NORTH CAROLINA DEPARTMENT OF
ENVIRONMENT AND NATURAL RESOURCES
DIVISION OF AIR QUALITY

NCDENR

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July 7, 1999

MEMORANDUM

TO: Alan Klimek, Director
Keith Overcash, Deputy Director

THROUGH: Lee Daniel, Chief, Technical Services Section

FROM: Lori Cherry, Supervisor, Toxics Protection Branch Lori Cherry

SUBJECT: Updated Guidelines for Implementing Acceptable Ambient Levels (AALs) for Chromium (VI) Compounds

The AALs for chromium (VI) compounds as contained in the current NC Air Toxic Rules differ from the recommendations of the North Carolina Scientific Advisory Board on Toxic Air Pollutants (SAB).[1] The Toxics Protection Branch is working with the Planning Section to revise the current rules to reflect the SAB's recommendations. This memorandum presents revised guidance for implementing AALs for chromium (VI) compounds and supersedes all previous memoranda on chromium (VI) compounds[2]. ***Please be advised that this memorandum outlines a significant departure from prior implementation of the chromium (VI) AALs.***

The SAB recommends two broad categories of chromium (VI) compounds based on the health effects of chromium (VI). The first category encompasses "bioavailable chromate pigments" that are human carcinogens. Calcium chromate and dichromate, strontium chromate and dichromate, and zinc chromate and dichromate are considered "bioavailable chromate pigments." The recommended AAL for this category is $8.3x10^{-8}$ mg/m^{3}. The second category applies to "soluble chromate compounds" that have been shown to cause nasal tissue ulceration. The SAB defines "soluble chromate compounds" as chromic acid, potassium chromate and dichromate, sodium chromate and dichromate, and ammonia chromate and dichromate. The recommended AAL is $6.2x10^{-4}$ mg/m^{3} for this category. In all, thirteen specific chromium VI compounds are grouped under the two broad chromium (VI) categories. Finally, the SAB specifically excludes lead chromate and lithium chromate in its AAL recommendations.

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[1] The recommendations of the SAB were submitted in a memorandum to the Environmental Management Commission dated January 11, 1991 and are contained in Attachment B to this document. Dr. Woodhall Stopford, on behalf of the SAB, further clarified their recommendation in a letter addressed to Jeff Hayward on January 29, 1999. This letter is also contained in Attachment B.

[2] Specifically, this memorandum supersedes the memorandum from Lori Cherry to Thomas Allen dated March 29, 1994 and the memorandum from Lori Cherry to Leslie Biller and Don van der Vaart dated July 11, 1994. This memorandum also supersedes a portion of the memorandum from Julie Woosley and Don Johnson to the Chromium Electroplating MACT Team dated June 20, 1997. The portion of the memorandum that deals with the implementation of chromium (VI) AALs is no longer valid. However, information discussed in the memorandum on other TAPs/HAPs emitted from chromium electroplaters and on last MACT is still valid and is not superseded by this memorandum.

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With the exception of lead chromate and lithium chromate, any chromium (VI) compound not specifically listed in the chromium (VI) categories is to be evaluated under a separate AAL for "non-specific chromium (VI) compounds." The AAL for this category is 8.3×10^{-8} mg/m^3, calculated as an annual average.

In summary, three chromium (VI) categories should be listed in the NC Air Toxic Rules. Table 1 presents an overview of the categories, their AALs, and their associated toxic permitting emission rates (TPERs).

Table 1. Overview of Categories of Chromium (VI) Compounds

Chromium (VI) Category	**Compounds Included in the Chromium (VI) Category**	**AAL for Chromium (VI) Category**	**TPER for Chromium (VI) Category**
Bioavailable Chromate Pigments	Calcium chromate (13765-19-0) Calcium dichromate (14307-33-6) Strontium chromate (7789-06-2) Strontium dichromate (77889-06-2) Zinc chromate (13530-65-9) Zinc dichromate (7789-12-0)	8.3×10^{-8} mg/m^3 (annual)	0.0056 lb/yr
Soluble Chromate Compounds	Ammonium chromate (7788-98-9) Ammonium dichromate (7789-09-5) Chromic acid (7738-94-5) Potassium chromate (7789-00-6) Potassium dichromate (7778-50-9) Sodium chromate (7775-11-3) Sodium dichromate (10588-01-9)	6.2×10^{-4} mg/m^3 (24-h)	0.013 lb/day
Non-specific Chromium (VI) Compounds	Any chromium (VI) compound not specified in other categories, with the exception of lead and lithium chromate	8.3×10^{-8} mg/m^3 (annual)	0.0056 lb/yr

Three important considerations must be taken into account when applying the AALs and TPERs:

1) The AAL and TPERs are applicable only to the broad chromium (VI) categories, not to the individual compounds listed under each category. In other words, the *sum* of the air concentration or emission rate for each compound within a category needs to be evaluated against the AAL or TPER. This sum cannot exceed the AAL or TPER for the entire category.

