Response to Peer Review Comments
Chapter 1: Executive Summary

Peer Reviewer: Paul Brant-Rauf

- *It is my opinion that the overall process followed by the workgroup in the generation of the report was thorough, rigorous and entirely appropriate, yielding a report that was responsive to the charge by the Commissioner. The recommendations of the workgroup were based on the best available scientific evidence, and the conclusions were reasonable and justified.*

    No response.

Peer Reviewer: Gregory Turk

No pertinent comments on Chapter 1.

Peer Reviewer: Gary Ginsberg

- *Is the recommendation for the 1998 proposed cleanup criteria based on valid science, particularly for hexavalent chromium?*

    Response: Yes, the criteria for oral, dermal, and inhalation pathways are based upon the best available science at the time and are still valid today. There is one difficulty, and this is with respect to how these various criteria are presented. From a risk management perspective it is unclear when a solid phase dermal ACD-based criterion of 400 mg/kg would ever be used. I know NJDEP would use the lowest criterion from among the ingestion, inhalation, and dermal numbers you've derived to determine a site-specific cleanup. Since the dermal 400 mg/kg standard is the highest among these, the document should state when it may come into play (e.g., acute exposure scenarios?). If never, then is it worth having the number?

    Response: This comment pertains to subject material in Chapter 3, Risk Assessment and is addressed in the peer review summary for that chapter.

Peer Reviewer: Gregory Turk

No pertinent comments on Chapter 1.

Peer Reviewer: Herman Gibb

- *Is the recommendation for the 1998 proposed cleanup criteria based on valid science, particularly for hexavalent chromium?*

    Response: Yes, it is based on valid science.

- *Was the process used by the workgroup valid for reviewing the criteria?*

    Response: Yes. The workgroup identified risk assessment questions and evaluated the data based on those questions. In that way, the group was able to focus on the important issues.

- *Did the workgroup adequately address the questions posed by Commissioner Campbell in his March 2004 memo?*

Response: Presumably this question is referring to the March 23 memo from Commissioner Campbell to Joseph Seebode (subject: Chromium) which was very brief. There were no questions posed in that letter. It is the only March memo identified on the web site. With regard to the charge to the risk assessment workgroup on the web site (http://www.state.nj.us/dep/dsr/chromium/subgroup-risk.htm), charge question #3 was modified by the Work Group (page 30 of the report). With the modification of question #3, the risk assessment charge questions appear to have been adequately addressed.

No further comments presented for Chapter 1.

Peer Reviewer: Chunming Su

● *This is a well-written report that outlines the review of New Jersey Chromium Workgroup on the application of the current chromium standards and proposed revision of the current standards. All four subgroups (Risk Assessment, Analytical Chemistry, Air and Dust Transport, and Chromium Environmental Chemistry) have done an excellent job in summarizing our current knowledge on chromium ore processing residue issues. Their suggestions appear to be scientifically sound. Technically, the report is in good shape. There are some editorial points that can be looked at in order to further improve the report.*

No response.

Peer Reviewer: Ken Stollenwerk

● *I found the report to be very thorough. Therefore, I did not have a lot of comments. Overall, I agree with the conclusions and recommendations presented in this report. I realize that some of the recommendations may go beyond the original charges made to the working group, particularly in the Chromium Environmental Chemistry Subgroup. However, I believe that the additional proposed research is necessary to address the questions relating to chromium behavior in these complex environments.*

Response: Comments specific to Chapter 6 are addressed in the response to that chapter.

Peer Reviewer: John Chorover

No comments on Chapter 1.

Peer Reviewer: C.P. Huang

● *The reviewer strongly agrees with the recommendations to continue support and review new and upcoming research that may improve the understanding of the toxicity of chromium-containing soils and the fate and transport of COPR in the environment.*

No response.

● *However, the reviewer is not clear about the role of UV radiation on Cr toxicity. One possibility of UV being a contributing factor to Cr toxicity is the oxidation of Cr(III) via UV-generated oxidants such as ozone and hydroxyl radicals. It is well known that UV radiation of oxygen will yield ozone and that further UV radiation of ozone in the* *presence of water will generate hydroxyl radical which is strong oxidation agent that can oxidize Cr(III) to Cr(VI) readily.*

Response: This comment pertains to subject material in Chapter 3, Risk Assessment and is addressed in the peer review summary for that chapter.

Response to Peer Review Comments
Chapter 2: Introduction

Peer Reviewer: Paul Brant-Rauf
No pertinent comments on Chapter 2.

Peer Reviewer: Gregory Turk
No pertinent comments on Chapter 2.

Peer Reviewer: Gary Ginsberg
No pertinent comments on Chapter 2

Peer Reviewer: Gregory Turk
No pertinent comments on Chapter 2.

Peer Reviewer: Herman Gibb
No pertinent comments on Chapter 2

Peer Reviewer: Chunming Su
No pertinent comments on Chapter 2

Peer Reviewer: Ken Stollenwerk
No pertinent comments on Chapter 2

Peer Reviewer: John Chovoer
- *P. 17, last line: The "respiratory tract" actually contains multiple "organs".*
  Response: Change has been made in the report to reflect this.

Peer Reviewer: C.P. Huang
The reviewer has no comment on this chapter. The chapter is very well presented.
No response.

Response to Peer Review Comments
Chapter 3 – Risk Assessment Sub-Group

General Comment (Executive Summary)

<u>Peer Reviewer: C.P.Huang</u>

●*The reviewer strongly agrees with the recommendations to continue support and review new and upcoming research that may improve the understanding of the toxicity of chromium-containing soils and the fate and transport of COPR in the environment.*

However, the reviewer is not clear about the role of UV radiation on Cr toxicity. One possibility of UV being a contributing factor to Cr toxicity is the oxidation of Cr(III) via UV-generated oxidants such as ozone and hydroxyl radicals. It is well known that UV radiation of oxygen will yield ozone and that further UV radiation of ozone in the presence of water will generate hydroxyl radical which is strong oxidation agent that can oxidize Cr(III) to Cr(VI) readily.

> **Response:** This is an interesting speculation although it is not clear whether the the free-radical chemistry that operates in the atmosphere or in free solution has direct relevance to the Cr(III) that may be present within the cell. In any event the specific mechanism involved cannot currently be ascertained, and the relevance of the Davidson et al. study to joint environmental exposures to UV and Cr(VI) remains uncertain.

●*Is the recommendation of the 1998 proposed cleanup criteria based on valid science, particularly for hexavalent Cr?*

<u>Peer Reviewer: Gary Ginsberg</u>

●*Yes, the criteria for oral, dermal, and inhalation pathways are based upon the best available science at the time and are still valid today. There is one difficulty, and this is with respect to how these various criteria are presented. From a risk management perspective it is unclear when a solid phase dermal ACD-based criterion of 400 mg/kg would ever be used. I know NJDEP would use the lowest criterion from among the ingestion, inhalation, and dermal numbers you've derived to determine a site-specific cleanup. Since the dermal 400 mg/kg standard is the highest among these, the document should state when it may come into play (e.g., acute exposure scenarios?). If never, then is it worth having the number?*

> **<u>Response</u>**: The charge to the Risk Assessment sub-group was to investigate whether an alternative to the existing solution-based ACD cleanup criterion was appropriate and to suggest a method for quantifying dose-response and exposure. The value that would result from that investigation was not known *a priori*. Therefore, the exercise, itself was an important step in order to determine where such a criterion would fall relative to the other criteria. However, as the solution-based ACD criterion does not have a fixed value, but depends on the extractability of the Cr^{+6} in a given sample, the 400 mg/kg value may be relevant for some samples.

Peer Reviewer: Paul Brandt-Rauf

● *In terms of the risk assessment part in particular, the workgroup addressed some difficult questions in a balanced fashion. For example, the question of Cr(VI) carcinogenicity by the ingestion route is raised by the Davidson et al. study, but there is no other direct evidence in the literature to support this. Furthermore, the methodology of the Davidson et al. paper was unusual, making its relevance for human health risk assessment hard to take into account. Since skin tumors are not typically associated with chromium exposure, and mixed exposures, such as chromium and UV light in this case, are not typically tested, this study by itself does not provide a sufficient basis for the development of a soil cleanup standard. Nevertheless, it would certainly be wise and prudent for the department to keep an open mind on this issue and follow the literature for any new developments that might shed light on this question in the future.*

Peer Reviewer: Herman Gibb

●*Yes, it is based on valid science*

●*Other than the Davidson et al. (2004) paper, are you aware of any evidence supporting the ingestion carcinogenicity of Cr (VI) that would support the development of a cleanup standard?*

Peer Reviewer: Gary Ginsberg

●*Yes, there are a number of CrVI genotoxicity studies which demonstrate the effectiveness of oral CrVI to induce a variety of genetic effects in vivo. The following is a listing of some examples:*

- DPC in rat liver and to a lesser degree lymphocytes from 100 or 200 ppm in drinking water for 3-6 weeks (Coogan, et al., TAP 109: 60-72, 1991);
- Increased SSB by 1.7 fold in rats given a single oral dose that was 50% the LD50 (Bagchi, et al., Comp Biochem Physiol C Pharmacol Toxicol Endocrinol 10:281-287, 1995);
- Increased LPO and DNA fragmentation in mice given an acute LD50 dose; the effects were measured in liver and brain and were more pronounced in p53 deficient mice (Bagchi, et al., Molec. Cell. Biochem. 222: 149-158, 2001).
- 2-4 fold increased liver SSB in rats given a low dose (2.5 mg/kg/d) by gavage for 120 days (Bagchi, et al., Free Radic Biol Med. 22(3): 471-478, 1997);
- Increased SSB/DSB in mouse leukocytes showing a clear dose response from 0.21 to 3.3 mg/kg/d in single oral doses (Devi, et al., Food Chem Toxicol. 39: 859-865, 2001). At higher doses the response was muted perhaps due to cytotoxicity.

