHs.

6) If the laboratory failed to record the pH data in a laboratory notebook, then the following actions are taken:

   a) The data are qualified with an unknown bias if the positive results exceed the clean-up action level.

   b) The data are suspect if the positive results are below the clean-up action level.

   c) The "non-detected" data are rejected because the possibility of false NDs exists.

7) If the temperature readings are not provided, then contact the laboratory. The data are conditionally rejected pending satisfactory verification of the digestion solution temperature.

8) If the laboratory failed to record the digestion solution temperature in a laboratory notebook, then the following actions are taken:

   a) The data are qualified with an unknown bias if the positive results exceed the clean-up action level.

   b) The data are suspect if the positive results are below the clean-up action level.

   c) The "non-detected" data are rejected because the possibility of false NDs exists.

## APPENDIX I - GLOSSARY OF TERMS

ABSORBANCE - a measure of decrease in incident light passing through a sample into the detector. It is defined mathematically as:

$$A = \frac{I\ (solvent)}{I\ (solution)} = \log \frac{Io}{I}$$

Where, I = radiation intensity

ALIQUOT- a measured portion of a field sample taken for analysis.

ANALYSIS DATE/TIME - the date and military time (24-hour clock) of the injection of the sample, standard, or blank into the analysis system.

ANALYTE - the element or ion an analysis seeks to determine; the element of interest.

AUTOZERO - zeroing the instrument at the proper wavelength. It is equivalent to running a standard blank with the absorbance set at zero.

AVERAGE INTENSITY - the average of two different injections (exposures).

BACKGROUND CORRECTION - a technique to compensate for variable background contribution to the instrument signal in the determination of trace elements.

BATCH - the basic unit for analytical quality control is the analytical batch. The analytical batch is defined as 20 samples or less which are analyzed together with the same method sequence and the same lots of reagents and the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g. groundwater, sludge, ash, etc.).

CALIBRATION - the establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of acid or concentration of acids as used in the sample preparation.

CALIBRATION BLANK - a volume of digestion solution/distilled water.

CALIBRATION CHECK STANDARD - analytical standard run every 1O analytical samples to verify the calibration of the analytical system.

COEFFICIENT OF VARIATION (CV) - the standard deviation as a percent of the arithmetic mean.

CONTROL LIMITS - a range within which specified measurement results must fall to be

compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged.

CORRELATION COEFFICIENT - a number (r) which indicates the degree of dependence between two variables (concentration - absorbance). The more dependent they are the closer the value to one. Determined based on the least squares line.

DAY - unless otherwise specified, day shall mean calendar day.

DIGESTION LOG - an official record of the sample preparation (digestion).

DUPLICATE - a second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

FIELD BLANK - any sample submitted from the field identified as such a blank.

HOLDING TIME - the elapsed time expressed in days from the date of sample collection until the date of its analysis.

Holding time = (sample analysis date - sampling date)

INDEPENDENT STANDARD - a laboratory-prepared standard solution that is composed of Hexavalent Chromium from a different source than that used in the standards for the initial calibration.

INJECTION - introduction of the analytical sample into the instrument excitation system for the purpose of measuring absorbance, emission or concentration of an analyte. May also be referred to as exposure.

INSTRUMENT DETECTION LIMIT (IDL) - determined by multiplying by three the standard deviation obtained for the analysis of a standard solution (each analyte in reagent water) at a concentration of 3x-5x IDL on three nonconsecutive days with seven consecutive measurements per day.

INTERFERENTS - substances which affect the analysis for the element of interest.

MATRIX - the predominant material of which the sample to be analyzed is composed.

MATRIX SPIKE - aliquot of a sample (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

METHOD DETECTION LIMIT (MDL) - The minimum concentration of a substance that can be measured and reported with 99 % confidence that the analyte concentration is greater than zero

and is determined from analysis of a sample in a given matrix containing the analyte. The procedures for determining the MDL are located in Chapter 1 of SW-846.

PREPARATION BLANK (reagent blank, method blank) - an analytical control that contains distilled, deionized water and reagents, which is carried through the entire analytical procedure (digested and analyzed). An aqueous method blank is treated with the same reagents as a sample with a water matrix; A solid method blank is treated with the same reagents as a soil sample.

PROTOCOL - a compilation of the procedures to be followed with respect to sample receipt and handling, analytical methods, data reporting and deliverables, and document control.

ROUNDING RULES - if the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 11.443 is rounded off to 11.44.

If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 11.446 is rounded off to 11.45.

If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 11.435 is rounded off to 11.44, while 11.425 is rounded off to 11.42.

If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

RUN - a continuous analytical sequence consisting of prepared samples and all associated quality assurance measurements as required by the USEPA, SW-846.

SOIL - synonymous with soil/sediment or sediment as used herein.

SPECTROMETER - An instrument with an entrance slit, a dispersing device, and one or more exit slits, which measurement are made at selected wavelengths within the spectral range, or by scanning over the range.

STOCK SOLUTION - a standard solution which can be diluted to derive other standards.

WET WEIGHT - the weight of a sample aliquot including moisture (undried).