2) Estimates of emissions and ambient air concentrations should be stated as chromium (VI) equivalents. In other words, only the molecular weight of the chromium (VI) portion of the compound needs to be considered when assessing an AAL or TPER. The use of chromium (VI) equivalents is applicable to *all* categories of chromium compounds.

3) Chromium (VI) compounds should not be "double counted" in the three categories. Instead, any chromium (VI) compound should be evaluated under only one category.

Attachment A to this document contains questions and answers that clarify the revised implementation guidance for chromium (VI) compounds.

ATTACHMENT A

Questions and Answers

QUESTIONS AND ANSWERS

1) A facility emits 0.01 lbs/year of calcium chromate. Does this facility exceed the TPER for "bioavailable chromate pigments?"

No. The TPERs for the thirteen chromate compounds included in the SAB's recommendation are applicable only to the chromium (VI) portion of the compounds. Thus, the emission rate of calcium chromate must be adjusted to account for the chromium (VI) portion. The following equation can be used to calculate the emission rate in terms of chromium (VI) equivalents:

Equation 1

$$\begin{aligned}
\text{Chromium (VI) Equivalent Emission Rate} &= \frac{\text{Chromium (VI) Molecular Weight}}{\text{Compound Molecular Weight}} \ x \ \text{Emission Rate} \\
&= \frac{52 \ g/mole}{156.1 \ g/mol} \ x \ 0.01 \ lbs/yr \\
&= 0.333 \ x \ 0.01 \ lbs/yr \\
&= 0.00333 \ lbs/yr
\end{aligned}$$

As seen in the above example, the emissions in terms of chromium (VI) are below the TPER of 0.0056 lbs/yr for "bioavailable chromate pigments," and so the facility does not exceed the TPER.

2) Air modeling for a facility resulted in an air concentration of potassium chromate estimated as $7.4 x 10^{-4}$ mg/m^3 on a 24-hour basis. Does this facility exceed the AAL for "soluble chromate compounds?"

No. The AALs for the thirteen chromate compounds included in the SAB's recommendation are applicable only to the chromium (VI) portion of the compounds. Thus, the air concentration of potassium chromate must be adjusted to account for the chromium (VI) portion. The following equation can be used to calculate the air concentration in terms of chromium (VI) equivalents:

Equation 2

$$\begin{aligned}
\text{Chromium (VI) Equivalent Air Concentration} &= \frac{\text{Chromium (VI) Molecular Weight}}{\text{Compound Molecular Weight}} \ x \ \text{Air Concentration} \\
&= \frac{52 \ g/mole}{194.2 \ g/mol} \ x \ 7.4 x 10^{-4} \ mg/m^3 \\
&= 0.268 \ x \ 7.4 x 10^{-4} \ mg/m^3 \\
&= 1.98 x 10^{-4} \ mg/m^3
\end{aligned}$$

As seen in the above example, the modeled air concentration in terms of chromium (VI) is below the AAL of $6.2 x 10^{-4}$ mg/m^3 for "soluble chromate compounds," and the AAL is not exceeded.

3) The updated guidance states that the AALs and TPERs should be evaluated in terms of chromium (VI) equivalents. Equations 1 and 2 show that the chromium (VI) equivalent can be calculated by applying a ratio of 0.333 for calcium chromate and 0.268 for potassium chromate. What are the appropriate ratios for the other chromium (VI) compounds included in the SAB's recommendations?