While none of these studies are suitable for quantitative cancer risk assessment, they provide support for a genotoxic and potentially a carcinogenic effect of CrVI at internal organs when administered orally in water.

> **Response:** We agree that these studies are consistent with the hypothesis of an ingestion carcinogenicity for CrVI. However, we also agree that these studies are not suitable for quantitative risk assessment because they are indirect predictors of mutagenicity and do not necessarily predict carcinogenicity. We will, however,

note the existence of such studies in the report (see last paragraph of Response to Charge #1).

Peer Reviewer: Paul Brandt-Rauf

● *In terms of the risk assessment part in particular, the workgroup addressed some difficult questions in a balanced fashion. For example, the question of Cr(VI) carcinogenicity by the ingestion route is raised by the Davidson et al. study, but there is no other direct evidence in the literature to support this.*

Response: We agree.

Peer Reviewer: Herman Gibb

There are some occupational studies of hexavalent chromium exposure that suggest that there may be an increased risk of cancer at sites other than the lung (e.g., digestive tract), and it is possible that these risks are the result of swallowing hexavalent chromium dust. The results are not consistent, however, and a causal association of ingested hexavalent chromium with an increased risk of cancer at any site cannot be concluded. It would certainly not be recommended doing anything quantitative with such data.

Response: We agree, and we believe that the current text of the sub-group report reflects this opinion. No change is needed to reflect this position.

Is the Davidson et al. study methodologically relevant to human co-exposure to Cr(VI) and UV light? This question includes, but is not limited to issues of UV light exposure [and] Cr exposure.

Peer Reviewer: Gary Ginsberg

● *I believe this to be an open question because the hairless mouse/UVR model has not been well characterized with respect to its relevance to human risk. A major uncertainty is the sensitivity of hairless mouse skin to UV damage and carcinogenicity. Mice do not normally experience intense UV irradiation and so their ability to contend with UV damage (repair of pyrimidine dimers and other DNA damage in the skin) may be limited. It may be possible that such repair systems are deficient or qualitatively distinct from human DNA repair systems in the skin. This becomes important when considering co-carcinogenesis studies in which CrVI on its own does not induce skin tumors but in some manner increases the tumor response caused by UVR. Since we don't know the mechanism for hairless mouse skin sensitivity to UVR or the mechanism for the CrVI/UVR interaction in mouse skin, it is difficult to say how relevant this type of bioassay is to human risk. Perhaps more confidence in the test system would be gained from an analysis of this group's former work with arsenic/UVR co-carcinogenesis. For example, if the arsenic dose response for inducing skin tumors in this co-carcinogenesis system was similar to that seen in epidemiology studies of arsenic-induced skin tumorigenesis, then one could begin to have more confidence that the quantitative results from this system could be extrapolated to human risk. However, we should also keep in mind that this would still apply mainly to arsenic which has a proven skin tumorigenic potential. The Davidson paper is the first to demonstrate a skin tumorigenic effect of CrVI.*

Response: We agree, and have added a paragraph to the text to this effect (see last paragraph on second-to-last page of Ingestion Carcinogenicity charge).

Peer Reviewer: Paul Brandt-Rauf

● *Furthermore, the methodology of the Davidson et al. paper was unusual, making its relevance for human health risk assessment hard to take into account. Since skin tumors are not typically associated with chromium exposure, and mixed exposures, such as chromium and UV light in this case, are not typically tested, this study by itself does not provide a sufficient basis for the development of a soil cleanup standard. Nevertheless, it would certainly be wise and prudent for the department to keep an open mind on this issue and follow the literature for any new developments that might shed light on this question in the future.*

Response: We agree and we believe that the recommendations of the Risk Assessment sub-group are consistent with the reviewer's advice.

Peer Reviewer: Herman Gibb

● *As indicated in the New Jersey document (page 35), the UV radiation administered in the Davidson et al. study may not be relevant to outdoor human exposure in New Jersey. Furthermore, there is no evidence in the literature even in case reports that chromium is associated with an increased risk of skin cancer. Davidson et al. indicate that Rossman et al. conducted a similar study using arsenic and found that arsenic and UV light increased the risk of skin cancer. Skin cancer in arsenic-endemic areas, however, has not appeared on the sun-exposed areas of the body such as the face and neck but on the palms of the hand, soles of the feet, and the trunk. In the areas where arsenic is endemic (e.g., Taiwan, Mexico, India), the trunk is generally covered because of the sun. Thus there is a question of the relevance of the Rossman et al., and in turn, the Davidson et al. data to the human situation. Also, as noted in the document, the Davidson et al. study was conducted in only one sex and one species. Finally, how to translate chromium and UVR exposure into a soil cleanup standard would itself be problematic. The New Jersey Work Group document was correct in not using these data for quantitative assessment.*

Response: We agree with the overall conclusions of the reviewer, and we believe that these comments largely reflect the existing text. However, we note that the reviewer appears to have mis-read our conclusion regarding the relevance of the UV exposure in Davidson et al. to human outdoor exposure. Page 35 of the draft report states: "The group, therefore, concluded that the UV exposures in Davidson et al. (2004) **were relevant** to consideration of human exposure *(emphasis added)*." However, as we concur with the overall response of the reviewer to this question, and as this statement does not alter that conclusion, we do not believe that a change to the text is warranted.

Is the health endpoint addressed by the Davidson et al. study – skin tumors from the interaction of ingested CrVI and UV light appropriate for the development of a soil cleanup standard?

Peer Reviewer: Gary Ginsberg

●*As pointed out above and below, this is unclear and this study should probably not be used on its own for quantitative risk assessment.*

Response: We agree, and this view is reflected in the Risk Assessment sub-group's report.

Peer Reviewer: Paul Brandt-Rauf

●*Since skin tumors are not typically associated with chromium exposure, and mixed exposures, such as chromium and UV light in this case, are not typically tested, this study by itself does not provide a sufficient basis for the development of a soil cleanup standard.*

Response: We agree.

Peer Reviewer: Herman Gibb - *As indicated in the answer to the previous question, the results of the Davidson et al. study would not be appropriate for a soil cleanup standard.*

Response: We agree.

Does the Davidson et al. study, by itself, provide a sufficient basis for the development of a soil cleanup standard?

Peer Reviewer: Gary Ginsberg

●*There is only a single oral study of CrVI carcinogenesis and it comes in a novel test system whose quantitative (and qualitative) relevance to human risk assessment needs further exploration. Therefore, these results cannot, on their own, or in combination with the oral genotoxicity data described above, be used to derive a cancer-based quantitative risk assessment for CrVI in soil.*

Since the oral genotoxicity studies and the Davidson study both point towards sufficient CrVI oral bioavailability to create some level of cancer risk, it is relevant to evaluate whether the 400 ppm CrVI proposed standard is at or below the genotoxicity and co-carcinogenic effect levels. A minimum effect level in the genotoxicity studies in mice was 210 ug/kg (Devi, et al., 2001) while the minimum cancer effect level in the Davidson study was 0.5 ppm (approx 15 ug/kg/d of CrVI). Both of these doses were the lowest dose tested so it could be that a wider range of doses would have identified a lower LOAEL or BMDL for genotoxic and carcinogenic effects. Nevertheless, these effect levels can be compared to an oral dose in children from 400 ppm in soil: 400 ug/g 0.2 g soil ingested/d * 1/15kg = 5.3 ug/kg/d. Thus a residential scenario could lead to a daily child's dose of CrVI that is within 3 fold of a cancer effect level (albeit in a test system of uncertain quantitative relevance to human risk) and within 40 fold of a dose capable of inducing genotoxicity from a single exposure in mice.*

The workgroup may want to consider whether an uncertainty factor should be added to the sensitization-based cleanup target to account for uncertainties in the oral cancer database. Specifically, it would address the possibility that oral CrVI can be genotoxic and co-carcinogenic in a dose range that is not all that different from the oral dose associated with 400 ppm in soil. Such an uncertainty factor could be instituted on an interim basis pending the results of the oral CrVI NTP study. In this manner, the cleanup standard could to some degree address a very important uncertainty, one that the NTP bioassay intends to resolve.

Response: We appreciate the reviewer's concern that whatever value is applied to protect against ACD not result in a significant ingestion cancer risk. However, given that the reviewer, having previously made the point that the available data do not permit the use of either the genotoxicity data or the Davidson et al. data in quantitative risk assessment, it is difficult to justify these calculations. Based on the reviewer's assessment of the data (with which we are in agreement), we believe that this analysis is over-reaching in an attempt to establish protectiveness. Given the many uncertainties in both datasets, we do not believe that even this relatively simple calculation is supportable. Furthermore, we note that even given the uncertainties in this calculation, the effect levels taken at face value, do not exceed the exposure at the 400 ppm ACD concentration. In the absence of a dose response relationship, and a determination of hazard identification for human exposure for either dataset, we do not believe that any conclusions, even semi-quantitative are warranted from these data. We also note that the as per the group's recommendations in the draft report, the 400 ppm value if adopted would be used in conjunction with the solution-based ACD cleanup value as well as in conjunction with the other cleanup endpoints. Therefore, the 400 ppm value would function as a ceiling, and would only constitute the cleanup value in limited number of cases, if at all. Nonetheless, we recognize the basis for concern in the reviewer's comment, and agree that such considerations should add to the overall recommendation of prudence in considering the overall Cr^{+6} cleanup policy.

Peer Reviewer: Paul Brandt-Rauf

●*Since skin tumors are not typically associated with chromium exposure, and mixed exposures, such as chromium and UV light in this case, are not typically tested, this study by itself does not provide a sufficient basis for the development of a soil cleanup standard.*

Response: We agree.

Peer Reviewer: Herman Gibb

● *No, it does not. The data is very limited, and as noted above, the translation of the data into a cleanup standard would be problematic*

Response: We agree.

Overall Response: We are in agreement with the consensus expressed by the reviewers that the Davidson et al. (2004) study should not form the basis for a soil cleanup standard. On the basis of these comments we have decided not to present the results of calculations conducted during group discussions and deliberations that might inappropriately suggest a quantitative risk-based cleanup standard based on the Davidson et al. data.

Does the available evidence support the derivation of an allergic contact dermatitis-based soil cleanup standard based on CrVI ingestion?

Peer Reviewer: Gary Ginsberg

●This is a good question. The preferable exposure scenario for evaluating risks and deriving soil cleanup levels across a range of sites would be oral ingestion. A dermal response is expected to be more variable and difficult to extrapolate between controlled patch test exposures and real-world exposures. This is because the amount of time of the patch test is typically exaggerated relative to the amount of time skin will remain exposed to a contaminant adhered to skin. Further, the form of the chemical may be quite different in terms of its complexation and binding to environmental media as opposed to patch test vehicles like petrolatum.

Thus it is worth taking a hard look at the oral sensitization studies available for CrVI. In combination, the 4 studies present a consistent profile of CrVI-induced elicitation of dermal reactions when sensitive subjects ingested solutions of potassium dichromate. Individually, all studies have very limited utility because they either involved only a single dose or a single subject or were reported in unclear fashion. There is a potential for dose response by combining data across studies since a fairly wide range of doses was administered. However, all of the studies found an elicitation effect and the effects were not reported in a quantitative fashion. This makes dose-response modeling impossible. Perhaps the most useful study was that of Kaaber and Veien (1977) because that involved the largest number of subjects, results were scored in double blind fashion, and it was quantitative in that the number of responders under different test conditions was reported. The oral dose was in the middle of the range used in these 4 studies (2.5 mg or approximately 36 ug/kg body wt). The elicitation response was 11/31 in the CrVI alone group and 2/31 in the placebo group suggesting that CrVI @ 0.1 mg/kg was responsible for 9/31 positive responses (29%). Unfortunately, there is no logical manner to extrapolate from these data to a point of departure 5 or 10% response rate. The conclusion one would draw is that it can be expected to be lower than 36 ug/kg.

These data are not sufficient for rigorous standard setting for soil cleanup criteria. However, they point in a direction that should be followed. Enough information is available to derive a crude estimate of oral potency and an oral hypersensitivity comparison value should be derived. The purpose of this would be to see whether its possible for an oral-based target to be lower than a dermal-based target. If so, this may indicate the need for an added uncertainty factor to a dermal-based target, should that type of target be deemed more robust.

*A hypothetical NOAEL can be constructed oral-based elicitation LOAEL of 36 ug/kg by dividing by 10 to yield 3.6 ug/kg. Uncertainty factors for cross-species and cross-individual would be unnecessary because the Kaaber and Veien study was conducted in sensitive humans. However, a 10 fold UF for database uncertainty given the limited number and vintage of studies available and because little is known about other types of toxicity from oral CrVI exposure. This would leave a comparison value of 0.36 ug/kg. This would convert to approximately 250 ppm in soil for an adult ingesting 100 mg/day for 70 kg body weight. (0.36 ug /kg body wt * 70 kg * 1/100E-06 kg soil ingestion *1/1000 conversion factor).*

This best guess ingestion-based soil comparison value (250 ppm) is in the same range as the value based upon the dermal studies. This suggests that an added UF to the dermal-based cleanup value to account for potentially greater sensitivity by the oral route would not be needed. The main caveats to this are the weakness in the oral *database and the fact that one study found an elicitation effect at a very low oral dose (18 ug or 0.26 ug/kg as reported in Fregert, 1965). This points out the need for follow-up testing of this kind. An animal model system (e.g., guinea pigs) may be appropriate for such testing, allowing direct comparison between dermal and oral elicitation threshold.*

It should be noted that this section of the NJ Chrome Workgroup Report draft document is mistaken when it reports NOELs in the range of 0.26 to 50 ug/kg (pg 39). I believe these values should be referred to as LOELs.

Response: The reviewer's rough comparison of the oral and dermal potencies was helpful and, to some extent, reassuring. However, we believe that this analysis has too many uncertainties for it to be formally integrated into the final report.

We agree with the reviewer that draft report was in error, and that the values referred to as being in the range of 0.26-50 ug/kg are, in fact, LOAELs rather than NOAELs. This has been changed in the report text.

Peer Reviewer: Paul Brandt-Rauf

●*Similarly, I think the literature does not support the derivation of an allergic contact dermatitis-based soil cleanup standard based on Cr(VI) ingestion.*

Response: We agree.

Peer Reviewer: Herman Gibb

●*Yes, it does. There is consistent evidence that allergic contact dermatitis can be elicited from skin contact with non-aqueous material and from solid material containing Cr(VI).*

Response: It appears that the reviewer has misread the question, and instead has interpreted the questions as referring to the appropriateness of deriving a *dermal*-based number for Cr(VI) in solid material.

●*Does the Nethercott et al. study provide a sound basis for the development of a soil cleanup standard?*

Peer Reviewer: Gary Ginsberg

● *The Nethercott, et al. 1994 study was appropriately chosen as the best of the available dermal elicitation studies for calculation of a soil CrVI criterion. It was designed for the derivation of elicitation thresholds applicable to soil cleanup criteria, it utilized a large number of sensitized individuals, dosed CrVI in patches in a semi-solid matrix (gel dried on the skin), it avoided some pitfalls that other studies likely experienced (too many challenge doses in a single subject; doses too high which might cause an irritation reaction; inexact dose quantitation), and it tested a wide range of doses on the skin (250 fold spread). A value added feature of this study is that it demonstrated that it is the intensity of the CrVI dose per skin SA and not the total dose on the skin that is the key determinant of elicitation threshold. The patch test results in Nethercott, et al.'s text figure are well suited for dose/response analysis. The calculation of a BMDL-0.10 of 0.08 ug/cm2 by NJDEP appears to be appropriate and consistent with the analysis of the study authors themselves and with the MassDEP treatment of the data. The use of this BMDL-0.10 in deriving a soil cleanup target of 400 ppm is reasonable, with the use of a* *soil loading on the skin of 0.2 mg/cm2 consistent with risk assessment guidelines and methodology.*

My only reservation with regards to this derivation is that there is only minimal consideration of variability and uncertainty and the application of UFs. It may in fact be appropriate to not apply any UFs. However, this needs clear justification. One uncertainty that comes immediately to mind is the large degree of inter-individual variability possible with respect to dermal allergy and thresholds for elicitation. Given that the test groups in all these studies represent sensitive populations, one can make an argument that an inter-individual UF is unnecessary. However, it is likely that the tested subjects fall within discrete sub-categories based upon responsiveness with 5/54 (9%) being sensitive at a dermal loading (0.088 ug/cm2) that is being considered equivalent to a NOAEL (Nethercott, et al., Table 4). It is equally likely that no NOAEL was established in this study (lowest loading had a response rate of 2%) and that in any population of sensitives, some finite percentage will respond to CrVI, even at very low levels. Thus, one could argue that the BMDL-0.1 of 0.08 ug/cm2 is a LOAEL for a certain segment of the sensitive population and that for them a lower criterion is needed. Perhaps this could be derived by using the BMD model to calculate the NOAEL as the BMDL-0.01. An argument against this would the what Proctor, et al.., (Regul Toxicol Pharmacol. 28:27-37, 1998) pointed out. They claimed that there is such a small percentage of the general population that is hypersensitive to CrVI, that protecting 90% of the sensitive population is a very conservative (in their mind over-conservative) approach. On the other side of the argument are analyses of consumer products which suggest that there is a sensitization risk from high ppm concentrations of Ni, Co or Cr in these products with the safety limit set at 1-10 ppm CrVI (Basketter, et al., Contact Dermatitis 49: 1-7, 2003).

The proposed cleanup criterion (400 ppm) needs to more explicitly take into account variability and uncertainty including considerations of general population risk vs. sensitive population risk vs. risk to high end responders within the sensitive population. This is needed to make the approach more defensible and transparent in terms of which members of the population it is protecting.

I noted an error in the soil target calculation on pg 46: the units in the middle part of the equation should be ug CrVI per gram soil not mg soil.

The manner in which the proposed cleanup standard will be used vis-à-vis the solution –based standard is unclear. Under what circumstances will one be used instead of the other? Since the solution-based standard is ultimately based upon a dose per skin surface area (e.g. as reported in Hansen, et al., 2003), the NJ Chrome Work Group should more systematically compare whether the solid matrix and solution tests are truly compatible and give a similar target criterion. For example, the Hansen study would suggest a solution results in a lower elicitation threshold than does a solid matrix. Is this reflected by a difference in the cleanup criteria calculations for the 2 methods?

It would seem confusing and unnecessary to retain two different approaches to calculating a health-based soil cleanup standard, especially since both are intended to protect against the same effect (dermal sensitivity). If there is good rationale for keeping both approaches, it needs to be clearly stated. The current document does not do this.