Table A-1. Ratios for Calculating Chromium (VI) Equivalents

Chromium (VI) Category	Compounds Included in the Chromium (VI) Category	Compound Molecular Weight (g/mol)	Chromium (VI) Ratios
Bioavailable Chromate Pigments	Calcium chromate ($CaCrO_4$)	156.09	0.333
	Calcium dichromate ($CaCr_2O_7$)	206.10	0.406
	Strontium chromate (CrO_4Sr)	203.64	0.255
	Strontium dichromate ($Cr2O_7Sr$)	303.62	0.342
	Zinc chromate ($ZnCrO_4$)	181.38	0.287
	Zinc dichromate ($ZnCr_2O_7$)	281.38	0.370
Soluble Chromate Compounds	Ammonium chromate ($CrH_8N_2O_4$)	152.09	0.342
	Ammonium dichromate ($Cr_2H_8N_2O_7$)	252.10	0.413
	Chromic acid - H_2CrO_4 CrO_3 (the anhydrous form)	 118 100	 0.441 0.52
	Potassium chromate (CrK_2O_4)	194.20	0.268
	Potassium dichromate ($Cr_2K_2O_7$)	294.21	0.354
	Sodium chromate ($CrNa_2O_4$)	161.97	0.321
	Sodium dichromate ($Cr_2Na_2O_7$)	261.96	0.397

4) A facility emits both strontium chromate and calcium chromate. The facility has recently conducted air modeling to determine compliance with the AAL for "bioavailable chromate pigments." The results of the air modeling indicate that the concentration of calcium chromate, in terms of its chromium (VI) equivalent, is 6.5×10^{-8} mg/m^3 on an annual basis. The modeled concentration of strontium chromate, in terms of its chromium (VI) equivalent, is 3.2×10^{-8} mg/m^3 on an annual basis. Does this facility exceed the AAL?

Yes. The AAL of 8.3×10^{-8} mg/m^3 is applicable to the category of "bioavailable chromate pigments." Thus, the modeled concentration of calcium chromate and strontium chromate expressed in terms of chromium (VI) equivalents must be combined to assess the AAL. The sum of the modeled values equals 9.7×10^{-8} mg/m^3, which exceeds the AAL for this category.

5) A facility emits lead chromate. How should this compound be evaluated?

Lead chromate is not one of the chromium (VI) compounds included in the SAB's recommendations and does not have to be evaluated under the NC Air Toxics rules. However, lead is a regulated compound under EPA's National Ambient Air Quality Standards (NAAQS). Lead accounts for 64.44% of lead chromate. This portion of the compound should be compared with the NAAQS (1.5 $\mu g/m^3$ per calendar quarter) to determine compliance for lead. Additionally, both lead and chromium compounds are hazardous air pollutants, and lead chromate may be regulated under certain NESHAPs as a result.

6) A facility emits lithium chromate. How should this compound be evaluated?

Lithium chromate is not one of the chromium (VI) compounds included in the SAB's recommendations and does not have to be evaluated under the NC Air Toxics rules. However, chromium compounds are considered a hazardous air pollutant, and lithium chromate may be regulated under certain NESHAPs as a result.

7) How should emissions from combustion sources be evaluated under these revisions?

Unless process data are available to indicate otherwise, the chromium emissions from combustion sources should be evaluated as chromic acid (CrO_3) under the "soluble chromate compounds" category. Emissions of chromic acid are first calculated in terms of the chromium (VI) equivalent, using a factor of 0.52 for the anhydrous form. The equivalent emissions are then compared with the TPER for "soluble chromate compounds" to determine compliance.

This recommendation is based on a literature review conducted to better understand the behavior of chromium in combustion reactions. (Attachment C summarizes the literature review.) Measuring specific chromium (VI) compounds present in combustion exhaust is not possible because test methods for hexavalent chromium cannot distinguish between different chromium(VI) compounds. Therefore, theoretical models describing chromium partitioning based on equilibrium data are the best way to determine which chromium (VI) compounds are present. An equilibrium model developed by Kashireninov and Fontijn showed that chromic acid is formed during combustion. According to their model, formation of chromium (VI) compounds - mainly as CrO_3 (g) - reached a maximum of 77% at 1650°K and 400% excess oxygen (Kashireninov and Fontijn, 1998). Although other equilibrium models have shown that different chromium (VI) compounds are dominant, these models considered only individual equilibria and not overall system equilibria, as was done in the Kashireninov and Fontijn model.

8) A facility conducted a stack test for a combustion source and reported emissions as _total_ chromium. How should the stack emissions of total chromium be evaluated?

As noted in Question 7, chromium emissions from combustion sources can be reported as chromic acid under the "soluble chromate compounds" category. In this case the facility tests for and reports the _total_ chromium from its combustion source. Therefore, the _total_ chromium measured should practically be considered as chromic acid and compared with the TPER for "soluble chromate compounds" to determine compliance.