Response: - We agree that the question of the application of uncertainty factors needs to be addressed explicitly. We have added paragraph discussing UFs immediately preceding the discussion of soil loading factors.

The reviewer's suggestion of calculating the BMDL-0.01 (BMDL-1%) rather than the BMDL-0.10 is not without merit. However, we decided not to follow that approach for two reasons. The first is that the lowest dose administered in the Nethercott et al. study corresponds to a response of 0.02 (2%). Thus, the a BMDL calculated on the basis of a 1% would be outside the range of the observed data. In general, the BMD approach seeks to identify minimal responses within the range of the observed data. Although the 1% response would be only moderately beyond the range of the data, we believe that the 10% response is more likely to reflect an accurate estimate of the true dose-response. Nonetheless, it should be pointed out that this is mitigated somewhat by the use of the BMDL, which is the *lower bound* on the 10% response. The corresponding BMD is 0.1 compared to the BMDL of 0.08. The second reason is that, consistent with the derivation of the existing ACD cleanup value calculated on the basis of solution concentration, the group believes that relatively mild adverse response at these levels of exposure does not justify the derivation of a more stringent criterion.

The reviewer is correct regarding the units on pg. 46. These have been corrected.

With respect to the comparison of the solution-based and soil concentration-based ACD standards, the reviewer was probably unaware of the extraction procedure that is used in conjunction with the solution-based approach. This procedure relates the soil concentration of CrVI to the corresponding solution concentration under defined conditions of extraction and fluid volume. The use of this procedure places the solution-based and soil concentration-based approaches on the same footing. We have also explicitly stated in the recommendations to sub-group report that both approaches should be used in parallel with the approach yielding the lower soil cleanup value being the most appropriate. However, we have now made this clear in the text, itself, in the last section of the ACD charge, "Consistency with the existing Cr $^{+6}$ACD standard."

The group has recommended that both the solution-based approach and the soil-concentration-based approach be retained and used in parallel because each addresses a different exposure scenario. This is stated in the section on Consistency with the existing Cr $^{+6}$ACD standard. However, we have now added language to make this point more explicitly.

Peer Reviewer: Paul Brandt-Rauf

● *On the other hand, the Nethercott et al. study was viewed as highly relevant and well-done so that it can provide a sound basis for the development of a soil cleanup standard.*

Response: We agree.

Peer Reviewer: Herman Gibb

●*The reason given for using the Nethercott et al. study is its "much larger sample size" of the three studies considered suitable for developing a dose response (N = 54 in*

Nethercott et al.; N = 18 in Hansen et al.; and N = 6 in Wass and Wahlberg). Estimates of the surface loading that would result in a 10% allergic response for both Hansen et al. and Wass & Wahlberg were only one third of that for the Nethercott et al. study, however. Given that the Work Group has recommended to NJDEP consideration of the Hansen et al. study to set a cleanup standard for Cr(III), it appears inconsistent to not factor the dose response from Hansen et al. and Wass and Wahlberg studies into the cleanup standard.

> **Response**: While this suggestion has merit, the primary consideration for combining dose-response data in a meta-analysis is that the data are mutually comparable. In the case of the three studies originally considered by the group, the studies each had significantly different study designs. The Nethercott et al. study used application of Cr^{+6} in a solid material. Hansen et al. used application of Cr^{+6} in solution, and Wass and Wahlberg used an indirect approach to estimate the mass of solid material deposited on a metal disc. While the mean and 10% response concentrations obtained from each study were roughly comparable, there is no *a priori* reason to expect that the differences in study design will result in similar dose response functions yielding a robust BMDL. There would be no simple way to determine if differences between the BMDL derived from the Nethercott study alone and the hypothetical BMDL derived from the meta-analysis of the three studies combined resulted from study incompatibilities or from a more robust assessment of compatible data. In addition, it should be noted that there is a question about the extent to which the Hansen et al. data reflects a more sensitive assessment of response. For these reasons we believe that it is most appropriate to base the BMDL on the Nethercott study alone.

●*Does the Hansen et al. study potentially provide a sound basis for the future development of a Cr(III) based allergic contact dermatitis standard?*

Peer Reviewer: Gary Ginsberg

● *No. The data are limited and of questionable use for risk assessment for a number of reasons:*

- ❖ *They are for CrIII in solution rather than as applied to skin in a solid matrix. Thus, one would have to apply solubility from soil matrix assumptions/tests to calculate a cleanup criterion from these data.*
- ❖ *The data suggest a relatively high degree of CrIII elicitation in Cr-sensitive subjects. The calculated MET 10% for CrIII was only 6 fold lower than the MET10% for CrVI. This runs counter to the biological properties of CrIII: it is believed to be much less able to pass membranes than CrVI. CrIII has generally been free of dermal sensitization/elicitation findings in the occupational literature. The Hansen results differ dramatically from the results obtained by Nethercott, et al., 1994. Hansen et al. demonstrated a MET10% for CrIII of 0.18 ug/cm2 in sensitive humans while Nethercott et al. report a lack of reaction to as much as a 33 ug/cm2 challenge in 54 sensitive subjects. This may have something to do with the fact that the Nethercott study applied the challenge substance in a semi-solid matrix (dried gel) while the Hansen results were for a solution. However, the large difference in results is striking given that CrVI can elicit*

reactions as a crystal and in solid matrix, and was clearly quite effective in the Nethercott dried gel matrix. The difference may thus lie in the very limited solubility of CrIII in human sweat so that it would not mobilize from a solid matrix. It may well be that solution testing of CrIII as performed by Hansen is unrealistic for under most environmental conditions.

- *Another issue with the Hansen study are that they describe some conversion of the CrIII solution to CrVI during the course of their use of the solution. Even though this was a low percent conversion, it may account for some of the positive response seen with CrIII.*
- *Finally, the Hansen study involved many CrIII and CrVI patch exposures in the same 18 subjects with some of the concentrations very high. This leads to the possibility of direct irritation reactions for CrIII and CrVI which may be mistaken as elicitation. The other issue with this protocol is the possible overtesting of a single individual leading to what Nethercott et al refer to as "excited skin syndrome". Given the high number of CrVI patches and the high concentration in some of these patches, it may be possible that these subjects were immunologically primed for reacting to CrIII in a manner that is unrealistic.*

Response: Other than the exposure to solid material versus solution, the major difference between the CrIII exposures in the Nethercott and Hansen studies is that Nethercott et al. used chromium trichloride, while Hansen et al. used chromium trichloride-hexahydrate. While ATSDR describes the solubility of chromium trichloride as "slightly soluble in hot water" the solubility of chromium trichloride-hexahydrate is given as 58.5 g/100 cc at 25 ^oC. Thus the CrIII used by Hansen et al. was inherently much more soluble than the CrIII used by Nethercott. Although Nethercott formed the solid gel used in the patches from CrIII in solution, the differences in inherent solubility could well have affected the availability of the material in the gel. The issue of irritant reactions or excited skin reactions in patch testing is well known in the dermatological literature. The authors specifically state that they excluded irritant reactions from their assessment of responses. While this may lead to some uncertainty, given prevalence of this concern, one is inclined to rely on the experience of the investigators in this regard. With regard to conversion of CrIII to CrVI in solution, the authors report a maximum of 0.6 ppm in the CrIII solution. As the lowest concentration of CrIII that was observed to give a response was 50 ppm, it is difficult to attribute any significant contribution to unintentional exposure to CrVI.

Peer Reviewer: Paul Brandt-Rauf

● *Nor does the Hansen et al. study provide a sound basis for the development of a Cr(III)-based allergic contact dermatitis standard.*

Response: We agree, and have modified the text to reflect this view.

Peer Reviewer: Herman Gibb

●*Hansen et al. appears to be a well done study; however, the results are inconsistent with those of Nethercott et al. with respect to Cr(III). This inconsistency would obviously* *need to be addressed by NJDEP before using Hansen et al. to set a cleanup standard, particularly considering potential differences between the TRUE-Test patches and the Finn chamber as indicated by Nethercott et al. (bottom of page 372 of Nethercott et al.).*

> **Response:** Although, as discussed in the response to Dr. Ginsberg, we think that the difference in the solubility of the Cr(III) salts used in the two studies is more likely to be the cause of the discrepency between the study results, we agree that Hansen study does not provide an adequate basis for the derivation of a Cr(III)-based ACD standard. We have modified the text to make this clear.

Overall Response regarding the use of Hansen et al. for development of a Cr(III) standard

There is no general level of support among the reviewers for the use of the Hansen et al. study as a basis for a future cleanup standard for Cr(III). While at least some of the specific concerns and objections raised by the reviewers appear to have reasonable explanations, it is clear that overall, the Hansen et al. study will not, by itself, provide a robust basis for deriving a Cr(III) risk based cleanup standard, particularly if the apparently contradictory Nethercott et al. study is used as the basis for a revised approach to a Cr(VI) cleanup standard. We have, therefore, eliminated recommendations and suggestions in the report to the use of the Hansen et al. study for the derivation of a Cr(III) standard.

Response to Peer Review Comments
Chapter 4: Analytical Chemistry

Peer Reviewer: Paul Brandt Rauf
No pertinent comments on Chapter 4.

Peer Reviewer: Jon Chorover
No pertinent comments on Chapter 4.

Peer Reviewer: Herman Gibb
No pertinent comments on Chapter 4.

Peer Reviewer: Gary Ginsberg
No pertinent comments on Chapter 4.

Peer Reviewer: Gregory Turk

● *The accurate measurement of Cr VI in environmental samples is one of the most difficult challenges in Analytical Chemistry. The subgroup has clearly demonstrated their understanding of the complexities of the measurement, and I find their recommendations to be logical, reasonable, and based on the present best scientific understanding of the measurement issues.*

> **Response:** No response

● *On pg 56, in the 3rd paragraph, the report states "… failure of the method to accurately quantify Cr(VI) in certain sample matrices." I think it would be helpful to list what these "certain sample matrices" are.*

> **Response:** The sentence is changed to read – "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 sample matrices that contain reducing conditions.

● *On pg 57, in the first complete paragraph, there is a discussion regarding subtle differences between NJDEP modified 3060 and EPA 3060A. What are the implications of these differences?*

> **Response:** The implications are addressed in Paragraph 2, Page 57.

● *Would the NJDEP modified method be more likely to report higher or lower Cr(VI) concentrations than 3060A?*

> **Response:** A sentence is added at Paragraph 2 – Page 57 to read "It is unknown what affect the differences between methods 3060 and 3060A may have on the measured amounts of Cr(VI).

● *Is Method 6800 really included in SW846? The EPA website at* http://www.epa.gov/epaoswer/hazwaste/test/6_series.htm *lists 2 methods in the 6000 series of SW846 methods, but not Method 6800.*

Response: Method 6800 is listed as a new method in Update IV, SW846. It can be found at http://www.epa.gov/epaoswer/hazwaste/test/pdfs/6800.pdf.

● *Regarding Method 6800, I agree with the subgroup's opinion that the method should generate reliable data under difficult matrix conditions, but even this rather sophisticated method is not infallible. Any method relying on isotopic spikes requires that the spike be "equilibrated" with the indigenous analyte in the sample. In situations where the indigenous Cr is solid, but the isotopic spike is dissolved in a solution, the spike cannot "equilibrate" until the solid material is dissolved. Thus the method cannot address any species conversions that might take place as the solid material is brought into solution. In the panel's recommendations for needed research, which I support, I suggest the addition of a study in which known amounts of solid water insoluble forms of Cr (perhaps minerals, ores, oxides, pure COPR) are added to various soil types, and the recovery of the known addition is calculated using Method 6800. Such a study would test the weakest aspect of the method.*

Response: The Subgroup agrees and the issue will be dealt with in the research proposal on methods evaluation..

● *On pg 63, I agree with the subgroup's recommendation that total Cr measurements be made in addition to Cr(VI) measurements. I only wish to make the obvious point that total Cr(VI) concentration can never be greater than total Cr, and thus total Cr measurements might be used as proof that Cr(VI) concentration are below required levels. In general I would think that total Cr measurements, being simpler to make, would be more reliable than a Cr(VI) measurement.*

Response:: No response, the Subgroup agrees with the comment.

● *Regarding the need for a reference material-- since I work for NIST my opinions might be considered somewhat biased on this topic, but there is clearly a great need here. As the report notes, NIST has budgeted some funds to collect and prepare a Cr(VI) in soil NIST Standard Reference Material (SRM). The report refers to a proposal that has been "agreed to by the USEPA, NIST, and EOHSI". This is a bit of an exaggeration. I am not aware of any formal agreement at this stage. NJDEP has been advising us on site selection of a COPR contaminated soil to be collected for production of the SRM, and has offered to help us with logistics.*

Response: The project to develop reference materials has been accepted by the NJDEP, USEPA, NIST and EOSHI, and is scheduled to begin June 2005. Revisions to the document to address this comment and this project have been made on page 63.

● *I strongly support the subgroup's recommendation and thoughts regarding research on a method to determine Cr(III) and Cr (VI) directly in soils without the need for sample digestion. Such a method would most likely be based on some form of X-Ray spectroscopy. I would point out that such a method would be of great benefit even if it never developed into a practical field testing method. The ability to use such a method to validate more practical extraction-based methods would very much improve our present* *understanding of this complex measurement. I believe that the X-Ray Photoelectron Spectroscopy is applicable only to the analysis of surfaces, so this could be a weak point.*

> **Response:** The Subgroup agrees with the comments. Additionally, the references to X-Ray Photoelectron Spectroscopy in the research proposal will be deleted from the document.

- *I also agree with the research recommendations regarding a systematic comparison of the various methods under different soil conditions. It would be of great benefit to identify correlations between measurable soil parameters (i.e. pH) and the performance of the various methods. If and when such correlations can be identified, the analytical method selection flowchart (Figure 4.1) should be updated so that measured soil properties can be used to guide decisions regarding the choice of method.*

> **Response:** The Subgroup agrees with the comment.

Peer Reviewer: C.P. Huang

- *Classification of COPR and COPR-soil materials. The Workshop has adequately addressed all charges within sound scientific context. The recommendations are appropriate, reasonable and sound. Regarding recommendations for research needs, it is agreed that non-wet chemistry methods are needed to better characterize COPR and COPR-soil mixture in terms of their Cr(VI) and Cr(III) distribution and transformation. But XPS can not provide quantitative information on the distribution of Cr(III) and Cr(VI), EDAX (X-ray dispersive spectrophotometry) technique does. Additionally, as far as the qualitative analysis of the surface Cr chemistry is concerned, other surface analysis techniques such as XRD (X-ray diffraction), NEXAF (Near edge X-ray absorption Fine Structure) and AFM (atomic force microscopy) can also be extremely useful. XPS will reveal the oxidation state of Cr but not its concentration.*

> **Response:** The Subgroup agrees with the comments. Additionally, the references to X-Ray Photoelectron Spectroscopy in the research proposal will be deleted from the document.

- *Soil sampling protocol. While laboratory analysis is important to remediation investigation, other important issue is the soil sampling protocols. EPA Soil Screening Levels for Superfund Sites is a good source of general information. But a specific soil sampling protocol is also useful. Soil sampling schedule should also consider economic constraints, i.e., is it affordable?*

> **Response:** The comment is outside the scope of responsibility for the Subgroup.

- *Eh and pH diagram. The reduction potential should be expressed as "E_h" not "eH" (Please make corrections on pages 61 and 64).*

> **Response:** The Subgroup agrees and revisions to the text will be made.

- *Figure 4.6 gives E_H versus pH plot of the reaction $HcrO_4^- + 4H^+ + 3e = Cr(OH)_3(s) + H_2O$. (Note the symbol E_h should be E_H). A more comprehensive Eh-PH diagram as shown in the left may be appropriate.*

Response: Although the suggested diagram is more detailed than the one currently in the document, the current diagram provides adequate information.

Peer Reviewer: Ken Stollenwerk

● *I agree with the subgroups recommendation to use USEPA Method 3060A for preparation of non-aqueous samples for analysis of Cr(VI). This would provide consistency among sites. However, there should be some room for flexibility given the potential for Cr redox state transformations in some sample matrixes. For example, if there is evidence for oxidation or reduction of Cr in a particular type of sample matrix and if a modification to Method 3060A can prevent the oxidation state conversion, then a modified method should be considered.*

Response: The Department has chosen to use USEPA Method 3060A, and expects to continue using this method until the USEPA develops a replacement method or until another method is shown to be more appropriate.

● *Development of standard reference samples for COPR would be useful. Until such standards can be developed for routine use, spike recovery data will be an important measure of analytical accuracy. Both Cr(III) and Cr(VI) should be considered to evaluate Cr(III) oxidation as well as Cr(VI) reduction during sample preparation.*

Response: The Subgroup agrees the comment.

● *Ch. 4, p. 61: The meaning of this sentence is unclear. It seems to imply that Fe(III) should oxidize Cr(VI) but is oxidizing DPC instead. How can Fe(III) oxidize Cr(VI) which is already oxidized?*

Response: The following sentence "Fe(III) has been shown to oxidize DPC (diphenlycarbizide), thus not allowing the DPC to react with the actual Cr(VI) present in the sample" will replace the sentence on page 61 that reads " Fe(III) has been shown to oxidize DPC(diphenlycarbizide) and not the actual Cr(VI) present."

● *Ch. 4, p. 67: Direct measurement of Cr in solids by techniques such as XPS would not necessarily determine worst case scenarios. If high concentrations of Cr occurred in discrete mineral phases that comprised a small percentage of the total sample, XPS types of analyses might miss these Cr-rich particles. Another example would be extensive coatings of Cr(VI) on iron oxide minerals that are below detection but soluble, potentially resulting in ground water contamination.*

Response: The Subgroup agrees with the comments. Additionally, the references to X-Ray Photoelectron Spectroscopy in the research proposal will be deleted from the document.

Peer Reviewer: Chunming Su

● *Chapter 4, page 54, line 30. Delete the extra word "that".*

Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 54, line 36. Insert the acronym "(SRWMP)" after the word "Program".*

  Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 55, line 6 from bottom. Change "eH" to "Eh".*

  Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 61, line 12 from bottom. Change "eH" to "Eh".*

  Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 61, line 3 from bottom. Should read "shown to oxidize".*

  Response: The sentence was previously changed in response to a separate comment.

- *Chapter 4, page 62, line 7 from bottom. Misspelled word for "species".*

  Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 62, line 1 from bottom. Should read "used to assess".*

  Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 63, line 6. Should read "has already had".*

  Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 64, line 3 from bottom. Change "copra" to "COPR".*

  Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 64, last paragraph. Another X-ray method, X-ray absorption spectroscopy, may also be useful for detecting Cr(III) and Cr(VI) in COPR waste. It has been used successfully in many cases to study chromium speciation in geological materials.*

  Response: The Subgroup agrees with this comment, but no change in the text of the document is necessary.