This recommendation is based on a literature review conducted to better understand the behavior of chromium in combustion reactions. (Attachment C summarizes the literature review.) Measured and experimental data indicate that only a fraction of the total chromium in combustion exhaust is chromium (VI). Experimental measurements of chromium (VI) ranged from less than 2% up to about 20%, while stack measurements at electrical utilities showed as much as 34% of total chromium can be chromium (V,I). Since formation of chromium (VI) depends on many factors (type of fuel, combustion temperature, presence of compounds, and etc.), developing any kind of chromium (VI) to total chromium ratio is not advised based on the limited data available. Therefore, as a practical matter when source testing is for *total* chromium from combustion sources, the entire result is considered as chromic acid (see Question 7) and compared to the AAL for "soluble chromate compounds," to be protective of public health. A source test for chromium (VI) compounds remains an option for facilities that may have difficulty applying the *total* chromium results as chromic acid (see Question 9).

9) Because test methods for hexavalent chromium cannot distinguish between different chromium(VI) compounds, how should source tests for hexavalent chromium emissions be evaluated?

In some cases, the facility that is testing for chromium (VI) emissions may be able to characterize which species of chromium (VI) are being emitted based on a knowledge of the process. If the facility does not know how to characterize its chromium (VI) emissions, then the emissions should be compared with the AAL and TPER for the "non-specific chromium (VI) compounds" to determine compliance.

10) How should chromium emissions from electroplaters using hexavalent chromium baths be evaluated under the SAB's recommendations?

Although powdered anhydrous chromic acid is used to make hexavalent baths at electroplating facilities, the hydrated form of chromic acid emitted from the baths is more of concern for air quality. Emissions from plating baths are caused by physical rather than chemical processes. When voltage is applied to the bath, hydrogen gas evolves from the bath and causes misting at the liquid surface. The mist is assumed to be composed of hydrated chromic acid (H_2CrO_4) and water in the same ratio as found in the bath. Emissions of H_2CrO_4 from the baths are first calculated in terms of the chromium (VI) equivalents, using the ratio of 0.441 for hydrated chromic acid. The equivalent emissions should be compared with the TPER for "soluble chromate compounds" to determine compliance.

ATTACHMENT B

SAB Recommendations for Chromium (VI) Compounds

THE UNIVERSITY OF NORTH CAROLINA
AT
CHAPEL HILL

The School of Public Health
Department of
Environmental Sciences and Engineering

The University of North Carolina at Chapel Hill
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January 11, 1991

Gladys VanPelt, PhD
Chair, Air Quality Committee
Environmental Management Commission
Department of Environment, Health,
and Natural Resources
P.O. Box 27687
Raleigh, NC 27611-7687

Dear Dr. VanPelt:

Re: Acceptable Ambient Levels for Chromium Compounds

In its meeting on November 15, 1990, the Scientific Advisory Board on Toxic Air Pollutants unanimously adopted a motion to recommend to the Environmental Management Commission that the following listed Acceptable Ambient Levels for chromium compounds be adopted by the Commission:

COMPOUND	EFFECT	AAL (mg/m^3)
Bioavailable pigments Chromate and dichromate salts of: Calcium Strontium Zinc	human cancer	8.3×10^{-8}
Soluble chromate compounds Chromic acid Chromate and dichromate salts of: Potassium Sodium Ammonium	nose ulceration	6.2×10^{-4}
Lithium chromate	none reported	none

The recomended AAL's for chromate and dichromate salts of calcium and strontium are unchanged from those listed in part .1104(b) of the current regulation.

The current regulation does not list chromate compounds of zinc. The new AAL recommended by the Board reflects the recognition of chromate salts of zinc as human carcinogens.

The compounds listed above in the category "soluble chromate compounds" are suspect carcinogens; the AAL calculated for this classification of carcinogens is more lenient than that for their known effect in nose ulceration. Adoption of the more stringent AAL based on nose ulceration is recommended.

No effect for exposure to chromate salts of lithium has been identified; the Board recommends that lithium salts be removed from the AAL list.

Documentation of the Board's recommendations was prepared by Woodhall Stopford, MD. A copy of Dr. Stopford's written review is appended to this letter.

Sincerely yours,

Robert L. Harris, PhD
Chair, Scientific Advisory Board
on Toxic Air Pollutants

Enclosure

cc: Members, Scientific Advisory Board
on Toxic Air Pollutants
Members, EMC Air Quality Committee
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January 29, 1999

Jeff Hayward
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USA

Dear Jeff:

This letter addresses your letter to me of January 7, 1998; your Email to me of December 4, 1998; and our meeting today, all concerning the interpretation of the SAB's recommendation for a change in the chromate AAL from a generic to a compound-specific AAL. We specifically recommended that calcium, strontium and zinc pigments of chromate or dichromate be considered human carcinogens with a summated AAL of 8.3 x 10-8 mg/m3. That is, if a factory emits more than one of these, the emissions of all in this class would be added and the total emissions should meet the AAL for this class.