- *Chapter 4, page 65, line 8. Change "COPRA" to "COPR".*

  Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 65, line 15. Change "specie" to "species".*

Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 65, line 25. Should read "distributed for".*

  Response: The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 67, line 4 and line 14. Change "copra" and "COPRA" to "COPR", respectively.*

  Response: The Subgroup agrees with the comment. The revision will be included. (Could not find language noted for line 4)

- *Chapter 4, page 68, References.*
Kingston, H.M., Huo, Lu ... should be read "Kingston, H.M., Huo, D., Lu…".
USEPA, (1996a) and (1996b), titles are mixed up.

  Response: The Subgroup agrees with the comment. The revisions will be included.

- *James et al., 1997. This paper is not cited in the text.*

  Response: The reference in the text of the document was inadvertently omitted. It has been inserted in the middle of page 61.

- *Griffing et al., 1997. Check the paper title, it does not seem right.*
Grove and Stollenwerk, 1985. Journal title and page numbers missing.
Korte et al., 1976. Paper title missing.
Ramos et al., 1994. Two journal names?
Schroeder et al., 1975. Check the names of authors.
Tzou et al., 2002. Change "want" to "Wang".

  Response: This group of references do not apply to Chapter 4.

Response to Peer Review Comments
Chapter 5: Air and Dust Transport

Peer Reviewer: Paul Brant-Rauf

- *The major issue under the air transport section seemed to be issue of whether or not the recommendation to include wind-blown dust in the model was justifiable, and I agree that it was.*

No response.

Peer Reviewer: Gregory Turk

No pertinent comments on Chapter 5.

Peer Reviewer: Jon Chorover

No pertinent comments on Chapter 5.

Peer Reviewer: Gary Ginsberg

No pertinent comments on Chapter 5.

Peer Reviewer: Herman Gibb

No pertinent comments on Chapter 5.

Peer Reviewer: C.P. Huang

- *The Workshop has adequately addressed the Commissioner's charges.*

No response.

Peer Reviewer: Ken Stollenwerk

- *Hexavalent chromium is listed as Cr(IV) instead of Cr(VI) throughout this chapter and the two attachments.*

Response: This has been corrected in the final report.

Peer Reviewer: Chunming Su

- *This is a well-written report that outlines the review of New Jersey Chromium Workgroup on the application of the current chromium standards and proposed revision of the current standards. All four subgroups (Risk Assessment, Analytical Chemistry, Air and Dust Transport, and Chromium Environmental Chemistry) have done an excellent job in summarizing our current knowledge on chromium ore processing residue issues. Their suggestions appear to be scientifically sound. Technically, the report is in good shape. There are some editorial points that can be looked at in order to further improve the report.*

Response: Two of the editorial comments have been incorporated into the final report. The other two are simply a matter of style preference and were not incorporated.

Response to Peer Review Comments
Chapter 6: Environmental Chemistry

Peer Reviewer: Paul Brant-Rauf

No pertinent comments on Chapter 6.

Peer Reviewer: Gregory Turk

No pertinent comments on Chapter 6.

Peer Reviewer: Gary Ginsberg

No pertinent comments on Chapter 6.

Peer Reviewer: Gregory Turk

No pertinent comments on Chapter 6.

Peer Reviewer: Herman Gibb

No comments presented for Chapter 6.

Peer Reviewer: Chunming Su

- *This is a well-written report that outlines the review of New Jersey Chromium Workgroup on the application of the current chromium standards and proposed revision of the current standards. All four subgroups (Risk Assessment, Analytical Chemistry, Air and Dust Transport, and Chromium Environmental Chemistry) have done an excellent job in summarizing our current knowledge on chromium ore processing residue issues. Their suggestions appear to be scientifically sound. Technically, the report is in good shape. There are some editorial points that can be looked at in order to further improve the report.*

No response.

Peer Reviewer: Ken Stollenwerk

- *I found the report to be very thorough. Therefore, I did not have a lot of comments. Overall, I agree with the conclusions and recommendations presented in this report. I realize that some of the recommendations may go beyond the original charges made to the working group, particularly in the Chromium Environmental Chemistry Subgroup. However, I believe that the additional proposed research is necessary to address the questions relating to chromium behavior in these complex environments.*

No response.

- *Determination of the fate and transport of chromium at COPR sites is particularly difficult because of the potential for changes in the oxidation/reduction state of chromium, and the dependency of Cr(VI) transport on physical and geochemical factors that can vary widely from site to site and within any given site. Therefore, defining generic cleanup standards for COPR is difficult.*

Response: We agree with reviewer's comment. The issue of oxidation/reduction and interconversion in the environment is significant and complex. Furthermore, the Department is no longer proposing a generic impact-to-groundwater cleanup standard for either COPR waste material or chromium-contaminated soil.

● *An important consideration is the rate of oxidation of Cr(III) to Cr(VI) in COPR contaminated soils. The Cr(VI) formed could then leach deeper into the subsurface, eventually reaching groundwater. The potential for Cr(III) oxidation should be better quantified in order to help determine COPR cleanup standards.*

Response: We agree with the reviewer's comment. This comment is consistent with the information that is presented in the report; that is, the potential for Cr(III) oxidation needs quantification in order to better address this issue in future clean-up standards. As information on this phenomenon becomes available, the clean-up standards will be revised, accordingly. However, given the relatively slow rate of chromium interconversion, the topic is difficult to study under laboratory conditions.

● *If not already in place, a procedure for evaluating COPR sites with respect to transport of Cr(VI) in the subsurface should be developed. Important considerations are site hydrology and geochemistry.*

Response: Understanding specific site hydrology and geochemistry is very complicated to evaluate in a predictive manner. We agree with the reviewer's suggestion and seek to address this issue through research. As information on this phenomenon becomes available, the clean-up standards will be revised, accordingly. We agree that our groundwater staff should continue to evaluate the transport of chromium in groundwater at these sites and provide more detailed documentation in the reports issued for COPR sites. Regarding the potential for chromium transport in the soil vadose zone or in COPR waste material, the SPLP test discussed in the document is the most practical tool for this assessment. Regarding the suggestion for more advanced geochemical assessment procedure, our current understanding of chromium geochemistry at these COPR sites is inadequate to develop such a procedure. Such an assessment would likely require detailed site-specific research.

● *Specific comments:*
Ch. 6, p. 95: A distinction between COPR waste material and COPR-waste contaminated soils would be justifiable from a geochemical viewpoint. High concentrations of COPR waste in a soil would result in elevated pH values and a difference in the behavior of Cr. For example, Cr(VI) would be less likely to adsorb. In mixtures where COPR concentrations are relatively low, the buffering capacity of the soil would maintain pH values near that of the soil and the adsorption behavior of Cr(VI) would be different. As mentioned, there are other parameters that could be used to make the distinction. However, I would expect many of the COPR-soil mixtures to fall somewhere in between, making clear-cut distinctions difficult. Perhaps a third category such as moderately contaminated soils would be appropriate.

Response: We will address reviewer's comment by adding clarifying language in the sections where the discussion focuses on distinguishing between COPR waste material and COPR-soil mixtures. Although identifying a third category seems theoretically useful, the parameters for distinguishing among three (versus two) categories is not feasible at this time. Rather, we seek to distinguish between the waste material and waste/soil mixtures as two broad categories. As we proceed, we can determine whether it is feasible to add a third or more categories.

- *Ch. 6, p. 101: The K_d given here is for hexavalent Cr. Suggest labeling chromium as hexavalent Cr here and throughout the subsequent discussion that relates to adsorption.*

  Response This section has been removed, because we are no longer proposing generic cleanup standards for chromium contamination. All numerical values for chromium K_d values have been removed from this discussion.

- *Ch. 6, p. 110: Should this be Cr(III) instead of Cr(VI)?*

  Response: Yes. This was a typographical error.

<u>Peer Reviewer: John Chorover</u>

1. The Nature of COPR.

General Comments:

- *In the context of the charge to describe the "nature of COPR", it would seem that the size of COPR particles, or more precisely, the specific surface area of the COPR particles, would be an important determinant in respect to the rate of Cr release at a given site. This is because the specific surface area determines the amount of reactive interface between solid and solution phases for a given mass of material. Thus, all other factors (mineralogy, pH, etc.) being equal, that COPR with higher specific surface area will be subjected to higher mass normalized rates of dissolution. In addition, the precise Cr-bearing mineralogy of the COPR would certainly be important to the rate of Cr(VI) release.*

  Response: We agree with the commenter's point that particle size, or surface area, is an important factor in defining COPR's behavior in the environment. Knowing the mineralogy of the COPR is vital to understanding the mechanisms of dissolution, and the work group has identified the need to conduct mineralogical assessments on COPR samples collected from NJ sites.

- *Specific Comments:*

P. 93 bottom through P. 94 top. I concur with the findings of the subgroup pertaining to the key processes that determine the fate and transport of Cr at COPR sites (dissolution of Cr-containing COPR materials, oxidation of Cr(III) to Cr(VI), reduction of Cr(VI) to Cr(III), adsorption-desorption of Cr species, and transport of Cr to groundwater). However, one process that should be added is the precipitation Cr containing solids, which is distinct from adsorption or accumulation at particle surfaces (e.g., reduction of Cr (VI) can result in solid phase incorporation of Cr(III), and the formation of Cr(VI) "blooms" apparently reflects precipitation of Cr salts). It is also true that modeling fate and transport of Cr in these systems is made difficult by an incomplete understanding of the relative kinetics of the processes in complex matrices.

Response: We agree with the comment that precipitation is an important fate and transport phenomenon. The language in the chapter has been changed to better emphasize that "concentration effect" includes precipitation.

- *P. 94, line 20: The statement that chromite ore contained "45 to 50 percent trivalent chromium" is unclear. Does this mean that roughly half the mass of the ore was Cr(III) or that half of the ore Cr was in the trivalent oxidation state?*

  Response: The statement has been clarified to state that chromite ore generally contains 45 to 50% Cr(III) by mass. 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).

- *P. 95, line 21: It is important to be clear on distinguishing issues such as "solubility" from the "rate" of dissolution. At this point in the report, it is stated that pH exerts significant control over solubility of Cr(VI) from COPR, which implies that pH exerts a control over the concentration of Cr(VI) in equilibrium with the solid phase. My impression is that none of the Cr(VI)-bearing mineral phases are thermodynamically stable under the environmental conditions where they reside, since the dissolved Cr(VI) is consistently lost from the open system with continuing throughput of fresh water. Rather, it seems more likely that the effects of pH are to alter the rate at which the Cr(VI)-bearing minerals undergo dissolution.*

  Response: We agree that a distinction should be made between "solubility" and "rate of dissolution." The sentence at line 21 discusses only results from equilibrium modeling, which did not take kinetics into account. We have clarified the discussion, particularly with respect to modeling and experimental results.

- *P. 95: In respect to the distinction between COPR and COPR-soil mixtures, it would seem that, in addition to the factors listed, mineralogy could provide an important distinction between these two materials. Those minerals present in the COPR are not typically found in nature, so their dilution relative to native soil minerals could be used as a proxy for distinguishing COPR from its soil mixture.*

  Response: We agree that mineralogy can be useful for this purpose and have added this as a possibility as appropriate in the chapter.

2. Transport to Groundwater.

- *General Comments:*

The studies by Geelhoed et al. (2002), Weng et al. (1994) and James (1994) show a fraction of the Cr that is "readily leached" from the COPR. However, none of the studies appear to address the long term effects of sequential leaching, weathering, drying, and re-leaching, as would be observed in the field. Dissolution may drive conversion of solid phase Cr to either more or less "labile" forms. The problem with the existing data is that the long-term transformation processes that control dissolution into groundwater over time scales of years, are not well represented by short term one-leach types of experiments. The solid phase speciation of Cr is key to the kinetics of Cr release (and this probably explains the poor correlations between total and eachable Cr reported by

NJDEP, 2004a), as is the change in solid phase speciation with time of COPR weathering in the field.

> **Response:** We agree. Laboratory studies are unable to reproduce processes that occur over long periods of time. Field studies to monitor these processes are difficult to conduct and require long-term funding commitments.

Specific Comments:

- *P 96. line 8: What was the duration of the batch leaching tests? The length of time for solid solution equilibration is an important factor influencing the mass fraction of Cr released.*

> **Response:** The tests were run for either 4 or 26 days. This has been added to the document.

- *P. 96, line 28: With regard to the statement that "these values are likely to be lower than field conditions because of the large volume of extractant employed", it is worth remembering that it is not easy to compare batch extractions with field data because of the much greater mixing afforded in the former case. Comparative studies have shown that weathering kinetics are generally accelerated in batch lab systems relative to field-scale measurements because of the greater contact between solution and reactive interface of the solids. This is despite the fact that the concentration in solution may indeed be lower for batch systems because of the dilution effect.*

> **Response:** We generally agree with the comment that the vigorous extraction conditions may partly cancel the effect of a large volume of extractant. However' we cannot speculate on this quantitatively and therefore have chosen not to modify the text here. Also, we feel the term "weathering kinetics" is best used for long term processes. We feel "dissolution kinetics" is a better term for batch experiments.

- *P 97, line 13: In addition to those characteristics listed, I would add that the solid phase speciation (i.e. the form or mineralogy) of the Cr is important.*

> **Response:** We agree. Language to reflect this has been added.

- *P 98, line 1-22: It would seem that this discussion assumes that reducing agents are exhausted following transfer of electrons to the Cr(VI). Whereas this may be true in some cases, it is often observed that these reducing agents can be re-established by their own subsequent reduction (by other reducing agents). For example, Fe(III) reduction to Fe(II) is catalyzed by iron reducing microorganisms that utilize Fe(III) as a terminal electron acceptor in respiration when labile organic matter is present, but molecular oxygen is unavailable. If Fe(II) is a principal reducing agent for Cr(VI), it is likely that each mole of Fe(II) will undergo several oxidizing and reducing cycles such that it may be "renewed" as a reducing agent, so long as molecular oxygen is limiting and sufficient organic matter is available for microbial respiration. Thus, in suboxic systems, each mole of Fe(II) would be available to reduce as many moles of Cr(VI) as can be accomplished by subsequent oxidation-reduction cycles of the Fe. In other words, the reducing power of the Fe(II) can be regenerated.*

Response: The discussion in the chapter refers to the ultimate source of the reducing agent, namely the organic carbon (the meadow mat). The meadow mat is specified in the discussion. A short discussion of redox cycling has been added to the paragraph.

- *P. 98, line 29-on: The transport of even nitrate and chloride can be retarded relative to water transport if the porous medium exhibits a net positive charge due to enrichment of Fe and Al oxides or hydroxides. If chromate exhibits a higher affinity for positively charged surfaces than nitrate or chloride, its retardation will be enhanced.*

  Response: While not necessarily as mobile as water itself, nitrate and chloride are known to be generally mobile in soils. Soils are generally negatively charged except at low pH. The language in this sentence has been revised to clarify that nitrate and chloride are generally transported readily through the soil. We do state that chromate is more readily retained by soil than nitrate and chloride.

- *P. 100-102: The use of soil-water partition coefficients (Kd values) to predict transport is problematic in cases where isotherm behavior is non-linear (e.g., Langmuir behavior), since in that case, the actual Kd will depend on the solution phase concentration. For example, if the isotherm follows the Langmuir shape, the Kd decreases with increasing aqueous phase concentration. Thus, in addition to exhibiting pH dependence (as indicated on p. 102) the Kd for Cr is dependent on aqueous phase Cr concentration. To complicate matters further, the pH and concentration dependence of the Kd will be strongly influenced by soil mineralogy. Soils containing high specific surface area of Fe and Al oxides tend to exhibit greater positive charge at a given pH, than those that have low interfacial areas of Fe and Al oxide. Thus, increasing amounts of Fe and Al solids are likely to enhance the Kd values, all else being equal.*

  Response: We acknowledge these comments. However these complicating factors are not characterized well enough in the scientific literature to incorporate them into models for routine use. This is why USEPA has suggested the simple partitioning model for its soil screening guidance, which only requires the Kd (with pH adjustment as necessary). The discussion on pages 100-102 is simply presenting the USEPA approach.

- *Saturation of adsorption sites is certainly a potential issue, and could lead to breakthrough as suggested here. It is worth remembering, however, that site saturation is not required for breakthrough to occur. Rather, sorption-desorption equilibria simply serve to slow or "retard" migration of the contaminant plume relative to the solvent water.*

  Response: We agree. Language to clarify has been added.

- *P 103, line 16: I think it would be better to state that "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."*

  Response: We agree. This change has been made.

- *P. 103: In the discussion of equilibrium solubility relationships, it must be kept in mind that this is a multi-component equilibrium. Thus if several solids are present, the concentration of Cr(VI) in solution at a metastable equilibrium will be that governed by the most soluble solid. The concentration can be reduced thereafter as Cr(VI) progressively precipitates into less soluble solids and the more soluble solids are transformed to these less soluble solids in the process known as "Ostwald ripening".*

  Response: We agree with the commenter. As with the simple partitioning equation, there are complicating factors that we feel are beyond the scope of this document, particularly since practical models are not available to account for these factors.

- *P. 104: It is stated that MINTEQA2 and related chemical speciation models may be "too advanced" for routine use. However, I would argue that this is not necessarily the case, and it would help to address the problem of multicomponent equilibria outlined just above, given that the person using the model was sufficiently trained (a few days for a chemist). The problem with these models on the other hand, is that they are only as good as the thermodynamic data they contain. Thus, it would be essential to confirm that sound thermo data are available for all species of interest. If the native database is insufficient, it can be modified. The other caveat is that these models assume achievement of equilibrium, which is often not the case in real field systems, as is indicated on p. 104.*

  Response: The MINTEQA2 model is best suited for Ph.D. academic inorganic chemists. It is not practical for use at NJDEP without training (as the reviewer points out), and this would only be worthwhile if the model offered a clear benefit. As the reviewer points out, the lack of needed input data can be a problem with the model. It is a certainty that adequate thermodynamic data is not available for several of the species present at COPR waste sites (some of which have been only recently discovered). Furthermore, the various species in solution at COPR sites and their concentrations have not been adequately characterized. Finally, the reviewer mentions that field conditions are not likely to be at equilibrium as the MINTEQ model requires. Considering all these issues, model is judged to be impractical for use at COPR sites.

- *P 105-106: The written assessment of alternative remediation standards seems reasonable, as does the treatment of COPR material as a continuing source.*

  Response: We agree.

- *P. 107: I am not convinced that material pH serves as an unambiguous proxy for source vs. soil material. I would imagine that COPR pH decreases with aging time even in the absence of soil. In this regard, the total Cr concentration criterion may be preferable. However, it would seem that quantitative mineralogical assessments would be least ambiguous, since solid phase Cr is present in unique mineral types. This approach would require a more intensive data acquisition for a given site/sample. I agree that research is needed in this area.*

  Response: We agree. The methodology for distinguishing between COPR and COPR-soil mixtures has not yet been developed, though it is anticipated that many factors in addition to pH will be used for this characterization. Mineralogical analysis would certainly be considered.