The second recommendation for compound-specific AALs was for the class made up of chromic acid and soluble potassium, sodium or ammonium salts of chromate or dichromate. We felt that the most protective end point for an AAL for chromium compounds in this class was for nose ulceration resulting in an AAL of 6.2 x 10-4. This AAL would also protect against cancer risk from exposures to soluble chromium salts in this class. We felt that emissions from one point source of soluble chromium salts in this class should also be summated as we recommended for chromium pigments.

Finally we felt that there should be no seperate AAL for lead chromate or lithium chromate, the AALs for lead and lithium being adequate to cover emissions of these compounds.

The SAB expected that these AAL recommendations would replace the generic chromate AAL. If NCDENR wishes to regulate the emissions of other chromate compounds, I suggest that the SAB advise NCDENR as to the appropriate AAL to be developed.

All of these AALs are considered "as chromium" and not as the total emission weight of the specific chromate compound.

Sincerely,

Woodhall Stopford, MD, MSPH
Consulting Toxicologist

ATTACHMENT C

Summary of Literature Review for Chromium (VI)

March 30, 1999

MEMORANDUM

TO: Lori Cherry

FROM: Betty Gatano

SUBJECT: Literature Review for Chromium (VI) from Combustors

Questions have been raised concerning the way facilities should evaluate chromium emissions from combustors. In response to these questions, a literature review was conducted to better understand the behavior of chromium in combustion reactions[1]. An overview of information obtained from the literature review is presented in this memorandum.

Conclusions Based on Literature Review

The literature review showed that only a fraction of the total chromium emitted from combustors is emitted as chromium (VI). Since formation of chromium (VI) depends on many factors (type of fuel, combustion temperature, presence of other compounds, and etc.), developing a chromium (VI) to total chromium ratio is not advised based on the limited data available. Additionally, because test methods for hexavalent chromium cannot distinguish between different chromium (VI) compounds, theoretical models describing chromium VI partitioning based on equilibrium data are the best way to determine which chromium (VI) compounds are formed in combustion reactions. One of the theoretical models considered in this literature review predicted that chromic acid is a dominant chromium (VI) compounds from combustion sources.

Theoretical Data

Current models describing chromium partitioning in combustion data are based on chemical equilibrium. In evaluating theoretical data, limitations in the modeling must be considered. It is important to note that equilibrium conditions may not be achieved in reality because of kinetic rate or mixing limitations. Additionally, any equilibrium prediction is only as good as the thermochemical information available (Linak, et. al, 1996).

Two papers on the equilibrium formation of chromium (VI) products were examined for this memorandum. In the first paper, the effects of chromium (VI) formation in the presence of chlorine and sulfur were examined. Inputs into the model were methane, oxygen, nitrogen, water, chromium, chlorine, and sulfur. The equilibrium model suggests the following (Linak, et. al, 1996):

1) In the absence of chlorine and sulfur, chromium (VI) is favored at high temperatures

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[1] The references reviewed for this memorandum do not represent an exhaustive literature search but include only those sources that were readily available from NCSU.

is emitted as chromium (VI). The average chromium (VI) emitted from the coal-fired utilities is 11% of the total chromium, and the average chromium (VI) from oil-fired utilities was 18% of the total chromium, based on the test data (US EPA, 1998).

References

Huggins, F.E., M. Najih, and G.P. Huffman. 1999. *Direct Speciation in Coal Combustion By-Products by X-Ray Absorption Fine-Structure Spectroscopy*. Fuel. Vol 78, pp. 233-242.

Kashireninov, O.E. and A. Fontijn. 1998. *Modeling of Chromium Combustion in Incineration: Thermochemistry of Cr-C-H-Cl Combustion in Air and Selection of Key Reactions*. Combustion and Flame. Vol 113, pp 498-506.

Linak, W.P., Ryan, J.V., and Wendt, J.O.L. 1996. *Formation and Destruction of Hexavalent Chromium in a Laboratory Swirl Flame Incinerator*. Combustion Science and Technology. Vol 134, pp 243-163.

US EPA. 1998. *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units -- Final Report to Congress.* Office of Air Quality Planning and Standards, RTP, NC. EPA-453/R-98-004a.