3. Interconversion

- *General Comments:*

This section emphasizes the role of various electron acceptors in promoting the oxidation of Cr(III) to Cr(VI). While the speciation and concentration of oxidizing agents is undoubtedly important, the speciation of Cr(III) is likely of equal importance. This review of the literature should specify which species of Cr(III) are being oxidized in each case cited. Were all studies conducted on aqueous phase Cr(III)? The kinetics of solid phase Cr(III) oxidation is likely highly variable depending on the form present in COPR.

Response: We agree. More specifics on the studies evaluated have been added.

- *At alkaline pH values characteristic of COPR (i.e., pH 10 and higher) the dominant aqueous species of Cr(III) are Cr(OH)30 and Cr(OH)4-. This is different than the speciation present at lower pH (conditions under which most of the cited studies have been conducted), a factor that is likely to impact oxidation rates.*

Response: We agree.

Specific Comments:

- *P. 110-112: This review of redox transformations of Cr suggests that systems containing significant Mn(IV) oxides have a greater tendency to oxidize Cr(III) whereas those systems comprising high concentrations of organic matter and Fe(III) oxides, have a greater tendency toward reduction of Cr(VI) (via Fe(II)-induced reduction). This seems consistent with the existing literature and so measures of these constituents in COPR sites might provide some utility for predicting interconversion. However, most of the cited research was conducted on model systems comprising Mn oxide or Fe oxide-humic suspensions. Further work is needed to verify the effects for COPR and COPR-soil mixtures.*

Response: We agree with the reviewer's comment that more work is needed. The recommendations include interconversion research. A sentence noting this has been added.

4. Concentration Effect

General Comments:

- *This portion of the review emphasizes adsorption as a function of particle size. However, the surface chemistry of the particles is a very important criterion for the production of surface excess. For example, HCrO4- and CrO42- will not accumulate on negatively-charged surfaces, such as structurally-charged layer silicate clay minerals or silica, whereas it will accumulate on positively-charged surfaces such as Fe and Al oxides and hydroxides, particularly when low pH promotes an increase in positive surface charge through surface protonation reactions. Thus, it is important to consider, not only the size of particles, but also their mineralogical composition and, hence, charge properties, when considering adsorption of anionic chromate.*

Response: We agree with the reviewer and have expanded the discussion to include the points about mineralogy of the adsorbate.

Specific Comments:

- *P. 118, 3rd paragraph: This discussion deals with pH dependency of Cr(III) and Cr(VI) adsorption. To elucidate the mechanisms governing this dependency it would be worth including some discussion of the speciation of aqueous phase Cr(III) and Cr(VI) as a function of pH. This aqueous phase speciation is what controls the affinity of Cr for surfaces under various chemical conditions. For example, the distribution of Cr(VI) species is pH dependent, with a pKa value for HCrO4- of 6.5. Similarly, the solubility of the hydrous solid phase Cr(OH)3 exhibits strong pH dependence because of aqueous phase speciation changes. Whereas the cationic species Cr(OH)2+ is predominant below pH 8, the neutral species Cr(OH)30 and anionic species Cr(OH)4- become increasingly prevalent at pH > 9. Thus, given the changing charge properties of the hydrolysis products for both Cr(VI) and Cr(III), we expect strong pH dependency of adsorption. Superimposed on this is the pH dependent charge properties of the Al and Fe oxides, which serve as important sorbents for hexavalent Cr. Much of the phenomenological description of pH dependency of "Cr(VI) solubility" can be understood in the context of acid-base chemistry of both the Cr species and the mineral surfaces.*

  Response: We agree that a discussion of pH, speciation, and adsorption would be useful here. A short discussion has been added as a preamble to the cited paragraph.

Recommendations (p. 121-124):

1. *Nature of COPR. Based on the documentation included in the report, I agree with the need for research on the nature (particularly mineralogy) of COPR, for the reasons stated throughout this review.*

   Response: We agree that the mineralogy is an important consideration. It has been added to the recommendation.

2. *Transport to Groundwater. Based on the documentation included in the report, I agree with the research needs listed.*

   No Response.

3. *Interconversion. Based on the documentation included in the report, I agree with the research needs listed. Relations between adsorption and redox transformation may prove to be particularly important.*

   No Response.

4. *Concentration Effect. Based on the documentation included in the report, I agree with the research needs listed. However, it seems that the most information will be obtained from the particle size concentration effect studies if Cr(VI) accumulations are correlated with both particle size and particle mineralogy/chemical composition. I am concerned that a focus solely on particle size will lead to equivocal results and*

relatively poor predictive power. Inclusion of data on solid phase composition across the particle size range should improve the predictive power significantly.

Response: An attempt will be made to include a mineralogical assessment of the material used in this research. However, it may be beyond the scope of the investigator's ability. This will depend in large part on the availability of the mineralogical techniques by the investigator. A request to incorporate mineralogical characterizations has been added to the research recommendation.

Other Specific Comments:

- *The term "blooms" is used in several locations throughout the report, presumably to denote visible surficial accumulations of Cr(VI) salts. However, the term is never fully defined, and it is not until P. 110 or so that it becomes somewhat clear what is intended by this term. The term "blooms" should be defined precisely whan it is first introduced, in terms of the precise chemical compositions or range of chemical compositions intended.*

Response: The term has been better and earlier defined.

<u>Peer Reviewer: C.P. Huang</u>

● *Comment #1. Cr release equations. Equations (1) and (2) were used to predict the release of chromium into the groundwater from organic and inorganic contaminants, respectively. These equations were derived on a simple adsorption equilibrium senior. A chemical transformation term, i.e., redox reaction, may be incorporated. For example:*

IGWSRS = C_{gw} (($K_{oc}F_{oc\,+}$ (0_w+0_aH')/p_b^{+} k)*DAF, *or organic contaminants and IGWSRS* = C_{gw} ((K_d + (0_w +0_aH')/p_b+k)*DAF, *or organic contaminants, where k is the rate of chemical transformation such as reduction or oxidation reaction.*

Response: The simple partitioning equation predicts equilibrium solution concentrations based on existing concentrations of contaminants in soil. These concentrations may be reduced as a function of time, but this would require an e^{-kt} term to be applied to the entire equation, not a rate constant k added to the denominator.

● *Comment #2. Dissolution-based guidance for cleanup. It is true that currently EPA does not have any guidance on dissolution-based models for calculating clean-up standards. But there are abundant literatures on chemical weathering of minerals that can be adopted to COPR and COPR-soil systems. Attached #1 is but one of the many current publications regarding chemical weathering process.*

Response: These are very general references, and they will not provide practical tools for use with COPR waste sites.

● *Comment #3. Classification of COPR and COPR-Soil Materials. It was suggested to use pH and total Cr as the two indicators for differentiating pure COPR from COPR-soil mixture. Other indicators such as Ca to Si (Ca/Si) and /or Ca to Al (Ca/Al) molar ratio or Cr to Si (Cr/Si) and/or Cr to Al (Cr/Al) molar ratios may also give useful information.*

Regardless of what indicators to be used, one most important issue to be addressed is the threshold value, that is, what is the dividing line between a COPR and a COPR-soil matrix. One suggestion to deal with the above question is to compare the indicator values, e.e., pH or Ca/Al against results from surface characteristics, e.g., XRD, XPS, and NEXAF. A threshold value can be drawn along the line where there is clear indication the presence of specific mineral phases intrinsic to the pure COPRs.

> **Response:** We agree. Research conducted toward separating COPR material from chromium contaminated soil should look into these possibilities. However, any techniques developed should be practical for routine use.

- *Comment #4. Chemical transformation of Cr. The geochemical cycle of chromium is complex. Many factors can affect the extent and the rate of the transformation of chromium, i.e., Cr(III)-Cr(VI). In the soil matrix, chemical species such as dissolved organic matter (e.g., soil humic substances), Mn, Fe, nitrogen (nitrate and ammonia) and sulfur are obvious ones. In the atmospheric side, chemical species such as oxygen, CO_2, SO_x and NO_x and ozone (from UV light reaction with water and atmospheric oxygen) call all participate at the geochemical transformation of chromium. Therefore, meteorological conditions may be as important as the soil chemical environment in the transformation of chromium.*

> **Response:** We have addressed issues of atmospheric oxygen in the discussion of interconversion. We have not found any studies that look at effects of ozone, NO_x or SO_x on chromium transformations. However, sulfate, whether in rainwater or other media, can compete with chromate ion for adsorption sites. The only study we have found so far that examines the effects of temperature on Cr (VI) leaching is Weng et.al., 2002. We have added a phrase referencing the results of this study to the discussion of Cr (VI) leaching. We do not have adequate information at present to address the effects of other meteorological phenomena or to indicate their importance relative to the soil chemical environment.

- *Overall, this report is very well prepared and documented. The Workshop has more than adequate in addressing all charges from the NJDEP Commissioners. Recommendations to NJDEP are rightfully proposed. The reviewer wishes to recommend the approval of this report.*

> **No Response.**

Attachment #1. Submitted by C.P. Huang
Chemical Weathering literature.
Volume 31, 1997 Mineralogical Society of America
CHEMICAL WEATHERING RATES OF SILICATE MINERALS
A.F. White & S.L. Brantly, Editors

Contents of Volume 31